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COMPLEXIMETRIC INDICATORS: CHARACTERISTICS AND APPLICATIONS

Prepared for publication by

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COMPLEXIMETRIC INDICATORS: CHARACTERISTICS AND APPLICATIONS

Abstract - Basic characteristics of 24 compleximetric indicators are presented. They include protonation and complexation equilibria, spectral characteristics of indicators and their complexes, purity tests and method of purification as well as typical applications.

CONTENTS

INTRODUCTORY REMARKS TO COLLECTED DATA ON COMPLEXIMETRIC INDICATORS

Up to the present, a large number of papers have been devoted to the study of complexation reactions between metal ions and indicator ligands. Several years ago,attempts were made to compile the data on reactions used in compleximetry (Ref. 1) , some of them may be extracted from general monographs (Ref. 2, 3) or tables of stability constants (Ref. 4, 5). There is however a constant need for an up-to-date survey which will allow a comparison of results obtained by various authors.

In spite of the large number of papers published recently, many gaps remain. A further significant defect being that some of the data are not reliable. The source of unreliability can be assigned to several factors:

- The investigated system shows a great complexity for example exhibits simultaneous formation of several complexes, or the formation of mixed or protonated complexes.

- The metals examined may be simultaneously involved in side reactions with hydroxyl ions or with buffer components.

- The indicators investigated are often of undefined purity. The contamination arises from their synthesis, unsufficient purification and/or instability of the reagents themselves.

- Experimental errors arise because the methods of investigation are not chosen properly or experimental conditions not fully defined. Random errors or measurement usually have a smaller contribution.

The first stage of the critical evaluation of the stability constant data there is their separation into two groups.

a) The first group includes systems where the authors formulate an equation and equilibrium constant for the reaction and defined as carefully as possible the experimental conditions under which the reaction was carried out.

b) The second group consists of systems where only the ratio, metal to ligand, has been indicated, the reaction equilibrium constant has been stated, but often the species taking part in the reaction and products were not unequivocally confirmed. Data in this group have been included herein as "Conditional Stability Constants" but because the exact experimental conditions are not defined they can not be considered as reliable characteristics of the system studied. They are useful in that they point out systems in which the reaction occurs and which need further investigation. Cases where the data are obviously contradictory to those of other authors, or appear to be nonrealistic, when taking into account the known properties of similar ligands and metal ions have been specially noted in the text. Recalculation of some of those data into true equilibrium constants seems possible occasionally but most often insufficient informations on solution composition were reported. The lack of constants for protonated or hydroxylated complexes presents additional difficulties.

When complexation and protonation equilibria for indicators are considered it must be kept in mind, that in some cases the sequence of losing protons in the absence and presence of metal ions is for steric reasons different. This occurs for Chromazurol S, Eriochrome Cyanine R, TAR and PAR (Ref. 6). In the latter case the proton in the p-OH group is more acidic than that in the o-OH group, however in the presence of complexed metal ions the o-OH proton is initially replaced by the metal ion because this is favoured by the chelate ring formation with the adjacent azo group.

It is obvious that only specially designed and very comprehensive experimental investigations will produce the true thermodynamic characteristics of the described species and their reactions. This was however, outside the scope of this project. Nevertheless, it is considered that a "semicritical" compilation will be also useful to practical analysts when chosing new working conditions and to the more physicochemically oriented investigators to check the existing discrepancies and gaps.

The compilation of equilibrium constants includes data which refer to aqueous solutions. Exceptions appear in the case of some azodyes and their complexes which are only slightly soluble in water. For such indicators data for mixed solvents are exceptionally presented.

The scope of this work does not cover data for mixed (ternary) complexes. Their occurence has been recently confirmed in a number of papers, but until now reliable data are available for a very few ligands only in spite of the fact that they are either practically exploited or considered as serious interferents in analytical procedures.

The manner of presentation of indicator characteristics follows the protocol suggested in a previous publication (Ref. 7).

The choice of indicators reviewed is somewhat arbitrary. However it was the subject of discussions on the Commission on Analytical Reactions and Reagents and it was decided to include indicators which are considered as most often used in practice.

<u>Note</u>: Following abbreviations have been used for solvents, when they are different from water:

BuOH - butanol
DMF - dimethylformamide
EtOH - ethanol
MeOH - methanol
PeOH - pentanol

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INDICATOR CHARACTERISTICS

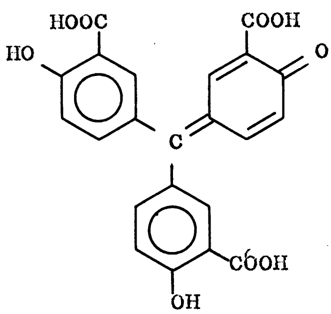
I. TRIPHENYLMETHANE INDICATORS

1. ALUMINON

Synonyms: Chrome Violet
Chrome Printing Violet
Ultra Violet
(some authors and producers use the name Aluminon for the triammonium salt)

Chemical names:
3-[Bis (3-carboxy-4-hydroxyphenyl) methylene] -6-oxo-1,4-cyclohexanediene-1-carboxylic acid
4,4'-Dihydroxyfuchsone-3,3' 3''-tricarboxylic acid
Aurintricarboxylic acid

Colour index: C.I. 43810, Mordant Violet 39



H_5L

Protonation constants of the indicator

log K_1 -OH	log K_2 -OH	log K_3 -COOH	Conditions	Ref.
13.7		3.89		1
13.0		3.9		2
8.85	8.65		0.1M $NaClO_4$, 25°C	3
9.76	8.93		I=0.02 25°C	4

The correlation of experimental values to ionisable groups seems to be doubtful. No critical study of these data has been published.

Stability constants of metal-indicator complexes

Metal ion	Reaction	log K	Conditions	Ref.
Al^{3+}	$Al^{3+}+H_4L^- = AlH_4L^{2-}$	16.6		5
Ga^{3+}	$Ga^{3+}+H_4L^- = GaH_4L^{2+}$	14.75		6

Conditional stability constants of complexes

Metal ion	Metal:Reagent ratio	log K	Conditions	Ref.
Al(III)	1:1	5.5	pH 4-5	2,7
	1:1	4.2	pH 4-6	8
Be(II)	1:1	4.5	pH 5.5	9
	1:1	4.2	pH 4-6	8
Ce(III)	1:1	4.2	pH 6	10
Cu(II)	1:2	8.8	pH 6	9
	1:1	8.3	pH 2-3.8; I=0.1	11
	1:2	3.5	pH 3.4 I=0.1	
	1:1	9.3	I=0.02	4
	1:2	3.8		
Dy(III)	1:1	4.9	pH 6	12
Er(III)	1:1	5.0	pH 6	12
Eu(III)	1:1	4.6	pH 6	12
Fe(III)	1:1	4.7	pH 4.5	9
Gd(III)	1:1	4.7	pH 6	12
Ho(III)	1:1	4.9	pH 6	12
Lu(III)	1:1	5.4	pH 6	12
Nd(III)	1:1	4.4	pH 6	12
Pr(III)	1:1	4.3	pH 6	12
Sc(III)	1:1	4.6	pH 5.5	13
Sm(III)	1:1	4.5	pH 6	12
Th(IV)	1:1	5.0	pH 5.0	9
	1:1	8.3	I=0.1, 25°C	3
	1:2	3.1		
	1:3	2.8		
Tb(III)	1:1	4.7	pH 6	12
Tm(III)	1:1	5.1	pH 6	12
UO_2(II)	1:1	4.8	pH 5.5	9
	1:1	7.4	I=0.1, 25°C	3
	1:2	3.0		
	1:3	2.7		
Yb(III)	1:1	5.2	pH 6	12

Spectral characteristics of the indicator

Ion	λ_{max}, nm	Colour	Ref.
H_2L^{3-}	535	pink-red	1
HL^{4-}	-	yellow	1
L^{5-}	545	red-violet	1
$L(OH)^{6-}$	-	colourless	1

Spectral characteristics of metal-indicator complexes

Metal ion	Metal:Reagent ratio	λ_{max} nm	$\epsilon_{max} \times 10^{-4}$	Colour	Ref.
Al (III)	1:1	510	1.4	red	2
Fe (III)	1:1	530	2.2	violet	14
In (III)	1:1	530	0.4	violet	14
Lanthanides (III)	1:1	540		violet	12
UO_2^{2+}	1:1 2:1	535	0.74 1.2	red	15

Purification of indicator has been carried out by extraction of impurities with hot ethanol (Ref. 16) or by precipitation of the free acid (H_5L) by hydrochloric acid from alkaline solutions. The precipitate was washed with water, ethanol and diethylether and dried at 25°C (Ref. 1).

The indicator is normally used as 0.5% aqueous solution.

Applications of the indicator. Direct titrations of: Al (pH 4.4), Cu (pH 8.5-9.9), Mg (pH 8.5-9.9), Fe (pH 1-2).

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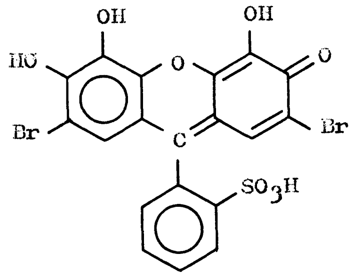
2. BROMOPYROGALLOL RED

Synonyms: -

Chemical names:

2,7-Dibromo-4,5,6-trihydroxy-3-oxo-9-(2'-sulphophenyl)-3H-xanthen-9-yl
2-(2,7-Dibromo-4,5,6-trihydroxy-3-oxo-3H-xanthen-9-yl) benzenesulphonic acid
3,3'-Dibromosulphongallein

Colour index:



H_4L

Protonation constants of the indicator

log K_1 -OH	log K_2 -OH	log K_3 -OH (at carbon 6)	log K_4 $=OH^+$	Conditions	Ref.
11.47	9.21	5.18	2.43		1[x]
11.27	9.3	4.39	0.16	0.2M KCl	2
		3.88			3
	9.13	4.39		0.1M $NaNO_3$	4
		5.2	0.9	0.1M $NaClO_4$	5
11.59	9.16	4.50		0.1M $NaNO_3$	6
11.44	9.03	4.37		0.3M $NaNO_3$	
11.25	8.95	4.30		0.6M $NaNO_3$	
	8.89	4.21	-0.10	1.0M $NaNO_3$	
11.30	9.39	4.33	0.19[xx]	I=0.1	7
		4.78		I=0.1; 30% EtOH	8
			0.24	I=2.0; 30% EtOH	

[x] Data, especially for log K_4 unreliable
[xx] I=0.5

Stability constants of metal-indicator complexes

Metal ion	Reaction	log K	Conditions	Ref.
$Ge(OH)_3^+$	$Ge(OH)_3^+ + 3H_2L^{2-} = Ge(OH)_3(H_2L)_3^{5-}$	12.9	0.1M $NaNO_3$	4
Th^{4+}	$Th^{4+} + H_3L^- = ThH_2L^{2+} + H^+$	4.36		3
UO_2^{2+}	$UO_2^{2+} + H_3L^- = UO_2H_2L + H^+$	-0.56[x]	2M $NaNO_3$; 30% EtOH	8
		0.02[xx]	0.1M $NaNO_3$; 30% EtOH	
	$UO_2^{2+} + UO_2H_2L = (UO_2)_2L + 2H^+$	3.18	0.1M $NaNO_3$; 30% EtOH	

[x] in presence of metal excess
[xx] in presence of ligand excess

Conditional stability constants of complexes

Metal ion	Metal:Reagent ratio	log K	Conditions	Ref.
Cu(II)	1:1	7.6		9
Co(II)	1:2	9.31	pH 5.5-7.0; I=0, 50% EtOH	10
Ni(II)	1:2	6.00	pH 6.0-7.5; I=0, 50% EtOH	10
Nb(V)	1:2	12.0	pH 6	11
	1:3	18.4	pH 6	11
Pb(II)	1:1	6.28	pH 5.5	12
Sb(III)	1:1	5.3	pH 6.6-6.8	13
Sn(IV)	1:2	11.12	pH 1.7	5
Th(IV)	1:2	10.2	pH 5	3
W(VI)	1:1	5.4	pH 4.7; I=0.1	14
Zr(IV)	1:1	9.05	pH 5.2	15

Spectral characteristics of the indicator

Ion	λ_{max} nm	$\epsilon_{max} \times 10^{-4}$	Colour	Ref.
H_5L^+	472	2.7	yellow	16
H_4L^-			yellow	6
	465	2.10(λ=440)		8
	472	2.6		16
H_3L^-	434-438	1.56	orange	6
	525-530	1.43	orange	6
	437	1.60		8
	436	1.3	red	16
H_2L^{2-}	558-564	5.81	red	6
	565	5.13		8
	557	4.4	violet	16
HL^{3-}	554-560	2.27	violet	6
	556	1.7	violet	16
	565	1.75	violet	8
L^{4-}	596-600	2.77	blue	6
	595	2.2	blue	16

Spectral characteristics of metal-indicator complexes

Metal ion	Metal:Reagent ratio	λ_{max} nm	$\epsilon_{max} \times 10^{-4}$	Colour	Ref.
Co(II)	1:2	620	2.9	blue	10
Cu(II)	1:1	619	1.25	blue	9
Er(III)	1:2	642	3.51		17
Ge(IV)	1:2	550	2.05	red-violet	18
La(III)	1:2	658	3.5	blue	17

Spectral characteristics of metal-indicator complexes (Cont.)

Metal ion	Metal:Reagent ratio	λ_{max} nm	$\epsilon_{max} x10^{-4}$	Colour	Ref.
Pb(II)	1:1	630	0.5	blue	12
Sb(III)	1:1	590	3.9	violet	13
Sn(IV)	1:2	493	2.0	red	5
Th(IV)	1:1	596	2.5	violet	3
	1:2	630	6.3	blue	3
	1:2	645	5.0		19
UO_2(II)	1:1	565	0.9	violet	8
	2:1	565	2.51	violet	8
W(VI)	1:1	530	0.8		14
Zr(IV)	1:2	670	7.0	violet	15

Purification of indicator has been carried out by crystallization from 50% ethanol. An efficient purification (Ref. 8) has been obtained by chromatographic separation on a polyamide column pre-washed with HCl (1+4). The indicator was dissolved in methanol with the addition of 1% hydrazine hydrate. After adsorption on the column yellow impurity was first eluted with HCl (1+4), then a red product which was identified as Pyrogallol Red was eluted. The column was finally washed with water and the pure Bromopyrogallol Red was eluted by ammonia (1+8), containing 1% hydrazine hydrate. The acid form of the indicator was immediately precipitated from the eluate using HCl (1+1) dissolved in ammonia containing 1% hydrazine hydrate and reprecipitated with HCl (1+1). The solution containing the precipitate was rapidly heated to 80°C and then cooled with ice. The precipitate was filtered off, washed with a small amount of cold water and dried over KOH and silica gel.

Purity check (Ref. 8). The purity may be checked by thin-layer chromatography on microcrystalline cellulose using butanol - acetic acid - water (4+1+5), n-propanol - water (1+1) and methanol - water (1+1) systems.

The indicator is normally used as 0.05% solution in 50% ethanol.

Typical application of the indicator. Direct titrations of Bi (pH 2-3), Cd (pH 9.3), Mg (pH 10), Mn (pH 10), Lanthanides (pH 7); it has been especially recommended for gallium determinations by back-titration of the excess of EDTA with Bi(III) at pH 2.2. Also in back-titration determination of Co, Cu, Ga, In, Pb, Th, Tl, VO^{2+} with Pb(II) solution as titrant at pH 5, and Bi, Fe(III), Ga, In, Tl with Bi(III) solution at pH 2-3.

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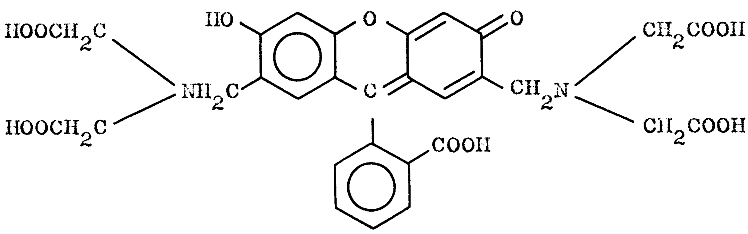
3. CALCEIN

Synonyms: Fluorescein Complexone
Fluorexon

Chemical names:
6-Hydroxy-2,7-bis(N,N-bis-carboxymethyl) aminomethyl-3-oxo-9-(2'-carboxyphenyl)-3H-xanthen-9-yl
2,7-Bis-[N,N-di(carboxymethyl) aminomethyl]-fluorescein
[(3',6'-Dihydroxy-fluoran-2',7'-diyl) bis-methylenenitrylo] tetraacetic acid
2',7'-Bis [N,N-bis (carboxymethyl) aminomethyl]-3',6'-dihydroxyfluoran
N,N'-{3',6'-Dihydroxy-3-oxo-1,3-dihydro-9'H-spiro [isobenzofuran-1,9'-xanthen]-2',7'-diyl-bis-methylene}-bis[N-(carboxymethyl) glycine]

Colour index:



H_6L

Protonation constants of the indicator

log K_1 ≡NH$^+$	log K_2 ≡NH$^+$	log K_3 -OH	log K_4 -COOH	log K_5 -COOH	log K_6 -COOH	Conditions	Ref.
12.0	10.1	5.4	4.1	2.9	2.1	0.1M KCl 30% EtOH	1
>12.0	10.5	9.0	5.4	<4		0.1M KCl	2

Stability constants of metal-indicator complexes

Metal ion	Reaction	log K	Conditions	Ref.
Cu^{2+}	$Cu^{2+}+H_4L^{2-}+H_3L^{3-} = Cu(H_4L)(H_3L)^{3-}$	10.4	I=0.1	3
	$Cu^{2+}+H_2L^{4-} = CuH_2L^{2-}$	8.3		
	$2Cu^{2+}+L^{6-} = Cu_2L^{2-}$	28.9		

Spectral characteristics of the indicator
The less protonated forms are yellow-rose coloured. No accurate spectral data are available.

Spectral characteristics of metal-indicator complexes

Metal ion	Metal:Reagent ratio	λ_{max} nm	ϵ_{max}x10^{-4}	Ref.
Cu(II)	2:1	490	3.91	3
	1:1	495	2.79	
	1:2	480	3.68	

The indicator is used as a fluorescent indicator, the calcium and sodium complexes exhibit a yellowish-green fluorescence. No reliable spectral data for this indicator are available.

Purification of the indicator may be achieved by crystallization or reprecipitation of commercially available calcein.

Crystallization: The commercially available calcein was dissolved in 50% aqueous methanol at 60°C and filtered using low ash filter paper. The filtrate was allowed to stand at 0°C for 1-2 days. Crystals formed on the glass walls were collected on a glass frit, washed with methanol and dried in a vacuum dessicator over sulphuric acid.

Reprecipitation: The commercially available calcein was dissolved in a small amount of 0.1M NaOH, diluted with 5-10% aqueous methanol, acidified to pH 2.5 with HCl and allowed to stand at 0°C overnight. The crystalline product was treated as described above.

The indicator is used in a solid form diluted with KNO_3 (1:100).

Typical applications of the indicator. Direct titration of Ca(II) at pH>13. Also in back-titration determination of Al, Cr, Cu, Fe(III), Mo(V), Th, VO^{2+} with Cu(II) solution as titrant at pH 4.5-5.

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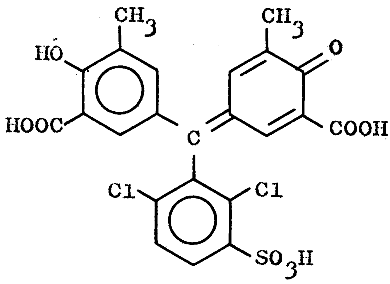
4. CHROMAZUROL S

Synonyms: Alberon
Chromoxan Pure Blue BLD
Eriochromazurol S
Gallochrome Brilliant Blue BLD
Polytrop Blue B
Solochrome Brilliant Blue B
Reinhellblau BLD

Chemical names:
3[(3-Carboxy-4-hydroxy-5-methyl-phenyl)-(2,6-dichloro-3-sulphophenyl)-methylene]-5-methyl-6-oxo-1,4-cyclohexanediene-1-carboxylic acid
3″-Sulpho-2″,6″-dichloro-3,3′-dimethyl-4-hydroxyfuchsone-5,5′-dicarboxylic acid

Colour index: C.I. 43825, Mordant Blue 29



H_4L

Protonation constants of the indicator

log K_1 -OH	log K_2 -COOH	log K_3 -COOH	log K_4 $=OH^+$	log K_5 $-SO_3H$	Conditions	Ref.
11.47	4.86	2.45			I=0.2	1
11.52	4.73	2.28	0.4	-2.2	0.1M KCl	2
11.81	4.71	2.25			0.1M KCl	3
11.79	4.88	2.37		-4.8	0.1M $NaNO_3$	4
12.4	5.0	2.3		-2	I=0.1	5
11.75	4.88	2.25	-1.2		I=0.1	6
12.21	4.92	2.27			I=0.1	7

Stability constants of metal-indicator complexes[x]

Metal ion	Reaction	log K	Conditions	Ref.
Al^{3+}	$Al^{3+}+L^{4-} = AlL^-$	5.20[xx]	0.6M $NaClO_4$	8
	$Al^{3+}+2L^{4-} = AlL_2^{5-}$	9.64		
	$Al^{3+}+2HL^{3-} = Al(HL)_2^{3-}$	16.82		9
	$Al^{3+}+2HL^{3-} = Al(HL)_2^{3-}$	16.1	I < 0.01	10
	$Al^{3+}+HL^{3-} = AlHL$	5.17	I=0.1	11
Be^{2+}	$Be^{2+}+HL^{3-} = BeHL^-$	11.84	0.1M $NaClO_4$	12
	$2Be^{2+}+2L^{4-} = Be_2L_2^{4-}$	26.8		
	$2Be^{2+}+L^{4-} = Be_2L$	15.8		
Cr^{3+}	$Cr^{3+}+L^{4-} = CrL^-$	4.0	0.1M $NaClO_4$	13
	$2Cr^{3+}+L^{4-} = Cr_2L^{2+}$	5.9		
	$Cr^{3+}+2L^{4-} = CrL_2^{5-}$	8.6		
Cu^{2+}	$2Cu^{2+}+L^{4-} = Cu_2L$	13.7	I=0.1	14
	$Cu^{2+}+HL^{3-} = CuHL^-$	4.02		
Fe^{3+}	$Fe^{3+}+L^{4-} = FeL^-$	15.6	I=0.1	3
	$2Fe^{3+}+L^{4-} = Fe_2L^{2+}$	20.2		
	$2Fe^{3+}+2L^{4-} = Fe_2L_2^{2-}$	36.2		

Stability constants of metal-indicator complexes (Cont.)

Metal ion	Reaction	log K	Conditions	Ref.
	$2Fe^{3+}+2L^{4-} = Fe_2L_2^{2-}$	37.6	0.1M KCl	15
	$Fe^{3+}+2HL^{3-} = Fe(HL)_2^{3-}$	6.4		16
Ni^{2+}	$Ni^{2+}+2L^{4-} = NiL_2^{6-}$	9.26	I=0.1	17
Pd^{2+}	$2Pd^{2+}+L^{4-} = Pd_2L$	9.80	0.1M $NaNO_3$	18
	$2Pd^{2+}+2L^{4-} = Pd_2L_2^{4-}$	15.27		
	$Pd^{2+}+HL^{3-} = PdHL^-$	4.9		
Sc^{3+}	$Sc^{3+}+HL^{3-} = ScHL$	5.12		19
	$Sc^{3+}+2HL^{3-} = Sc(HL)_2^{3-}$	11.94		
Ti^{4+}	$Ti(OH)_2^{2+}+HL^{3-} = Ti(OH)_2HL^-$	5.64		20
UO_2^{2+}	$UO_2^{2+}+HL^{3-} = UO_2HL^-$	11.6	I=0.1	4
	$2UO_2^{2+}+L^{4-} = (UO_2)_2L$	18.3		

x in the case of formation of monoprotonated complexes the sequence of replacement of protons through metal ion is different than that in the case of deprotonation in absence of metal ion.

xx probably this is a constant for AlHL.

Conditional stability constants of complexes

Metal ion	Metal:Reagent ratio	log K	Conditions	Ref.
Al (III)	1:1	4.3	pH 4.0, 0.2M KCl	21
Be (II)	1:1	4.5	pH 6.0, 0.1M $NaClO_4$	22
Cd (II)	1:2	9.0	pH 11.0	23
Co (II)	1:2	8.0	pH 10.5-11.5	24
Cu (II)	1:1	4.1	pH 6.5, 0.1M $NaClO_4$	25
Dy (III)	1:1	4.4	pH 6.0	26
Eu (III)	1:1	4.6	pH 6.0	26
Fe (III)	1:1	4.9	pH 3.0, 0.1M $NaClO_4$	21
	1:1	4.5	pH 3.44, 0.1M $NaClO_4$	27
	2:2	14.7	pH 3.44, 0.1M $NaClO_4$	27
Ga (III)	1:1	6.3		28
Gd (III)	1:1	4.7	pH 6.0	26
Hf (IV)	1:1	4.8	pH 2.0	29
Ho (III)	1:1	6.4	pH 6.0	26
In (III)	1:1	4.6	pH 4.0	21
Mg (II)	1:2	9.3	pH 11.0	21
Pd (II)	1:1	4.9	pH 4.0	21
	1:1	4.75	pH 3.5-8.0	30
Sc (III)	1:1	5.6	pH 5.0	21
Sm (III)	1:1	5.1	pH 6.0	26

Conditional stability constants of complexes (Cont.)

Metal ion	Metal:Reagent ratio	log K	Conditions	Ref.
Tb (III)	1:1	4.8	pH 6.0	26
Th (IV)	1:1	~4.5	pH 4.5, 0.15M NH_4NO_3	31
	1:2	11.3	pH 5.6	32
Ti (IV)	1:1	4.5	pH 4.5	29
U (VI)	1:1	4.6	pH 5.0	33
Y (III)	1:1	4.3	pH 6.0	21
Zr (IV)	1:1	5.0	pH 2.5	29

Spectral characteristics of the indicator

Ion	λ_{max} nm	ϵ_{max}x10^{-4}	Colour	Ref.
H_5L^+	542	7.8	pink	2
	545,399		red-violet	12
H_4L	466	2.3		2
	541,399	5.53(λ=540)	red-violet	12
H_3L^-	466	2.3	orange	2
	469	1.15(λ=500)	orange	12
H_2L^{2-}	490	2.24	red	2
	499	1.49(λ=500)	red	12
HL^{3-}	430	2.24	yellow	2
	429		yellow	12
L^{4-}	598	7.56	blue	2
	598	5.53(λ=600)	blue-violet	12

Spectral characteristics of metal-indicator complexes

Metal ion	Metal:Reagent ratio	λ_{max} nm	ϵ_{max}x10^{-4}	Colour	Ref.
Al (III)	1:1	545		red	21
	1:1 (AlHL)	570	8.5		11
	1:1 (AlL^-)	546	6.4		
	1:2	545	7.6^x 5.9^{xx}	red	10
	1:3	585	5.1		34
Be (II)	1:1 (2:2, ?)	540		red	22
	1:1 (BeL^{2-})	490	2.7	red	12
	1:1 ($BeHL^-$)	568	5.1	red-violet	
	2:1 (Be_2L)	565		red-violet	
	2:2 ($Be_2L_2^{4-}$)	540	7.0	red	
Cd (II)	1:2	540		red	23
Co (II)	1:1	567	3.9	blue	35
	1:2	567	3.3		36
Cr (III)	1:2	560		red-violet	37
	2:3	610		blue	
Cu (II)	1:1	580		violet	25
	1:1	540		red	14
	2:1	586		violet	14

Spectral characteristics of metal-indicator complexes (Cont.)

Metal ion	Metal:Reagent ratio	λ_{max} nm	ϵ_{max}x10^{-4}	Colour	Ref.
Fe (III)	1:1	570		red-violet	21
	1:1	570	7.0		38
	1:1	596		blue-violet	3
	1:3	630	5.5		39
	2:2	582		violet	3
Ga (III)	1:2	547	5.0		40
Hf (IV)	1:1	510		red	29
In (III)	1:1	530		red	21
	1:1	580	1.8	violet	41
La (III)	1:2	500			26
Mg (II)	1:2	545		red	21
Ni (II)	1:1	567	3.9	violet	35
Pd (II)	1:1	585		violet	21,30
	1:2	610	4.3		40
Sc (III)	1:1	560		red-violet	21
	1:2	550	2.7	red-violet	42
Th (IV)	1:1	550		red-violet	31
	1:2	554	3.2	red-violet	32
Ti (IV)	1:1	520		red	29
U (VI)	1:1	585		violet	33
	1:1	590	5.8	violet	4
	2:1	585			
	1:1	582	2.0(λ=590)	red	
Y (III)	1:1	490		red	21
Zr (IV)	1:1	530		red	29
	1:2	560	4.1		43

x in urotropin buffer

xx in acetate buffer

Purification of the indicator (Ref. 44). The sodium salt of Chromazurol S (commercial product) is converted into free acid by precipitation with hydrochloric acid (1+1). The non-sulphonated dye is removed by repeated extraction with ethyl ether. Extraction of Chromazurol B, as an impurity, is possible also from aqueous acetic solution of commercial Chromazurol S with several portions of acidified (HCl) and pure ethyl ether. Afterwards the free acid of Chromazurol S is precipitated from aqueous solution by hydrochloric acid (1+1). Purification in small amounts is possible by using paper chromatography (Ref. 45).

Purity check (Ref. 44) was carried out by thin layer chromatography on silica gel using as solvent 0.05M EDTA in n-butanol - acetic acid - water(7+1+3) or i-propanol - 25% ammonia - water (8+1+2). Several spots are usually obtained, the highest is the non-sulphonated Chromazurol B present in variable amounts.

The indicator is normally used as a 0.1-0.4% aqueous solution.

Typical applications of the indicator. Direct titration of Al (pH 4), Ca (pH 11), Cu (pH 6-6.5), Fe (pH 2-3), Mg (pH 10-11), Ni (pH 8-11), Lanthanides (pH 8), Th (pH 2-3), V (pH 4); especially recommended for Al (pH 4), Fe (pH 2-3), Th (pH 2-3). Also in back-titration determination of Al with Fe(III), Cu(II) or Zn(II) solution as titrants at pH 6.

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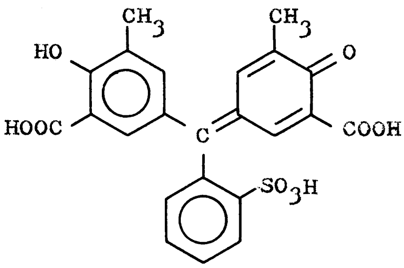
5. ERIOCHROME CYANINE R

Synonyms: Alizarol Cyanine RC
Chromoxane Cyanine RA
Omega Chrome Cyanine GR
Pontachrome Blue ECR
Solochrome Cyanine R
Eriochrome Cyanine RC
(the commercial product is usually a trisodium salt)

Chemical names:

3[(3-Carboxy-4-hydroxy-5-methyl-phenyl)-(2-sulphophenyl) methylene] -5-methyl-6-oxo-1,4-cyclohexanediene-1-carboxylic acid
2″-Sulpho-3,3′-dimethyl-4-hydroxyfuchsone-5,5′-dicarboxylic acid
3,3′-Dicarboxy-phenolsulphophthalein
5-[α(3-Carboxy-5-methyl-4-oxo-2,5-cyclohexanediene-1-ylidene)-o--sulphobenzyl]-3-methylsalicylic acid

Colour index: C.I. 43820, Mordant Blue 3



H_4L

Protonation constants of the indicator

log K_1 -OH	log K_2 -COOH	log K_3 -COOH	log K_4 =OH^+	Conditions	Ref.
11.83	5.74	1.46		0.2M KNO_3	1
12.1	5.45	2.32	<1.0	I=0.1	2
11.85	5.47	2.23	-4.9	0.1M $NaClO_4$	3

Stability constants of metal-indicator complexes [x]

Metal ion	Reaction	log K	Conditions	Ref.
Al^{3+}	$Al^{3+}+H^++L^{4-} = AlHL$	14.1	I=0.1	2
	$AlHL+2HL^{3-} = Al(HL)_3^{6-}$	8.1		
	$Al^{3+}+L^{4-} = AlL^-$	13.66	I=0.1	4
	$Al^{3+}+H^++L^{4-} = AlHL$	18.25		
	$Al^{3+}+2H^++L^{4-} = AlH_2L^+$	22.29		
Be^{2+}	$Be^{2+}+HL^{3-} = BeHL^-$	11.85	0.1M $NaClO_4$	3
	$2Be^{2+}+2L^{4-} = Be_2L_2^{4-}$	28.3		
Fe^{3+}	$Fe^{3+}+L^{4-} = FeL^-$	17.9	0.1M KCl	5
	$2Fe^{3+}+L^{4-} = Fe_2L^{2+}$	22.5		
	$2Fe^{3+}+2L^{4-} = Fe_2L_2^{2-}$	37.9		
Mg^{2+}	$Mg^{2+}+OH^-+L^{4-} = MgOHL^{3-}$	8.65	I=0.1	4

[x] In the case of formation of monoprotonated complexes the sequence of replacement of protons through metal ion is different than that in the case of deprotonation in absence of metal ion.

Conditional stability constants of complexes

Metal ion	Metal:Reagent ratio	log K	Conditions	Ref.
Al(III)	1:1	4.6–5.1	pH 4.5	6
Ga(III)	1:1	5.8	pH 3.5	7
	1:1	4.5–5.1	pH 3.5	6
Gd(III)	1:2	9.8		8
Ho(III)	1:2	9.8		8
Hf(IV)	1:1	5.0	pH 1.0	9
	1:2	9.5	pH 1.8	
In(III)	1:1	5.5	pH 3.5	7
Lu(III)	1:2	9.2		8
Nd(III)	1:2	9.6		8
Pr(III)	1:2	10.6		8
Rh(III)	1:2	9.7–10.3	pH 4.0	10
Sm(III)	1:2	9.6		8
Ti(III)	1:1	5.9–6.9	pH 3.8–4.5	11
	1:2	10.4–11.6	pH 3.8–4.5	
Tl(III)	1:1	5.1	pH 3.5	7
Tm(III)	1:2	9.6		8
V(III)	1:1	5.0–6.0	pH 3.8–4.5	11
	1:2	10.2–10.3	pH 3.8–4.5	
V(V)	1:1	4.6	pH 3.0–5.5	12
Yb(III)	1:2	9.1		8

Spectral characteristics of the indicator

Ion	λ_{max} nm	$\epsilon_{max} x10^{-4}$	Colour	Ref.
H_5L^+	510		red-orange	1
	522,398		red-violet	3
H_4L	510		red-orange	1
	510	5.99 (λ=512)	red-violet	3
H_3L^-	480		red-orange	1
	476		orange	3
H_2L^{2-}	520		red	1
	517	1.33 (λ=512)	red	3
HL^{3-}	445		yellow	1
	444		yellow	3
L^{4-}	585		violet	1
	585	3.85	blue-violet	3

Spectral characteristics of metal-indicator complexes

Metal ion	Metal:Reagent ratio	λ_{max} nm	ϵ_{max}x10^{-4}	Colour	Ref.
Al(III)	1:1	540	3.2	violet	13
	1:1	550	4.3	violet	2
	1:3 ($Al(HL)_3^{6-}$)	535	8.4	red-violet	
Be(II)	1:1 ($BeHL^-$)	547	4.65	red	3
	2:2	522	7.98	red	
	1:1 (BeL^{2-})	500			
	2:1 (Be_2L)	547		red	
Cr(III)	1:1	540	2.6	violet	14
Ga(III)	1:1	550	2.2	violet	13
Hf(III)	1:1	520	1.9	red	8
	1:2	560	0.75	violet	
Mg(II)	1:1	570	0.22	violet	4
Th(IV)	1:2	530	4.0		19
Tl(III)	1:1	650	1.02	blue	15
Zr(IV)	2:1	540	3.2	violet	16

Purification of the indicator has been carried out as follows (Ref. 17): 4 g Eriochrome Cyanine R were dissolved in 60 cm^3 water and 40 cm^3 of concentrated hydrochloric acid was added with stirring. The precipitated acid was filtered using a Büchner funnel and washed with 10 cm^3 of (1+1) HCl. The moist precipitate was dissolved in about 100 cm^3 of chloroform and filtered to remove the remaining aqueous phase. The chloroform solution was extracted with two 100 cm^3 portions of water, the combined aqueous extracts were evaporated to dryness. The product was ground and dried for 1 hour at 60°C.

Purity check (Ref. 18) has been carried out by thin layer chromatography on silica gel using as solvent 0.05M EDTA in n-butanol - acetic acid - water (7+1+3) or i-propanol - 25% ammonia-water (8+1+2). Always appear two spots of variable relative intensity belonging to two structural forms of the dye.

The indicator is normally used as 0.1-0.4% aqueous or 0.1% ethanolic solution.

Typical applications of the indicator. Direct titration of: Al (pH 5-6), Ca (pH 11.5), Fe (pH 2-3), Mg (pH 10), Th (pH 2-2.5), Zr (pH 1.3-1.5).

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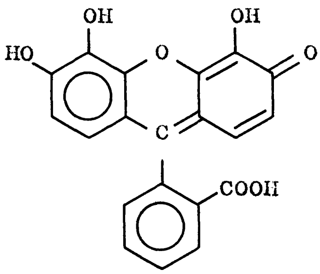
6. GALLEIN

Synonyms: Pyrogallolphthalein
Galleina

Chemical names:
4,5,6-Trihydroxy-3-oxo-9-(2′-carboxyphenyl)-3H-xanthen-9-yl
3′,4′,5′,6′-Tetrahydroxyfluoran
4,5-Dihydroxyfluorescein
3′,4′,5′,6′-Tetrahydroxy-3-oxo-1,3-dihydro-9′H-spiro[isobenzofuran-1,9-xanthene]

Colour index: C.I. 45445, Mordant Violet 25



H_4L

Protonation constants of the indicator

log K_1 -OH	log K_2 -OH	log K_3 -OH (at carbon 6)	log K_4 -COOH	log K_5 $=OH^+$	Conditions	Ref.
	11.5	6.7	4.6	1.5	I=0.45, 10% EtOH	1
12.75	9.37	5.92		1.75		2
		6.3		1.8	0.1M $NaClO_4$	3
		6.11	4.80	1.53	I=1.0	4[x]
11.24	9.20	5.87	4.63	1.48	I=1.0, 10% EtOH	5[x]

[x] also data for other ionic strengths were given.

Stability constants of metal-indicator complexes

Metal ion	Reaction	log K	Ref.
$InOH^{2+}$	$InOH^{2+} + 2H_5L^+ = InOH(H_3L)_2 + 4H^+$	10.3	6

Conditional stability constants of complexes

Metal ion	Metal:Reagent ratio	log K	Conditions	Ref.
Bi (III)	1:1	5.2	pH 2.3	7
Zr (IV)	3:2	4.79	pH 2.3	8

Spectral characteristics of the indicator

Ion	λ_{max} nm	ϵ_{max}x10^{-4}	Ref.
H_6L^{2+}	452	2.46	1
H_5L^{+}	460 466	2.40 2.67	1 5
H_4L	460-480	2.6	1,5
H_3L^{-}	507	1.00	5
H_2L^{2-}	530 540	3.32 3.82	1 5
HL^{3-}	567 532	2.00 1.55	1 5
L^{4-}	575 580	2.2 2.07	1 5

Spectral characteristics of metal-indicator complexes

Metal ion	Metal:Reagent ratio	λ_{max} nm	ϵ_{max}x10^{-4}	Colour	Ref.
Bi (III)	1:1	574	1.57	violet	7
In (III)	1:1 1:2	534 530	1.22 1.8	red-violet red	9 6
Sn (IV)	1:4	495	6.5	red	4
Zr (IV)	3:2	530	0.77	red	8

Purification of the indicator (Ref. 1). The crude product may be purified by acetylation. The acetyl derivative was crystallized twice from benzene, m.p. of product 247-248°C. The acetyl derivative was hydrolyzed in alkaline solution and the free product precipitated with hydrochloric acid, washed with water, diethyl ether and dried. The product was further recrystallized three times from ethanol.

Purity check by potentiometric titration with sodium hydroxide in presence of ascorbic acid (to prevent oxidation).

Typical applications of the indicator: Titrations of Bi (pH 1-2.3) and Cd pH (6.8-10).

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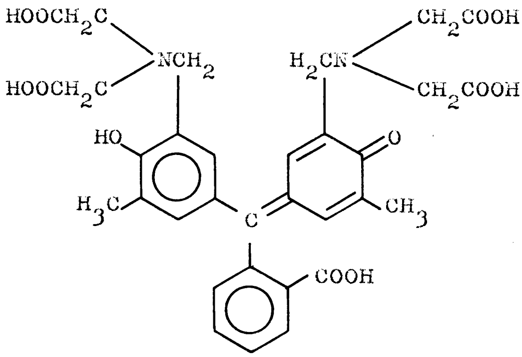
7. METALPHTHALEIN

Synonyms: o-Cresolphthalein Complexone
Phthalein Complexone
Phthalein Purple
Metylphthalexon

Chemical names:
4{[3-(N,N-Bis-carboxymethyl)-aminomethyl-4-hydroxy-5-methyl-phenyl] (2-carboxyphenyl) methylene}-2[(N,N-bis-carboxymethyl) aminomethyl] -6--methyl-1,4-cyclohexanediene-1-one
3,3'-Bis[N,N'-di(carboxymethyl)-aminomethyl] -o-cresolphthalein
3,3'-Dimethyl-5,5'-[N,N'-di (carboxymethyl) -aminomethyl] -phenolphthalein
o-Cresolphthalein-5,5' bis[(methylimino) diacetic acid]
N,N'-[(3-Oxo-1,3-dihydro-isobenzofuran-1-yliden) bis-(6-hydroxy-5-methyl-phen-3,1-ylene) methylene] bis [N-(carboxymethyl) glycine]

Colour index: -



H_6L

Protonation constants of indicator (Ref. 1) in 0.1M KCl, t=20°C

log K_1 $\equiv NH^+$	log K_2 $\equiv NH^+$	log K_3 -OH	log K_4 -COOH	log K_5 -COOH	log K_6 -COOH
12.0	11.4	7.8	7.0	2.9	2.2

Stability constants of metal-indicator complexes (0.1M KCl, t=20°C)

Metal ion	Reaction	log K	Ref.
Ba^{2+}	$Ba^{2+}+L^{6-} = BaL^{4-}$	6.2	1
	$2Ba^{2+}+L^{6-} = Ba_2L^{2-}$	9.2	
	$Ba^{2+}+HL^{5-} = BaHL^{3-}$	4.8	
	$Ba^{2+}+H_2L^{4-} = BaH_2L^{2-}$	2.3^x	
	$Ba^{2+}+H_3L^{3-} = BaH_3L^{-}$	1.3	
Ca^{2+}	$Ca^{2+}+L^{6-} = CaL^{4-}$	7.8	1
	$2Ca^{2+}+L^{6-} = Ca_2L^{2-}$	12.8	

Stability constants of metal-indicator complexes (0.1M KCl, t=20°C) (Cont.)

Metal ion	Reaction	log K	Ref.
	$Ca^{2+}+HL^{5-} = CaHL^{3-}$	6.9	
	$Ca^{2+}+H_2L^{4-} = CaH_2L^{2-}$	3.2	
	$Ca^{2+}+H_3L^{3-} = CaH_3L^{-}$	2.3	
Mg^{2+}	$Mg^{2+}+L^{6-} = MgL^{4-}$	8.9	1
	$2Mg^{2+}+L^{6-} = Mg_2L^{2-}$	14.1	
	$Mg^{2+}+HL^{5-} = MgHL^{3-}$	7.5	
	$Mg^{2+}+H_2L^{4-} = MgH_2L^{2-}$	3.6	
	$Mg^{2+}+H_3L^{3-} = MgH_3L^{-}$	2.2	
Zn^{2+}	$Zn^{2+}+L^{6-} = ZnL^{4-}$	24.9	1
	$2Zn^{2+}+L^{6-} = Zn_2L^{2-}$	15	
	$Zn^{2+}+HL^{5-} = ZnHL^{3-}$	13.8	
	$Zn^{2+}+H_2L^{4-} = ZnH_2L^{2-}$	10.2	
	$Zn^{2+}+H_3L^{3-} = ZnH_3L^{-}$	6.0	
	$Zn_2L^{2-}+H^{+} = Zn_2HL^{-}$	5.9	

x The constant for reaction $BaHL^{3-}+H^{+} = BaH_2L^{2-}$ given in the paper as log K =6.7 seems to be wrong (probably printing error).

Conditional stability constants of complexes

Metal ion	Metal:Reagent ratio	log K	Conditions	Ref.
Ba(II)	1:1	4.6	pH 11.3, I=0.1	2
Sr(II)	1:1	5.0	pH 11, I=0.1	2

Spectral characteristics of the indicator (Ref. 1)

Ion	λ_{max} nm	ϵ_{max}x10^{-4}	Colour
H_2L^{4-}	575	0.2	light rose
HL^{5-}	575	1.1	red
L^{6-}	575	6.0	red

Species containing three or more protons do not absorb in visible spectral region.

Spectral characteristics of metal-indicator complexes

Metal ion	Metal:Reagent ratio	λ_{max} nm	ϵ_{max}x10^{-4}	Colour	Ref.
Ba (II)	2:1	570	7.0	red	1
Ca (II)	2:1	560	6.5	red	1
Mg (II)	2:1	550	2.5	red	1
Mo (VI)	1:1	370	0.5		3

Purity of indicator (Ref. 1) may be examined by paper chromatography using as eluent ethanol - water - phenol (6+3+1) ; for colour development is taken NaOH.

Purification (Ref. 1) from unsubstituted and monosubstituted cresolphthaleins has been carried out by dissolving the dye in sodium acetate solution followed by careful fractional precipitation with HCl. The precipitates obtained at higher acidities contain the pure indicator. These were washed with cold water and dried in vacuum at 30°C, the product being a monohydrate m.p. 186°C.

The indicator is used either as a 0.5% aqueous solution or as a screened indicator solution having 0.1 g of the dye, 0.005 g Methyl Red and 0.005 g Diamine Green B in 100 ml water containing a few drops of aqueous ammonia. Both solutions are stable for one week. The screened indicator is used in amounts 0.2 ml for (Ca) or 0.4 ml for (Ba and Sr).

Typical applications of the indicator: Titration of Ba (pH 10.5-11), Ca (pH 10-11), Sr (pH 10.5-11). It has been especially recommended for Sr at pH 10.5-11 (Ref. 4). Also in back-titration determination of Ni with Cu(II) solution as titrant at pH 10.

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8. METHYL THYMOL BLUE

Synonyms: Methylthymol Blue Complexone
(the commercial product is usually a tetrasodium salt)

Chemical names:

4{[3-(N,N-Bis-carboxymethyl)-aminomethyl-4-hydroxy-5-isopropyl-2-methyl-phenyl] -(2-sulphophenyl) methylene} -2[(N,N-bis-carboxymethyl)-aminomethyl] -3-methyl-6-isopropyl-1,4-cyclohexanediene-1-one

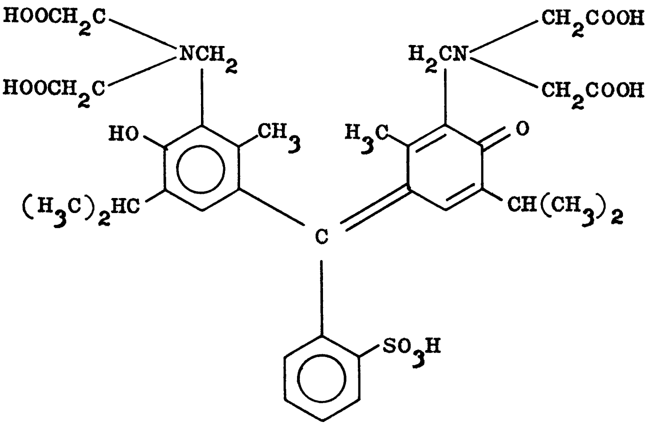
3,3'-Bis[N,N -di(carboxymethyl)-aminomethyl] -thymolsulphonphthalein

[4' -Hydroxy-5,5 -diisopropyl-2,2 -dimethyl-2 -sulphofuchsone-3,3 -diyl-bis-methylenenitrilo] tetraacetic acid

Thymolsulphonphthalein-3',3"-bis[(methyleneimino) diacetic acid]

{3H-2,1-Benzoxathiol-3-ylidene-bis[(6-hydroxy-5-isopropyl-2-methyl-phen-3,1-ylene) methylene]} bis[N-carboxymethyl-glycin] -S,S-dioxide

Colour index: -



H_6L

Protonation constants of indicator

log K_1	$\equiv NH^+$	12.9		13.4	12.5
log K_2	$\equiv NH^+$	11.1		11.2	10.6
log K_3	-OH	6.9	7.4	7.2	7.02
log K_4	-COOH	3.0	3.8	4.5	3.1
log K_5	-COOH	2.0	3.3		1.9
log K_6	-COOH	1.8[x]	3.0[x]		-1.9 (in 8M $HClO_4$)
log K_7	-COOH				
Conditions		0.1M KNO_3	0.2M KNO_3		0.1M $NaClO_4$, 25°C
Reference		1	2	3	4

x Doubtful as potentiometric measurements

Stability constants of metal-indicator complexes

Metal ion	Reaction	log K	Conditions	Ref.
Ba^{2+}	$Ba^{2+}+L^{6-} = BaL^{4-}$	6.93	0.1M KNO_3	5
	$2Ba^{2+}+L^{6-} = Ba_2L^{2-}$	11.58		
	$BaL^{4-}+H^+ = BaHL^{3-}$	11.2		
	$BaHL^{3-}+H^+ = BaH_2L^{2-}$	8.06		
	$Ba_2L^{2-}+H^+ = Ba_2HL^-$	8.5		
Bi^{3+}	$Bi^{3+}+H_3L^{3-} = BiH_3L$	12.49	0.5M $NaClO_4$	6
Ca^{2+}	$Ca^{2+}+L^{6-} = CaL^{4-}$	8.25	0.1M KNO_3	5
	$2Ca^{2+}+L^{6-} = Ca_2L^{2-}$	13.63		
	$CaL^{4-}+H^+ = CaHL^{3-}$	10.9		
	$CaHL^{3-}+H^+ = CaH_2L^{2-}$	7.35		
	$Ca_2L^{2-}+H^+ = Ca_2HL^-$	7.7		

Stability constants of metal-indicator complexes (Cont.)

Metal ion	Reaction	log K	Conditions	Ref.
Co^{2+}	$Co^{2+}+L^{6-} = CoL^{4-}$	12.69	0.1M KNO_3	1
	$2Co^{2+}+L^{6-} = Co_2L^{2-}$	23.69		
	$CoL^{4-}+H^+ = CoHL^{3-}$	10.84		
	$CoHL^{3-}+H^+ = CoH_2L^{2-}$	6.33		
	$Co_2L^{2-}+H^+ = Co_2HL^-$	3.8		
Cr^{3+}	$Cr^{3+}+H_3L^{3-} = CrH_3L$	3.9	0.1M $NaClO_4$	4
	$2Cr^{3+}+H_3L^{3-} = Cr_2H_3L^{3+}$	8.2		
Cu^{2+}	$Cu^{2+}+L^{6-} = CuL^{4-}$	14.05	0.1M KNO_3	1
	$2Cu^{2+}+L^{6-} = Cu_2L^{2-}$	26.45		
	$CuL^{4-}+H^+ = CuHL^{3-}$	10.18		
	$CuHL^{3-}+H^+ = CuH_2L^{2-}$	6.08		
	$Cu_2L^{2-}+H^+ = Cu_2HL^-$	2.2		
	$Cu_2L^{2-}+2OH^- = Cu_2(OH)_2L^{4-}$	2.9		
Fe^{3+}	$Fe^{3+}+H_2L^{4-} = FeH_2L^-$	20.56	0.1M $NaClO_4$	7
Ga^{3+}	$Ga^{3+}+H_3L^{3-} = GaH_3L$	11.43		8
	$GaH_3L+H_5L^- = Ga(H_4L)_2^-$	4.88		
In^{3+}	$In^{3+}+H_2L^{4-} = InH_2L^-$	13.60	0.1M $NaClO_4$	9
	$In^{3+}+H_3L^{3-} = InH_3L$	5.3	1M $NaClO_4$	10
	$In^{3+}+2H_3L^{3-} = In(H_3L)_2^{3-}$	9.5		
	$2In^{3+}+HL^{5-} = In_2HL^+$	23.6		
Lu^{3+}	$Lu^{3+}+2H_2L^{4-} = Lu(H_2L)_2^{5-}$	11.1		11
Mg^{2+}	$Mg^{2+}+L^{6-} = MgL^{4-}$	8.87	0.1M KNO_3	5
	$2Mg^{2+}+L^{6-} = Mg_2L^{2-}$	14.67		
	$MgL^{4-}+H^+ = MgHL^{3-}$	10.8		
	$MgHL^{3-}+H^+ = MgH_2L^{2-}$	7.04		
	$Mg_2L^{2-}+H^+ = Mg_2HL^-$	7.3		
	$MgL^{4-}+OH^- = Mg(OH)L^{5-}$	2.69		
	$Mg_2L^{3-}+2OH^- = Mg_2(OH)_2L^{5-}$	3.44		
Nd^{3+}	$Nd^{3+}+H_2L^{4-} = NdH_2L^-$	5.0		11
Ni^{2+}	$Ni^{2+}+L^{6-} = NiL^{4-}$	12.66	0.1M KNO_3	1
	$2Ni^{2+}+L^{6-} = Ni_2L^{2-}$	23.93		
	$NiL^{4-}+H^+ = NiHL^{3-}$	10.56		

Stability constants of metal-indicator complexes (Cont.)

Metal ion	Reaction	log K	Conditions	Ref.
	$NiHL^{3-}+H^+ = NiH_2L^{2-}$	6.59		
	$Ni_2L^{2-}+H^+ = Ni_2HL^-$	3.51		
Pr^{3+}	$Pr^{3+}+H_2L^{4-} = PrH_2L^-$	5.2		11
Sc^{3+}	$Sc^{3+}+H_3L^{3-} = ScH_3L$	12.55	0.1M $NaClO_4$	12
	$Sc^{3+}+H_2L^{4-} = ScH_2L^-$	16.55		
Sr^{2+}	$Sr^{2+}+L^{6-} = SrL^{4-}$	7.05	0.1M KNO_3	5
	$2Sr^{2+}+L^{6-} = Sr_2L^{2-}$	11.63		
	$SrL^{4-}+H^+ = SrHL^{3-}$	11.1		
	$SrHL^{3-}+H^+ = SrH_2L^{2-}$	7.93		
	$Sr_2L^{2-}+H^+ = Sr_2HL^-$	8.3		
Th^{4+}	$Th^{4+}+H_3L^{3-} = ThH_3L^+$	6.7	1M $NaClO_4$	13
	$Th^{4+}+2H_3L^{3-} = Th(H_3L)_2^{2-}$	10.8		
	$2Th^{4+}+HL^{5-} = Th_2HL^{3+}$	25.3		
UO_2^{2+}	$UO_2^{2+}+H_2L^{4-} = UO_2H_2L^{2-}$	6.0	0.5M $NaClO_4$	13
	$2UO_2^{2+}+H_2L^{4-} = (UO_2)_2H_2L$	7.3		
Y^{3+}	$2Y^{3+}+2L^{6-} = Y_2L_2^{6-}$	37.0	I=0.2	2
Yb^{3+}	$Yb^{3+}+2H_2L^{4-} = Yb(H_2L)_2^{5-}$	11.2		11
Zn^{2+}	$Zn^{2+}+L^{6-} = ZnL^{4-}$	13.31	0.1M KNO_3	1
	$2Zn^{2+}+L^{6-} = Zn_2L^{2-}$	24.41		
	$ZnL^{4-}+H^+ = ZnHL^{3-}$	10.56		
	$ZnHL^{3-}+H^+ = ZnH_2L^{2-}$	6.11		
	$Zn_2L^{2-}+H^+ = Zn_2HL^-$	3.3		

Conditional stability constants of complexes

Metal ion	Metal:Reagent ratio	log K	Conditions	Ref.
Be (II)	1:1	5.8	pH 5.0	14
	?	11.7	pH 8.0	15
Ce (III)	1:1	6.2	pH 6.5	16
Cr (III)	1:1	5.8	pH 4-5	17[x]
Fe (III)	1:1	5.5	pH 2.5	18
	1:2	9.5	pH 5.8	
Gd (III)	1:1	5.6	pH 5.6, I=0.4 ($GdHL^{2-}$)	19
	2:1	8.4	pH 3.2-5.2, I=0.4 ($Gd_2H_2L^{2-}$)	
	1:1	5.1	pH 8, I=0.4, (GdH_2L^-)	

Conditional stability constants of complexes (Cont.)

Mtal ion	Metal:Reagent ratio	log K	Conditions	Ref.
La(III)	1:1	4.8	pH 6.5, I=0.4 ($LaHL^{2-}$)	19
	2:1	7.5	pH 3.2-5.2, I=0.4 ($La_2H_2L^{2+}$)	
	1:1	3.8	pH>8 (LaH_2L^-)	
	1:1	6.1	pH 6.5	16
	2:2	35.8	pH 5.7-6.7, 0.2M $NaNO_3$	20
Mg(II)	1:1	6.9	pH 10.8	14
Mn(II)	1:1	6.9	pH 7.0	21
Nb(V)	1:1	4.6	pH 2	22
Nd(III)	1:1	5.1	pH>8, I=0.4, ($NdHL^{2-}$)	19
	2:1	7.9	pH 3.2-5.2, I=0.4 ($Nd_2H_2L^{2+}$)	
	1:1	4.5	pH 6.5 (NdH_2L^-)	
Ni(II)	1:1	6.7	pH 7.0	23
Pb(II)	1:1	5.7	pH 5.8	24
Pd(II)	1:1	4.1	pH 6.8-7.5	25
	1:2	9.8	0.02-0.05M $HClO_4$	
Pr(III)	1:1	4.9	pH>8, I=0.4 ($PrHL^{2-}$)	19
	2:1	7.7	pH 3.2-5.2, I=0.4, ($Pr_2H_2L^{2+}$)	
	1:1	4.3	pH 6.5, I=0.4 (PrH_2L^-)	
Sc(III)	1:1	4.1	pH 2.75-3.55	26
	1:2	7.3		
Sm(III)	1:1	5.4	pH>8, I=0.4 ($SmHL^{2-}$)	19
	2:1	8.1	pH 6.5, I=0.4 ($Sm_2H_2L^{2+}$)	
	1:1	5.0	pH 6.5, I=0.4 (SmH_2L^-)	
Th(IV)	1:2	11.6	pH 4-4.5	27[x]
Tl(III)	1:1	13.1	pH 2.5, I=0.1	28
	1:2	6.8	pH 5.5, I=0.1	
V(V)	1:1	4.3	pH 4-4.7, I=0.01	29
	1:2	10.05	pH 6-6.5, I=0.01	
Y(III)	1:1	6.9	pH 6.5	16
	1:1	5.8	pH>8, I=0.4 (YHL^{2-})	19
	2:1	8.7	pH 3.2-5.2, I=0.4 ($Y_2H_2L^{2+}$)	
	1:1	5.2	pH 6.5, I=0.4 (YH_2L^-)	
Yb(III)	1:1	6.3	pH 5.6	30
Zn(II)	1:1	6.7	pH 5	31[x]
Zr(IV)	1:1	5.0	1M $HClO_4$	32

[x] Data not quite consistent with those in previous Table.

Spectral characteristics of the indicator

Ion	λ_{max} nm	$\epsilon_{max}x10^{-4}$	Colour	Ref.
H_6L	545 435	2.45(λ=550) 1.89	red	4 1
H_5L^-	445 435	1.13(λ=475) 1.89	yellow	4 1
H_4L^{2-}	445 435	0.98(λ=475) 1.89	yellow	4 1
H_3L^{3-}	595 435	0.08(λ=580) 1.89	yellow-green	4 1
H_2L^{4-}	600 607	1.8 (λ=600) 2.15	green-blue	4 1
HL^{5-}	600 458	0.67(λ=600) 1.2	pale-blue	4 1
L^{6-}	605 617	2.9 (λ=600) 4.29	blue	4 1

The given colours are in various papers different, particularly for the higher protonated species.

Spectral characteristics of metal-indicator complexes

Metal ion	Metal:Reagent ratio	λ_{max} nm	$\epsilon_{max}x10^{-4}$	Colour	Ref.
Al (III)	1:1	590	1.9	violet	33
Be (II)	1:1	500		orange	14
Bi (III)	1:1 1:2	590 500			6
Ca (II)	1:1	610	1.7	blue	34
Ce (III)	1:1	600	2.1	blue	16
Co (II)	1:1 (CoH_2L^{2-})	440	1.76	yellow	1
	1:1 ($CoHL^{3-}$)	611	2.70	blue	
	1:1 (CoL^{4-})	584	2.08	violet	
	2:1 (Co_2L^{2-})	618	3.57	blue	
Cr (III)	1:1 1:1	580 525	0.6	violet	17 4
Cu (II)	1:1 1:1 (CuH_2L^{2-})	595 450	1.3 1.88	violet yellow	34 1
	1:1 ($CuHL^{3-}$)	583	2.15	violet	
	1:1 (CuL^{4-})	538	1.88	red	
	2:1 (Cu_2L^{2-})	611	1.93	blue	
Fe (III)	1:1 1:2 1:1 1:2	610 515 600 510	1.73 0.3 0.65 1.2	blue brown-red blue red	7 18
Ga (III)	1:1	580	1.95	violet	35
Hf (IV)	1:1	570	1.87	red	32
In (III)	1:1 1:2 1:1 (InH_3L)	600 510 530;570	1.75 0.55 1.12;1.8	blue red 	9 10

Spectral characteristics of metal-indicator complexes (Cont.)

Metal ion	Metal:Reagent ratio	λ_{max} nm	ϵ_{max}x10^{-4}	Colour	Ref.
	1:2 $In(H_3L)_2^{3-}$	530	2.15		
	2:1 (In_2HL^+)	585	2.6		
La(III)	1:1	600	1.7	blue	16
Mg(II)	1:1	605	2.0	blue	34
	1:1	610	1.52	blue	36
Mn(II)	1:1	615	1.9	blue	34
	1:1	582	0.64	violet	21
Nb(V)	1:1	560	1.3	red	22
Ni(II)	1:1	615	2.1	blue	34
	1:1	580	1.3	blue-violet	23
Pb(II)	1:1	600	1.95	blue	24
	1:1	620	1.5	blue	34
Pd(II)	1:1	530	2.1	red	25
	1:2	500	1.5	red	
Sc(III)	1:1	588	2.4	violet	26
Th(IV)	1:2	585	3.9	violet	27
	1:2	580	5.0	violet	37
U(VI)	1:1	510	1.1	red	38
V(V)	1:1	590		blue	29
	1:2	520		red	
Y(III)	1:1	600	1.6	blue	16
	1:2	606	2.3	blue	2
Yb(III)	1:1	570	2.1	blue	30
Zn(II)	1:1	596	1.9	blue	31
	1:1	595	1.4	blue	34
Zr(IV)	1:1	600	5.0	blue	39
	1:1	580	2.17	red	32

Purification of the indicator (Ref. 40) The sample of the commercial product was dissolved in water placed on a cellulose column and eluted with butanol containing 0.1% acetic acid. Three fractions were obtained, the third being the indicator contaminated with sodium iminodiacetate. The crude product was separated on an acid from cation - exchange column from iminodiacetic acid and a small amount of semi-Methyl Thymol Blue. The ion-exchange purification was repeated several times until the obtained product had a purity of at least 97%. The purity was checked by a pH titration.

The indicator is used as a 1% aqueous solution or solid, diluted 1:100 with KNO_3.

Typical application of the indicator. Direct titration of: Bi (1M HNO_3 or pH 3), Mg (pH 10), Mn (pH 6-6.5), Pb (pH 6), Sc (pH 6.5), Th (pH 1-3.5), and Zn (pH 6-6.5); It has been especially recommended for Pb at pH 6. Also in back-titration determination of Pb with Pb(II) solution as titrant at pH 5.5-6 and Cd with Ca(II) solution at pH 12.

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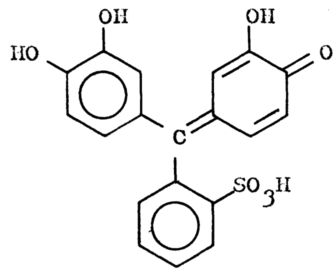
9. PYROCATECHOL VIOLET

Synonyms: **Catechol Violet**
Catecholsulphonephthalein
Brenzcatechinviolett

Chemical names:
4[3,4-Dihydroxyphenyl-(2'-sulphophenyl)methylene]-2-hydroxy-1,4 cyclohexanediene-1-one
3,3'',4''-Trihydroxy-fuchsone-2'-sulphonic acid
4,4'-(3H-2,1-Benzoxathiol-3-ylidene) dipyrocatechol-S,S-dioxide
3,4-Dihydroxy-α-(3-hydroxy-4-oxo-cyclohexa-2,5-dienylidene) diphenyl -methane-2-sulphonic acid

Colour index:



H_4L

Protonation constants of the indicator

log K_1 m-OH	log K_2 m-OH	log K_3 p-OH	log K_4 $=OH^+$	Conditions	Ref.
11.73	9.80	7.82		I=0.2	1
12.50					2
11.7	9.75		0.1		3
11.93	10.00	8.01		I=0	4
	10.230	7.921		I=0.01	5
10.86	7.87	6.91		0.2M KNO_3	6[x]
	8.33	7.51	0.26		7[x]
12.8	9.76	7.80	0.8	0.1M $NaClO_4$	8

[x] these values seem to be too low (?)

Stability constants of metal-indicator complexes

Metal ion	Reaction	log K	Conditions	Ref.
Al^{3+}	$Al^{3+}+L^{4-} = AlL^-$	19.1	I=0.2	9
	$2Al^{3+}+L^{4-} = Al_2L^{2+}$	24.1	I=0.2	
	$Al^{3+}+HL^{3-} = AlHL$	25.1	I=0.2	10
	$AlHL+HL^{3-} = Al(HL)_2^{3-}$	22.3		
	$Al(HL)_2^{3-}+HL^{3-} = Al(HL)_3^{6-}$	20.7		
	$Al^{3+}+H_2L^{2-} = AlH_2L^+$	7.9	0.1M $NaClO_4$	11
	$Al^{3+}+H_2L^{2-}+HL^{3-} = AlH_3L_2^{2-}$	19.4		
	$Al^{3+}+H_2L^{2-}+2HL^{3-} = AlH_4L_3^{5-}$	27.3		
	$2Al^{3+}+HL^{3-} = Al_2HL^{3+}$	17.3		
Bi^{3+}	$Bi^{3+}+L^{4-} = BiL^-$	27.1	I=0.2	9
	$2Bi^{3+}+L^{4-} = Bi_2L^{2+}$	32.3		
Cd^{2+}	$Cd^{2+}+L^{4-} = CdL^{2-}$	8.1	I=0.2	12
	$CdL^{2-}+H^+ = CdHL^-$	9.5		
Co^{2+}	$Co^{2+}+L^{4-} = CoL^{2-}$	9.0	I=0.2	12
	$CoL^{2-}+H^+ = CoHL^-$	9.2		

Stability constants of metal-indicator complexes (Cont.)

Metal ion	Reaction	log K	Conditions	Ref.
Cr^{3+}	$Cr^{3+}+H_2L^{2-} = CrH_2L^+$	8.70	0.1M $NaClO_4$	13
	$CrH_2L^++HL^{3-} = CrH_3L_2^{2-}$	11.15		
	$CrH_3L_2^{2-}+HL^{3-} = CrH_4L_3^{5-}$	8.96		
Cu^{2+}	$Cu^{2+}+L^{4-} = CuL^{2-}$	16.5	I=0.2	12
	$CuL^{2-}+H^+ = CuHL^-$	6.4		
Fe^{3+}	$Fe^{3+}+H_2L^{2-} = FeH_2L^+$	7.5	0.1M $NaClO_4$	11
	$Fe^{3+}+H_2L^{2-}+HL^{3-} = FeH_3L_2^{2-}$	19.3		
	$Fe^{3+}+H_2L^{2-}+2HL^{3-} = FeH_4L_3^{5-}$	27.2		
	$2Fe^{3+}+HL^{3-} = Fe_2HL^{3+}$	22.2		
	$FeOH^{2+}2H_2L^{2-} = FeOH(H_2L)_2^{2-}$	13.80	0.5M KNO_3	14
Ga^{3+}	$Ga^{3+}+2H_2L^{2-} = Ga(H_2L)_2^-$	17.05	0.1M NaCl	15
	$Ga^{3+}+L^{4-} = GaL^-$	11.2	I=0.2	9
	$2Ga^{3+}+L^{4-} = Ga_2L^{2+}$	26.8		
In^{3+}	$In^{3+}+L^{4-} = InL^-$	18.1	I=0.2	9
	$2In^{2+}L^{4-} = In_2L^{2+}$	22.9		
	$In(OH)_2^++H_2L^{2-} = In(OH)_2(H_2L)^-$	17.05		16
	$InOH^{2+}+2H_2L^{2-} = InOH(H_2L)_2^{2-}$	9.10		
Mg^{2+}	$Mg^{2+}+L^{4-} = MgL^{2-}$	4.4	I=0.2	12
	$MgL^{2-}+H^+ = MgHL^-$	11.0		
Mn^{2+}	$Mn^{2+}+L^{4-} = MnL^{2-}$	7.1	I=0.2	12
	$MnL^{2-}+H^+ = MnHL^-$	10.0		
Ni^{2+}	$Ni^{2+}+L^{4-} = NiL^{2-}$	9.4	I=0.2	12
	$NiL^{2-}+H^+ = NiHL^-$	9.2		
Pb^{2+}	$Pb^{2+}+L^{4-} = PbL^{2-}$	13.3	I=0.2	12
	$PbL^{2-}+H^+ = PbHL^-$	8.7		
Sn^{4+}	$Sn^{4+}+H_2L^{2-} = SnH_2L^{2+}$	15.31	1.0M NaCl pH 3.0	7
	$Sn^{4+}2H_2L^{2-} = Sn(H_2L)_2$	29.92		
	$2Sn^{4+}+H_2L^{2-} = Sn_2H_2L^{6+}$	20.43		
Th^{4+}	$Th^{4+}+L^{4-} = ThL$	23.4	I=0.2	9
	$2Th^{4+}+L^{4-} = Th_2L^{4+}$	27.8		
	$Th^{4+}+H_2L^{2-} = ThH_2L^{2+}$	9.83	0.1M $NaClO_4$	8
	$ThH_2L^{2+}+HL^{3-} = ThH_3L_2^-$	15.38		

Stability constants of metal-indicator complexes (Cont.)

Metal ion	Reaction	log K	Conditions	Ref.
	$ThH_3L_2^- + HL^{3-} = ThH_4L_3^{4-}$	13.62		
	$2Th^{4+} + HL^{3-} = Th_2HL^{5+}$	20.04		
UO_2^{2+}	$UO_2^{2+} + H_2L^{2-} = UO_2H_2L$	7.05	0.1M $NaClO_4$	8
	$UO_2H_2L + H_2L^{2-} = UO_2H_4L_2^{2-}$	5.60		
	$2UO_2^{2+} + HL^{3-} = (UO_2)_2HL^+$	14.7		
Zn^{2+}	$Zn^{2+} + L^{4-} = ZnL^{2-}$	10.4	I=0.2	12
	$ZnL^{2-} + H^+ = ZnHL^-$	8.5		
Zr^{4+}	$Zr^{4+} + L^{4-} = ZrL$	27.4	I=0.2	9
	$2Zr^{4+} + L^{4-} = Zr_2L^{4+}$	31.6		

Conditional stability constants of complexes

Metal ion	Metal:Reagent ratio	log K	Conditions	Ref.
Ga(III)	1:2	14.7	in presence of acetate, pH 5.75-6.7	17
Ge(IV)	1:2	8.7-9.2	pH 6.5	18
Nb(V)	2:1	5.4	pH 1.5-4.7	19
V(IV)	2:1	9	pH 4.2	20
W(VI)	1:1	5.5	pH 1.5-2.5	19

Spectral characteristics of the indicator

Ion	λ_{max}, nm	$\epsilon_{max} \times 10^{-4}$	Colour	Ref.
H_5L^+, H_4L	550^x, 560^+	2.0^x, 2.0^+	red	1^x, 6^+
H_3L^-	445^x, 445^+	1.49^x 1.40^+	yellow	1^x, 6^+
H_2L^{2-}	590^x, 600^+	3.03^x 1.96^+	violet	1^x, 6^+
HL^{3-}	560-580	1.59	red-violet	6
HL^{3-}, L^{4-}	560	1.55	red-violet	1
L^{4-}	660		blue	2

^{x} values from (Ref. 1) $^+$ values from (Ref. 6)

Spectral characteristics of metal-indicator complexes

Metal ion	Metal:Reagent ratio	λ_{max}, nm	$\epsilon_{max} x 10^{-4}$	Colour	Ref.
Al(III)	1:1	620	2.5-2.9	blue	9
	1:1 (pH 3)	550			21
	1:1 (pH 4-7)	580			
	1:1 (pH 8-10)	640			
	1:2	560	4.5		23
	1:2	580	6.8		35
Bi(III)	1:1 (pH 1-4)	550-610			21
	1:1	610	2,5-2.9	blue	9
Cd(II)	1:1	610		blue	12
Cr(III)		590	2.63	violet	24
Cu(II)	1:1	630		blue	12
	1:1 (pH 5-10)	650			21
	1:2 (pH 5-7)	580			
Fe(III)	1:2	610	6.24	blue	25
Ga(III)	1:1	615	2.5-2.9	blue	9
	1:2	620	3.33	blue	26
	1:1 (pH 2)	550			21
	1:1 (pH 3-10)	640			
	1:2 (pH 3-7.5)	550			
	1:2 ($Ga(H_2L)_2$)	580	7.3		15
Ge(IV)	1:1 (pH 5-9)	620			21
	1:2 (pH 5-9)	560			
	1:2	555	5.5	purple	27
In(III)	1:1	620	2.5-2.9	blue	9
	1:1 (pH 5.5-7.5)	630			21
	1:1 (pH 8-10)	630			
	1:2 (pH 5.5-7.5)	580			
Mg(II)	1:1	640		blue	12
Mn(II)	1:1	640		blue	12
Nb(III)	1:1	575	2.5		36
Nb(V)	2:1	600		blue	19
Ni(II)	1:1	650		blue	12
	1:1 (pH 8-10)	650			21
Pb(II)	1:1 (pH 6-9)	650			
	1:2 (pH 6-7)	580			
Sb(III)	1:1	580		violet	28
	1:1 (pH 1-5)	560			21
Sc(III)	1:1 (pH 5-10)	550,640			21
	1:2 (pH 5-8)	600			
Sn(IV)	1:1	555	6.5	red	29
	1:1 (pH 1-7)	550			21
	1:1 (pH 3-8)	640			
	1:2 (pH 1-7)	600			
		552	6.85		30
Th(IV)	1:1	615		blue	9
Ti(IV)	1:2	690			32
Zn(II)	1:1	630		blue	12
	1:1 (pH 7-10)	650			21
Zr(IV)	1:1	610	2.5-2.9	blue	9
	1:2 (pH 2-6)	625	3.5		33
R.E.	1:1 (pH 6-10)	650			21
	1:2 (pH 6)	580			

Purification of the indicator (Ref. 34) has been achieved by crystalization from hot ethanol (brownish-green crystals) or by crystallization from glacial acetic acid (green crystals). Both crystaline forms were dried at room temperature under reduced pressure.

The indicator is normally used as a 0.1% solution in water. It may be also used in the presence of cetyltrimethylammonium bromide (Ref. 22).

Typical applications of the indicator: Direct titration of Bi (pH 2-3), Th (pH 2-3), Cd (pH 10), Cu (pH 5-6.3, 9,3), Mn (pH 9.3), Ni (pH 8-9.3), Zn (pH 10). It has been especially recommended for Th (pH 2-3) and Bi (pH 2-3). Also in back-titration determination of Al, Fe(III), In with Cu(II) solution as titrant at pH 6-7 and Bi, Fe(III), Ga, In, Ni, Th, Tl, with Bi(III) solution at pH 2-3.

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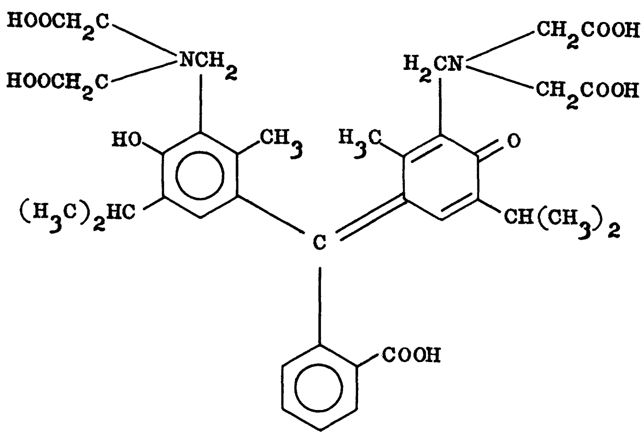
10. THYMOLPHTHALEXON

Synonyms: Thymolphthalein complexone

Chemical names:

4-[[2-Methyl-3-(N,N'-bis-carboxymethyl)-aminomethyl-4-hydroxy-5-isopropyl][2-carboxyphenyl] methylene]-2-[(N,N-bis-carboxymethyl) aminomethyl] -3-methyl-6-isopropyl-1,4-cyclohexanediene-1-one
3,3'-Bis[N,N'-di(carboxymethyl)-aminomethyl] thymolphthalein
Thymolphthalein-bis-(methylaminodiacetic acid)
3',3"-Bis[N,N-bis (carboxymethyl) aminomethyl] -5',5"-diisopropyl-2',2"-dimethyl-phenolphthalein
N,N'-[(3-Oxo-1,3-dihydro-isobenzofuran-1-ylidene) bis(6-hydroxy-5-isopropyl-2-methyl-phen-3,1-ylene) methylene] bis[N-(carboxymethyl) glycine]

Colour index: -



H_6L

Protonation constants of the indicator

log K_1 $\equiv NH^+$	log K_2 $\equiv NH^+$	log K_3 -OH	log K_4 -COOH	Conditions	Ref.
13.0	10.8	8.7	7.0	I=0.3	1
12.3^x	7.4^x			0.2M $NaNO_3$	2

x. These results appear to be "averages" of K_1, K_2 and K_3, K_4 values, respectively.

Stability constants of metal-indicator complexes

Metal ion	Reaction	log K	Conditions	Ref.
Ca^{2+}	$Ca^{2+}+L^{6-} = CaL^{4-}$	7.2	I=0.3	3
	$CaL^{4-}+H^{+} = CaHL^{3-}$	10.7		
	$CaHL^{3-}+H^{+} = CaH_2L^{2-}$	9.1		
	$2Ca^{2+}+2L^{6-} = Ca_2L_2^{8-}$	42.7^{x}	0.2M $NaNO_3$	2

x This value is probably based on the wrong protonation constants of the indicator.

Conditional stability constants of complexes

Metal ion	Metal:Reagent ratio	log K	Conditions	Ref.
Ti (III)	1:1	4.42	i-BuOH	4

Spectral characteristics of the indicator

Ion	λ_{max}, nm	$\epsilon_{max} x10^{-4}$	Colour	Ref.
H_2L^{4-}	605	0.12	light blue	1
HL^{5-}	605	1.05	blue	
L^{6-}	605	2.6	blue	

Species containing three or more protons do not absorb in visible spectral region.

Spectral characteristics of metal-indicator complexes

Metal ion	Metal:Reagent ratio	λ_{max}, nm	$\epsilon_{max} x10^{-4}$	Colour	Ref.
Ba (II)	1:1	605	4.3	blue	2
Ca (II)	1:1	605	4.1	blue	2
Mg (II)	1:1	605	2.8	blue	2
	1:1	605	1.6		5
Nd (III), Pr (III), Sm (III), Yb (III)	2:3	594		blue	6,7
Sr (II)	1:1	605	3.5	blue	2
Mo (VI)	1:1	370	0.3		8

Purification of the indicator (Ref. 3) has been achieved by dissolving the dye in sodium acetate solution followed by fractional precipitation with HCl.

The indicator is normally used as solid mixture diluted with KNO_3

Typical application of the indicator. Direct titration of Ba (pH 10-11), Ca (pH 10.5-11), Mn (pH 10). It has been recommended for Ba (pH 10-11). Also in back titration determination of Ba, Mn, Sr with Ca(II) solution as titrant at pH 12.

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11. XYLENOL ORANGE

Synonyms: -

Chemical names:

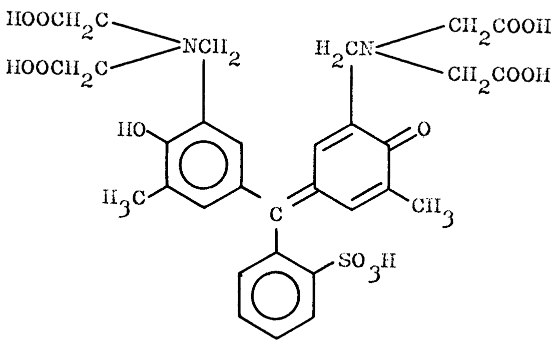
3{[3-N,N-bis-carboxymethyl aminomethyl] -4-hydroxy-5-methylphenyl}(2-sulphophenyl)methylene -2[(N,N-bis-carboxymethyl) aminomethyl -6-methyl-1,4-cyclohexanediene-1-one

3,3′-Bis[N,N-di(carboxymethyl) aminomethyl] -o-cresol-sulphonphthalein

4′-Hydroxy-5,5′-dimethyl-2″ sulpho-fuchsone-3,3′-diyl-bis(methylene nitrilo) tetraacetic acid

{3H-2,1-Benzoxathiol-3-ylidene-bis[(6-hydroxy-5-methyl-phen-3,1-ylene)methylenenitrilo]}tetraacetic acid, -S,S-dioxide

Colour index: -



H_6L

Protonation constants of indicator

log K_1	$\equiv NH^+$	12.23	12.28		12.20		12.00	10.58
log K_2	$\equiv NH^+$	10.56	10.46	10.0	8.4	10.35	10.30	9.34
log K_3	-OH	6.74	6.46	6.1	6.4	6.66	7.50	6.09
log K_4	-COOH	2.85	3.23	3.20	3.7	2.79	4.49	2.56
log K_5	-COOH	2.32	2.58	2.15	2.6	2.11	2.74	2.24
log K_6	-COOH	<1.5	1.15	1.25			2.00	1.45
log K_7	-COOH	-1.04	0.76					1.43

Protonation constants of indicator. (Cont.)

log K_8	$=OH^+$	-1.83	-1.09					-1.24
log K_9	$-SO_3H$	-3.32	-1.74					
Conditions		I=0.1	I=0.2			I=0.1		I=1.0
Reference		1	2	3	4	5	6	7

Stability constants of metal-indicator complexes

Metal ion	Reaction	log K	Conditions	Ref.
Al^{3+}	$Al^{3+}+H_2L^{4-}+H_3L^{3-} = AlH_5L_2^{4-}$	11.79	0.1M $NaClO_4$	8
	$2Al^{3+}+H_3L^{3-} = Al_2H_3L^{3+}$	13.64		
Ba^{2+}	$Ba^{2+}+L^{6-} = BaL^{4-}$	6.67	0.1M KNO_3	9
	$2Ba^{2+}+L^{6-} = Ba_2L^{2-}$	11.24		
	$BaL^{4-}+H^+ = BaHL^{3-}$	10.5		
	$BaHL^{3-}+H^+ = BaH_2L^{2-}$	7.54		
	$Ba_2L^{2-}+H^+ = Ba_2HL^-$	8.0		
Bi^{3+}	$Bi^{3+}+H_3L^{3-} = BiH_3L$	9.80	I=1.0	10
	$Bi^{3+}+2H_3L^{3-} = Bi(H_3L)_2^{3-}$	15.53		
	$2Bi^{3+}+2L^{6-} = Bi_2L_2^{6-}$	75.6	0.2M $NaNO_3$	11
Ca^{2+}	$Ca^{2+}+L^{6-} = CaL^{4-}$	8.65	0.1M KNO_3	9
	$2Ca^{2+}+L^{6-} = Ca_2L^{2-}$	14.67		
	$CaL^{4-}+H^+ = CaHL^{3-}$	10.4		
	$CaHL^{3-}+H^+ = CaH_2L^{2-}$	6.71		
	$Ca_2L^{2-}+H^+ = Ca_2HL^-$	6.9		
Dy^{3+}	$2Dy^{3+}+2L^{6-} = Dy_2L_2^{6-}$	47.6	0.2M $NaNO_3$	12
Fe^{3+}	$2Fe^{3+}+L^{6-} = Fe_2L$	39.8	0.2M $NaNO_3$	13
	$Fe^{3+}+H_3L^{3-} = FeH_3L$	8.85	I=0.5	14
	$Fe^{3+}+H_2L^{4-} = FeH_2L^-$	14.16		
	$Fe^{3+}+H_4L^{2-}+H_3L^{3-} = FeH_7L_2^{2-}$	13.87		
	$Fe^{3+}+2H_3L^{3-} = Fe(H_3L)_2^{3-}$	15.55		
Ga^{3+}	$Ga^{3+}+H_2L^{4-} = GaH_2L^-$	15.16	I=0	15
	$Ga^{3+}+H_2L^{4-} = GaH_2L^-$	11.92	I=0.2	16
	$Ga^{3+}+H_5L^- = GaH_5L^{2+}$	7.0	I=0.01	17
	$Ga(H_5L)^{2+}+H_5L^- = Ga(H_5L)_2^+$	4.5		
	$Ga^{3+}+H_4L^{2-} = GaH_4L^+$	9.37	I=0.1	8

Stability constants of metal-indicator complexes. (Cont.)

Metal ion	Reaction	log K	Conditions	Ref.
	$Ga_2(H_2L)_2^{2-}+2H_2L^{4-}=2Ga(H_2L)_2^{3-}$	12.49		
Gd^{3+}	$2Gd^{3+}+2L^{6-} = Gd_2L_2^{6-}$	43.1	0.2M $NaNO_3$	12
In^{3+}	$In^{3+}+H_2L^{4-} = InH_2L^-$	14.2	I=0	15
	$In^{3+}+H_2L^{4-} = InH_2L^-$	14.31	0.1M $NaClO_4$	18
	$In^{3+}+2H_2L^{4-} = In(H_2L)_2^{5-}$	24.63		
La^{3+}	$La^{3+}+HL^{5-} = LaHL^{2-}$	12.9		6
Mg^{2+}	$Mg^{2+}+L^{6-} = MgL^{4-}$	9.02	0.1M KNO_3	9
	$2Mg^{2+}+L^{6-} = Mg_2L^{2-}$	15.16		
	$MgL^{4-}+H^+ = MgHL^{3-}$	10.3		
	$MgHL^{3-}+H^+ = MgH_2L^{2-}$	6.56		
	$Mg_2L^{2-}+H^+ = Mg_2HL^-$	6.8		
	$MgL^{4-}+OH^- = Mg(OH)L^{5-}$	2.43		
	$Mg_2L^{2-}+2OH^- = Mg_2(OH)_2L^{4-}$	3.21		
Pb^{2+}	$Pb^{2+}+L^{6-} = PbL^{4-}$	15.24	I=0.1	5
	$Pb^{2+}+H^++L^{6-} = PbHL^{3-}$	25.32		
	$Pb^{2+}+2H^++L^{6-} = PbH_2L^{2-}$	30.01		
	$2Pb^{2+}+L^{6-} = Pb_2L^{2-}$	26.70		
Sc^{3+}	$Sc^{3+}+H_2L^{4-} = ScH_2L^-$	13.04	I=0.1	19
	$Sc^{3+}+H_3L^{3-} = ScH_3L$	5.95	I=0.1	20
	$2Sc^{3+}+2L^{6-} = Sc_2L_2^{6-}$	61.2	0.2M $NaNO_3$	11
Sm^{3+}	$2Sm^{3+}+2L^{6-} = Sm_2L_2^{6-}$	47.0	0.2M $NaNO_3$	12
Sr^{2+}	$Sr^{2+}+L^{6-} = SrL^{4-}$	7.71	0.1M KNO_3	9
	$2Sr^{2+}+L^{6-} = Sr_2L^{2-}$	12.60		
	$SrL^{4-}+H^+ = SrHL^{3-}$	10.4		
	$SrHL^{3-}+H^+ = SrH_2L^{2-}$	7.36		
	$Sr_2L^{2-}+H^+ = Sr_2HL^-$	7.6		
Th^{4+}	$Th^{4+}+H_2L^{4-} = ThH_2L$	12.35	I=0.1	21
	$Th^{4+}+2H_2L^{4-} = Th(H_2L)_2^{4-}$	19.31		
	$2Th^{4+}+H_2L^{4-} = Th_2H_2L^{4+}$	9.71		
	$2Th^{4+}+2L^{6-} = Th_2L_2^{4-}$	59.8	I=0.001	22
	$2Th^{4+}+2L^{6-} = Th_2L_2^{4-}$	52.5	0.2M $NaNO_3$	11
Ti^{3+}	$2Ti^{3+}+2L^{6-} = Ti_2L_2^{6-}$	57.8	0.2M $NaNO_3$	11

Stability constants of metal-indicator complexes. (Cont.)

Metal ion	Reaction	log K	Conditions	Ref.
Tl^{3+}	$2Tl^{3+}+2H_2L^{4-} = Tl_2(H_2L)_2^{2-}$	8.0	I=0.1	23
UO^{2+}	$2UO^{2+}+2L^{6-} = (UO)_2L_2^{8-}$	69.1	I=0.1	22
UO_2^{2+}	$2UO_2^{2+}+2L^{6-} = (UO_2)_2L_2^{8-}$	38.6	0.2M $NaNO_3$	13
VO^{2+}	$VO^{2+}+H_2L^{4-} = VOH_2L^{2-}$	10.48	0.1M $NaClO_4$	24
	$VO^{2+}+H_2L^{4-}+H_5L^{-} = VOH_7L_2^{3-}$	15.67		
VO_2^{+}	$2VO_2^{+} + 2L^{6-}=(VO_2)_2L_2^{10-}$	63.1	0.2M $NaNO_3$	11
Yb^{3+}	$2Yb^{3+}+2L^{6-} = Yb_2L_2^{6-}$	45.7	0.2M $NaNO_3$	12
Zn^{2+}	$Zn^{2+}+L^{6-} = ZnL^{4-}$	15.41	I=0.1	5
	$Zn^{2+}+H^{+}+L^{6-} = ZnHL^{3-}$	24.91		
	$Zn^{2+}+2H^{+}+L^{6-} = ZnH_2L^{2-}$	29.84		
	$2Zn^{2+}+L^{6-} = Zn_2L^{2-}$	25.37		
	$Zn^{2+}+HL^{5-} = ZnHL^{3-}$	12.3	I=0.1	25
	$2Zn^{2+}+L^{6-} = Zn_2L^{2-}$	26.3		
Zr^{4+}	$Zr^{4+}+H_3L^{3-} = ZrH_3L^{+}$	37.80	I=3	7
	$Zr^{4+}+H_4L^{2-} = ZrH_4L^{2+}$	38.68		
	$2Zr^{4+}+L^{6-} = Zr_2L^{2+}$	43.37[x]		
	$2Zr^{4+}+L^{6-} = Zr_2L^{2+}$	31.0[x]	0.2M $NaNO_3$	11

[x] Discrepancy of data is not obvious.

Conditional stability constants of complexes

Metal ion	Metal:Reagent ratio	log K	Conditions	Ref.
Al(III)	2:2	14.3	pH 2.3, I=0.2	26
Bi(III)	1:1	5.1	pH 1-2.3, I=0.02	27
	1:1	5.5	0.1M HNO_3	28
	1:1	5.4	0.05M H_2SO_4	29
Cd(II)	1:1	3.8	pH 5.5, 0.3M KNO_3	30
Ce(III)	1:1	5.5	pH 6.1, 0.1M acetate	31
	1:1	6.4	pH 6.0	32
Co(II)	1:1	18.5	pH 5.8	33
Cr(III)	1:1	6.4	pH 4-5	34
	1:1	3.6	pH 1.7	35
Cu(II)	1:1	18.9	pH 5.5	33
Fe(III)	1:1	5.7	0.05M $HClO_4$	36
Ga(III)	1:1	7.0	pH 2	30
	1:2	4.5		
Gd(III)	1:1	4.7	pH 5.5, I=0.1	4

Conditional stability constants of complexes. (Cont.)

Metal ion	Metal:Reagent ratio	log K	Conditions	Ref.
Hf(IV)	1:1	6.5	0.3M $HClO_4$	37
Hg(II)	1:2	11.5	pH 7.1	38
Ho(III)	1:1	5.3	pH 5.5, I=0.1	4
La(III)	1:1	6.4	pH 6.0	32
	1:1	5.8	pH 6.1, 0.1M acetate	31
Lu(III)	1:1	4.9	pH 5.5, I=0.1	4
Mn(II)	1:1	5.9	pH 6.6	39
	1:1	15.1		33
Mo(VI)	2:2	17.0	pH 3.6	26
Nb(V)	1:1	6.7	pH 2.5	40
Nd(III)	1:1	6.0	pH 6.8, 0.1M acetate	31
	1:1	5.0	pH 5.5, I=0.1	4
	1:1	6.8	I=0.1	41
Ni(II)	1:1	4.8	pH 3.0, 0.1M KCl	42
	1:1	7.2	pH 5	43
	1:1	18.0		33
Pd(II)	1:2	10.3	1.1-1.7M $HClO_4$	44
Pr(III)	1:1	5.2	pH 5.5, I=0.1	4
Rh(III)	1:1	3.4	pH 2.5	45
Ru(III)	1:2	9.6	pH 4	46
Sm(III)	1:1	5.0	pH 5.5, I=0.1	4
Th(IV)	1:1	6.17^{x}	pH 2.0, I=0.01	47
	1:2	12.13^{x}	pH 4-5, I=0.01	
Ti(IV)	1:1	3.5	0.02M $HClO_4$, I=0.5	48
Tl(III)	1:1	4.9	pH 1.4	49
Tm(III)	1:1	5.2	pH 5.5, I=0.1	4
U(IV)	1:2	11.5	pH 3.5-3.7	50
V(IV)	1:1	6.4	pH 2.9	51
Y(III)	1:1	5.5	pH 6.1, 0.1M acetate	31
	1:1	6.5	pH 6.0	32
	1:1	7.6^{xx}	0.8M $HClO_4$	52
Yb(III)	1:1	5.1	pH 5.5, I=0.1	4
Zn(II)	1:1	6.1	pH 5.8-6.2	53
	1:1	6.2	pH 6.5	54
Zr(IV)	1:1	7.6	0.8M $HClO_4$	37

x Disagreement with data in Ref. 21.

xx Disagreement with data in Ref. 31, 32.

Spectral characteristics of the indicator

Ion	λ_{max}, nm	$\epsilon_{max}x10^{-4}$	Colour	Ref.
H_9L^{3+}	515	8.08^{x}	red	1
	518	5.58^{x}	red	2
H_8L^{2+}	515	6.54^{x}	red	1
	518	1.19^{x}	red	2
H_7L^{+}	480	1.78^{x}	orange	1

Spectral characteristics of the indicator. (Cont.)

Ion	λ_{max}, nm	ϵ_{max}x10^{-4}	Colour	Ref.
	518	0.149^x	red	2
H_6L	?			
H_5L^-	439	2.62	yellow	1
H_4L^{2-}	434	2.62	yellow	1
H_3L^{3-}	?			
H_2L^{4-}	578	6.09	violet	1
HL^{5-}	578	3.66	violet	1
L^{6-}	582	6.54	violet	1

^{x} Large differences in ϵ_{max} may be due to uncertain purity.

Spectral characteristics of metal-indicator complexes

Metal ion	Metal:Reagent ratio	λ_{max},nm	ϵ_{max}x10^{-4}	Colour	Ref.
Al (III)	1:2	480	2.45	red	8
	2:1	550	3.16	violet	8
	2:2	555	1.53		26
Bi (III)	1:1	560	2.85	red-violet	27
	1:1	530	1.6		55
	1:1	540-545	2.4	red	29
	1:1	510	1.55		56
	2:2	560	1.4	red-violet	11
Cd(II)	1:1	575	1.8	violet	30
Ce (III)	1:1	575	3.1	violet	31
	1:1	570	5.3	violet	32
Cr (III)	1:1	550	1.6	red	34
Dy (III)	2:2	570	2.35		12
Fe (III)	2:1	575			13
	1:1	550	2.7	purple	36
Ga (III)	1:1	530	2.3	red	57
	1:1	545	3.3		58
	1:1	556	3.15	raspberry red	17
	1:2	502	1.6	red	54
	1:2	480	2.4	red	8
	1:2	483	1.7		17
	2:2	550	2.2	violet	8
	3:2	555	4.4		58
Gd (III)	2:2	570	2.1		12
Hf (IV)	1:1	530	1.6	red	37
Hg(II)	1:2	580	1.7	violet	38
In (III)	1:1	560	3.3	violet	59
La (III)	1:1	576	3.2	violet	31
	1:1	570	3.6	violet	32
Mn (II)	1:1	582	2.26	violet	39
Mo (VI)	2:2	490	0.52		26
Nb (V)	1:2	530	2	red	60
Nd (III)	1:1	578	3.8	violet	31

Spectral characteristics of metal-indicator complexes. (Cont.)

Metal ion	Metal:Reagent ratio	λ_{max}, nm	$\epsilon_{max} x10^{-4}$	Colour	Ref.
Ni(II)	1:1	580	1.7	violet	43
Pb(II)	2:1	580	7.74	violet	5
	1:1	584	1.94		61
Ru(III)	1:2	540	1.2		46
Sc(III)	1:1	553	2.4	red-violet	62
	1:1	556	2.9	red-violet	20
	1:1	555	3.34		19
	1:2	500	1.8		19
	1:2	525		red	62
	2:2	560	2.16	red-violet	11
Sm(III)	2:2	570	2.3		12
Sn(IV)	1:2	536	0.2		63
Th(IV)	1:1	535	2.8		47
	1:1	570	3.9		21
	1:2	565	5.5		47
	1:2	580	6.4		21
	2:2	560	3.8		11
	2:1	570	4.5		21
Ti(III)	1:1	502	1.8	red	48
	2:2	485	0.49	orange	11
Tl(III)	1:1	580	1.98		49
	1:1	586	2.68		59
	1:1	590	1.8	red-violet	64
U(IV)	2:2	550		red-violet	22
	1:2	568			50
U(VI)	2:2	510		red	13
V(IV)	1:1	570	3.6		24
	1:2	520	2.4		24
V(V)	1:1	590	2.0		65
	1:2	520	1.3		65
	2:2	560	1.8		11
Y(III)	1:1	578	4.8		31
	1:1	570	4.3		32
Yb(III)	2:2	570	2.2		12
Zn(II)	1:1	574		violet	53
	1:1	570	2.7		50
	2:1	570	6.63		5
Zr(IV)	1:1	535	2.4	red	37
	1:1	550(λ_{opt})	5.3	red-violet	66
	1:1 (ZrH_3L^+)	485	3.1		6
	1:1 (ZrH_4L^{2+})	528	5.98		6
	2:1	560	5.2	red-violet	67
	2:1	560	1.2		11
	2:1	551	9.5		6

Purification of the indicator (Ref. 1). Commercial Xylenol Orange has been purified by dissolving the dye in water followed by separation on a cellulose column using butanol containing 10% acetic acid as eluent. Three fractions were obtained, the third being Xylenol Orange contaminated with a small amounts od sodium iminodiacetate and Semixylenol Orange. The crude product was separated on the cation-exchange column in the acid form. This purification stage was repeated several times until the Xylenol Orange obtained had a purity of 97%.

For purification of Xylenol Orange Sato and coworkers (Ref. 5) propose ion-exchange chromatography on the DEAE-cellulose column with 0.1M NaCl as an eluent.

Purity check by partition chromatography; the indicator assay was controlled by pH titration.

The indicator is normally used as a 0.1% solution in aqueous ethanol.

Typical applications of the indicator. Direct titration of: Bi (pH 1-3), Th (pH 1.6-3.5), Sc (pH 2.2-5), Pb (pH 5-6), Zn (pH 5-6), Cd (pH 5-6), Hg (pH 5-6). It has been especially recommended for Zr in 1M HNO_3. Also in back-titration determination of Al, Bi, Fe(III), Ga, In, Pd, Sn, Th, VO_2^{2+} with Th(IV) solution as titrant at pH 2-3. Tl(III) solution as titrant is used in determination of Al and Ga (pH 3), Fe(III), In, Pd and Sb (pH 4), Ti(IV) (pH 2). Bi(III) solution as titrant is used in determination of Ni and Th (pH 2) and Ti and Zn (pH 4.5). Pb(II) solution as titrant is used in determination of Al and Cu (pH 5) or Sn (IV) (pH 2.5-3.5).

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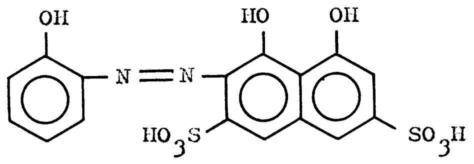
II. AZO INDICATORS

12. ACID CHROME DARK BLUE

Synonyms: Acid Chrome Blue T
Fast Mordant Blue R

Chemical name: 2-(2- Hydroxyphenylazo)-1,8-dihydroxynaphthalene-3,6-disulphonic acid
(the commercial product is a monosodium salt)

Colour Index: 16670



H_5L

Protonation constants of the indicator

log K_1 -OH	log K_2 -OH	log K_3 -OH	Conditions	Ref.
12.4	9.30	7.56		1

Stability constants of the metal-indicator complexes

Metal ion	Reaction	log K	Conditions	Ref.
Ba^{2+}	$Ba^{2+}+2HL^{4-} = Ba(HL)_2^{6-}$	6.2	I~0.002	2
Ca^{2+}	$Ca^{2+}+2HL^{4-} = Ca(HL)_2^{6-}$	9.28	I~0.002	2
Mg^{2+}	$Mg^{2+}+2HL^{4-} = Mg(HL)_2^{6-}$	8.5	I~0.002	3
Sr^{2+}	$Sr^{2+}+2HL^{4-} = Sr(HL)_2^{6-}$	7.11	I~0.002	2
Zn^{2+}	$Zn^{2+}+ 2HL^{4-} = Zn(HL)_2^{6-}$	10.5		4

Spectral characteristics of the indicator

Ion	λ_{max}, nm	ϵ_{max}x10^{-4}	Colour	Ref.
H_2L^{3-}	525			1
HL^{4-}	550			1
L^{5-}	570	1.34	violet	1

Spectral characteristics of metal-indicator complexes

Metal ion	Metal:Reagent ratio	λ_{max}, nm	ϵ_{max}x10^{-4}	Ref.
Ba (II)	1:2	590	3.0	2
Ca (II)	1:2	550	3.7	2
Mg (II)	1:2	550	3.0	3
Sr (II)	1:2	550	3.4	2
Zn (II)	1:2	570	4.54	4

Purification of the indicator -

Purity check -

The indicator is normally used as a 0.1% aqueous solution.

Typical applications of the indicator. Direct titration of: Ca (pH 12), Mg (pH 10), Pb (pH 10), Zn (pH 10).

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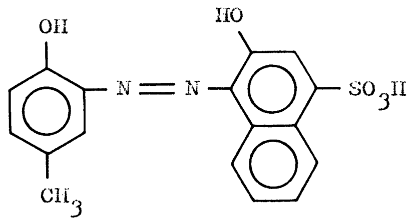
13. CALMAGITE

Synonyms: -

Chemical names:

1-(2-Hydroxy-5-methyl-phenylazo)-2-naphthol-4-sulphonic acid
3-Hydroxy-4-[(6-hydroxy-m-tolyl)azo]-1-naphthalenesulphonic acid
(the commercial product is a monosodium salt)

Colour index: -



H_3L

Protonation constants of the indicator

log K_1 -OH (β-naphthol)	log K_2 -OH (phenol)	Conditions	Ref.
12.35	8.14	I=0.1	1
12.50	7.92	I=0.1	2
12.08	7.84	I=1.0	2
12.87	7.01	I=0.2	3
11.98	8.52		4
12.30	8.15	I=0.1	5

Stability constants of metal-indicator complexes

Metal ion	Reaction	log K	Conditions	Ref.
Al^{3+}	$Al^{3+}+L^{3-} = AlL$	16.58	0.1M $NaClO_4$	5
	$AlL+L^{3-} = AlL_2^{3-}$	16.80		
	$AlL_2^{3-}+L^{3-} = AlL_3^{6-}$	9.90		
Ca^{2+}	$Ca^{2+}+L^{3-} = CaL^-$	6.1	I=0.1	1
Cd^{2+}	$Cd^{2+}+L^{3-} = CdL^-$	12.59	I=0.3	6
Co^{2+}	$Co^{2+}+L^{3-} = CoL^-$	21.03	I=0.3	6
Cu^{2+}	$Cu^{2+}+L^{3-} = CuL^-$	21.70	I=0.3	6
Ga^{3+}	$Ga^{3+}+L^{3-} = GaL$	18.30	I=0.1	5
	$GaL+L^{3-} = GaL_2^{3-}$	16.80		
	$GaL_2^{3-}+L^{3-} = GaL_3^{6-}$	14.30		
In^{3+}	$In^{3+}+L^{3-} = InL$	18.58	I=0.1	5
	$InL+L^{3-} = InL_2^{3-}$	16.82		

Stability constants of metal-indicator complexes. (Cont.)

Metal ion	Reaction	log K	Conditions	Ref.
	$InL_2^{3-}+L^{3-} = InL_3^{6-}$	14.50		
	$In^{3+}+L^{3-} = InL$	17.09	I=0.2	3
	$InL+L^{3-} = InL_2^{3-}$	14.87		
La^{3+}	$La^{3+}+L^{3-} = LaL$	14.60	0.1M $NaClO_4$	4
	$LaL+L^{3-} = LaL_2^{3-}$	7.50		
	$LaL_2^{3-}+L^{3-} = LaL_3^{6-}$	6.07		
Mg^{2+}	$Mg^{2+}+L^{3-} = MgL^-$	8.1	I=0.1	1
Ni^{2+}	$Ni^{2+}+L^{3-} = NiL^-$	21.63	I=0.3	6
Pb^{2+}	$Pb^{2+}+L^{3-} = PbL^-$	12.90	I=0.3	6
Th^{4+}	$Th^{4+}+2L^{3-} = ThL_2^{2-}$	33.2		7
Y^{3+}	$Y^{3+}+L^{3-} = YL$	15.70	0.1M $NaClO_4$	4
	$YL+L^{3-} = YL_2^{3-}$	7.85		
	$YL_2^{3-}+L^{3-} = YL_3^{6-}$	5.9		
Zn^{2+}	$Zn^{2+}+L^{3-} = ZnL^-$	12.31	I=0.3	6
	$Zn^{2+}+L^{3-} = ZnL^-$	12.52	I=0.1	2
	$Zn^{2+}+2L^{3-} = ZnL_2^{4-}$	20.23	I=0.1	
		19.57	I=1.0	

Spectral characteristics of the indicator

Ion	λ_{max}, nm	ϵ_{max}x10^{-4}	Colour	Ref.
H_2L^-	520	2.0	red	1
HL^{2-}	610	1.9	blue	1
L^{3-}	500	1.0	red	1

Spectral characteristics of metal-indicator complexes

Metal ion	Metal:Reagent ratio	λ_{max},nm	ϵ_{max}x10^{-4}	Colour	Ref.
Al(III)	1:3	570	4.2	violet	8
Ca(II)	1:1	520	4.0	red	1
Cd(II)	1:1	560	1.6	red-violet	6
Co(II)	1:1	570	1.8	violet	6
Cu(II)	1:1	520	1.8	red	6
Ga(III)	1:3	545			5
In(III)	1:3	545			5

Spectral characteristics of metal-indicator complexes. (Cont.)

Metal ion	Metal:Reagent ratio	λ_{max}, nm	ϵ_{max}x10^{-4}	Colour	Ref.
Mg(II)	1:1	540	4.6	red-violet	1
Ni(II)	1:1	560	2.3	red-violet	6
Pb(II)	1:1	560	1.5	red-violet	6
Zn(II)	1:1	560	1.2	red-violet	6
	1:2	550	4.0	red-violet	2
Zr(IV)	1:2	600	0.68		9

Purification of the indicator (Ref. 10) from inorganic impurities has been carried out by crystallization from ethanol. The sample of calmagite was converted into the acid form and crystallized from isopropanol + hexane.

Purity check (Ref. 10) by thin layer chromatography on cellulose using as eluent n-propanol-ethyl acetate - water (5+1+4).

The indicator is normally used as 0.05% aqueous solution or 0.1% ethanolic solution.

Typical applications of the indicator. Direct titrations of Ca (pH 10), Mg (pH 10), Zn (pH 8.5-10.5).

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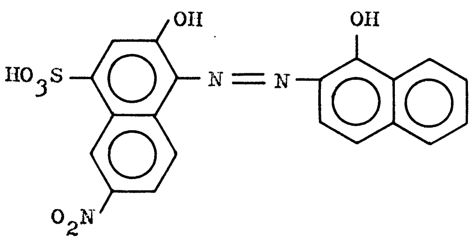
14. ERIOCHROME BLACK T

Synonyms: Calcochrome Black T, Chrome Black TK, Chromogenblack ET, Diamond Blue Black EBS, Omega Chrome Black T, Pontachrome Black TA, Potting Black C, Solochrome Black T

Chemical names:
1-(1-Hydroxy-2-naphthylazo)-6-nitro-2-naphthol-4-sulphonic acid
3-Hydroxy-4-(1-hydroxy-2-naphthylazo)-7-nitro-1-naphthalene sulphonic acid
(the commercial product is a sodium salt)

Colour Index: 14645, Mordant Black 11



$\cdot H_3L$

Protonation constants of the indicator

log K_1 -OH (α-naphthol)	log K_2 -OH (β-naphthol)	log K_3 $-SO_3H$	Conditions	Ref.
11.5	6.35	3.85	I=0.1	1
	6.3		I=0.008	2
11.55			I=0.008	
11.50	6.91		I=0.1	3,4
11.31	6.80		I=0.3	5
10.71	7.16		I=0.1	6

Stability constants of metal-indicator complexes

Metal ion	Reaction	log K	Conditions	Ref.
Ba^{2+}	$Ba^{2+}+L^{3-} = BaL^-$	3.0	I~0.1	7
Ca^{2+}	$Ca^{2+}+L^{3-} = CaL^-$	5.4	I~0.02	2
	$Ca^{2+}+L^{3-} = CaL^-$	5.3	I=0.1	3
Cd^{2+}	$Cd^{2+}+L^{3-} = CdL^-$	12.74	I=0.3	5
Co^{2+}	$Co^{2+}+L^{3-} = CoL^-$	20.0	I=0.3	8
Cu^{2+}	$Cu^{2+}+L^{3-} = CuL^-$	21.38	I=0.3	9
La^{3+}	$La^{3+}+L^{3-} = LaL$	8.80	I=0.1	6
	$LaL+L^{3-} = LaL_2^{3-}$	5.25		
	$LaL_2^{3-}+L^{3-} = LaL_3^{6-}$	4.30		
Mg^{2+}	$Mg^{2+}+L^{3-} = MgL^-$	7.0	I=0.008	2
	$Mg^{2+}+L^{3-} = MgL^-$	7.2	I=0.1	3
	$Mg^{2+}+HL^{2-} = MgL^-+H^+$	-4.85	I=0.15	10
Mn^{2+}	$Mn^{2+}+L^{3-} = MnL^-$	9.6	I=0.1	11
	$MnL^-+L^{3-} = MnL_2^{4-}$	8.0		
Ni^{2+}	$Ni^{2+}+L^{3-} = NiL^-$	20.8	I=0.3	8
Pb^{2+}	$Pb^{2+}+L^{3-} = PbL^-$	13.19	I=0.3	5
VO_2^+	$VO_2^++L^{3-} = VO_2L^{2-}$	14.4	I=0.1	12
	$VO_2L^{2-}+L^{3-} = VO_2L_2^{5-}$	10.9		
Y^{3+}	$Y^{3+}+L^{3-} = YL$	10.70	I=0.1	6
	$YL+L^{3-} = YL_2^{3-}$	9.17		
	$YL_2^{3-}+L^{3-} = YL_3^{6-}$	5.35		
Zn^{2+}	$Zn^{2+}+L^{3-} = ZnL^-$	12.9	I=0.1	11
	$ZnL^-+L^{3-} = ZnL_2^{4-}$	7.1		
	$Zn^{2+}+L^{3-} = ZnL^-$	12.31	I=0.3	9

Spectral characteristics of the indicator

Ion	λ_{max}, nm	ϵ_{max}x10^{-4}	Colour	Ref.
H_3L			red	3
H_2L^-			red	3
HL^{2-}	615	3.2	blue	3
L^{3-}			orange	3

Spectral characteristics of metal-indicator complexes

Metal ion	Metal:Reagent ratio	λ_{max},nm	ϵ_{max}x10^{-4}	Colour	Ref.
Cd(II)	1:1	580	2.9		5
Cu(II)	1:1	500	1	red	9
Er(III)	1:1	640	2.3	blue	13
Gd(III)	1:1	640	2.2	blue	13
La(III)	1:1	640	1.9	blue	13
Mg(II)	1:1	550	2.8		7
	1:1	550	2.2	red	14
Nd(III)	1:1	640	2.1	blue	13
Pb(II)	1:1	580	2.6	violet	5
V(V)	1:2	570			12
Yb(III)	1:1	640	2.4	blue	13
Zn(II)	1:1	580	3.3	violet	9

Purification of the indicator (Ref. 3) has been carried out by crystallization of the indicator (in the acid form) from methanol.

Purity check. -

The indicator is normally used as solid mixture with NaCl (1:200).

Typical application of the indicator. Direct titration of Mg (pH 10), Mn (pH 8-10), Pb (pH 10), lanthanides (pH 8-9), Zn (pH 7-10). It has been especially recommended for Mg (pH 10) and Zn (pH 7-10). Also in back titration determination of Ba and Sr, Bi, Ca, Hg(II), In, Mn, Ni with Mg(II) or Zn(II) solution as titrant at pH 10. Mg(II) solution as titrant is used in determination of Cu (pH 10), Ga (pH 6.5-9.5), Sn(IV)(pH 9), Tl (pH 8). Zn(II) solution as titrant is used in determination of Al (pH 7-8), Cr (pH 9-10), Fe(III)(pH 7), Ga (pH 8-10), Mo(V)(pH 10), Pd (pH 10), lanthanides (pH 8-9), Sn(IV)(pH 9), Tl (pH 8). Mn(II) solution as titrant is used in determination of Al (pH 9-10), Cr (pH 9-10), Cu (pH 6.5), Fe(III) (pH 9), In (pH 10), Ni (pH 10), Pd (pH 8-10), VO_2^+ (pH 10). Pb(II) solution as titrant is used in determination of Ga (pH 8-10), In (pH 10).

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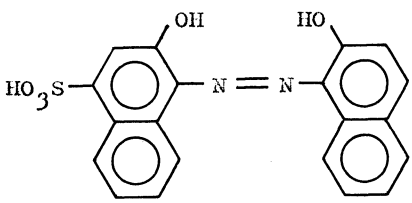
15. ERIOCHROME BLUE BLACK R

Synonyms: Acid Chrome Blue Black
Alizarine Blue OCR
Anthracene Blue Black ERN
Calcon
Chrome Blue Black RC
Chromechtschwarz RN
Chrome Dark Blue ERM
Diamond Blue Black R
Erio R
Eriochrome Blue Black RSS
Solochrome Dark Blue B

Chemical names:
1-(2- Hydroxy-1-naphthylazo)-2-naphthol-4-sulphonic acid
3-Hydroxy-4-[(2-hydroxy-1-naphthyl)-azo]-1-naphthalene sulphonic acid
(the commercial product is a monosodium salt)

Colour Index: 15705, Mordant Black 17



H_3L

Protonation constants of the indicator

log K_1 -OH	log K_2 -OH (in sulphonated ring)	log K_3 $-SO_3H$	Conditions	Ref.
13.5			I=0.08	1
	7.0		I=0.008	1
13.5	7.36	1.0	I=0.1	2,3
12.87	7.01		I=0.2	4

Stability constants of metal-indicator complexes

Metal ion	Reaction	log K	Conditions	Ref.
Al^{3+}	$Al^{3+}+L^{3-} = AlL$	22.5	0.1M NaCl, pH 3-6	5
Be^{2+}	$Be^{2+}+L^{3-} = BeL^-$	~12	0.1M NaCl, pH<7	5
Ca^{2+}	$Ca^{2+}+L^{3-} = CaL^-$	5.25	I=0.02	1
	$Ca^{2+}+L^{3-} = CaL^-$	5.58	I=0.1	2

Stability constants of metal-indicator complexes. (Cont.)

Metal ion	Reaction	log K	Conditions	Ref.
Cd^{2+}	$Cd^{2+}+L^{3-} = CdL_2^{4-}$	10.4	0.1M NaCl, pH>11.5	5
Co^{2+}	$Co^{2+}+2L^{3-} = CoL_2^{4-}$	19.0	0.1M NaCl, pH<9	5
	$Co^{2+}+HL^{2-} = CoHL$	8.7	0.1M NaCl, 100^{o}	
Cu^{2+}	$Cu^{2+}+L^{3-} = CuL^{-}$	21.2	0.1M NaCl, pH~9, (NH_3)	6
	$CuL+OH^{-} = Cu(OH)L^{2-}$	4		
Fe^{3+}	$Fe^{3+}+L^{3-} = FeL$	20.6	0.1M NaCl, pH~4	5
	$FeL+L^{3-} = FeL_2^{3-}$	17-18	0.1M NaCl, pH 6-9	
Ga^{3+}	$Ga^{3+}+2L^{3-} = GaL_2^{3-}$	12.4	I=0	7
In^{3+}	$In^{3+}+L^{3-} = InL$	16.48	I=0.2	4
	$InL+L^{3-} = InL_2^{3-}$	14.66		
	$In^{3+}+L^{3-} = InL$	16.9	0.1M NaCl, pH 4-9	5
La^{3+}	$La^{3+}+HL^{2-} = LaHL^{+}$	5.4	0.1M NaCl, pH 5-7[xx]	5
Mg^{2+}	$Mg^{2+}+L^{3-} = MgL^{-}$	7.56	I=0.08	1
	$Mg^{2+}+L^{3-} = MgL^{-}$	7.64	I=0.1	2
Mn^{2+}	$Mn^{2+}+L^{3-} = MnL^{-}$	10.6	0.1M $NaNO_3$, pH 10	5
[Mo][x]	$[Mo] +H_2L^{-}+2H^{+}=[MoL]$	13.8	0.1M NaCl	5
Ni^{2+}	$Ni^{2+}+L^{3-} = NiL^{-}$	15.4	0.1M NaCl, pH<10	5
Pb^{2+}	$Pb^{2+}+L^{3-} = PbL^{-}$	13.2	0.1M $NaNO_3$, pH~10	5
Th^{4+}	$Th^{4+}+L^{3-} = ThL^{+}$	19.8	0.1M NaCl, pH 4-8	5
Ti^{3+}	$Ti^{3+}+L^{3-} = TiL$	23.4	0.1M NaCl, pH~5	5
Tm^{3+}	$Tm^{3+}+HL^{2-} = TmHL^{+}$	5.6	0.1M NaCl, pH~6[xx]	5
UO_2^{2+}	$UO_2^{2+}+L^{3-} = UO_2L^{-}$	18.9	0.1M NaCl, pH 5-11	5
V^{3+}	$V^{3+}+L^{3-} = VL$	21.7	0.1M NaCl, pH~5	5
VO_2^{2+}	$VO_2^{2+}+L^{3-} = VO_2L^{-}$	16.3	0.1M $NaNO_3$, pH 5-10	5
[W][x]	$[W] + H_2L^{-}+ H^{+} =[WL]$	5.4	0.1M NaCl	5
Y^{3+}	$Y^{3+}+L^{3-} = YL$	13.6	0.1M NaCl, pH 7	5
Zn^{2+}	$Zn^{2+}+L^{3-} = ZnL^{-}$	12.5	I=0.1	2
	$Zn^{2+}+NH_3+L^{3-} = Zn(NH_3)L^{-}$	16.4	I=0.1	8

x The exact composition of Mo(VI) and W(VI) species has not been reported.

xx In presence of 0.1M α-hydroxyisobutyric acid.

Spectral characteristics of the indicator

Ion	λ_{max}, nm	$\epsilon_{max}x10^{-4}$	Colour	Ref.
H_2L^-			pink	2
HL^{2-}			blue	2
L^{3-}			pink	2

Spectral characteristics of metal-indicator complexes

Metal ion	Metal:Reagent ratio	λ_{max}, nm	$\epsilon_{max}x10^{-4}$	Colour	Ref.
Ca (II)	1:1			pink	2
Ce (IV)	1:1	530		brown	9
Ga (III)	1:2	580			7
La (III)	1:1	530		brown	9
Mg (II)	1:1			pink	2
Nd (III)	1:1	530		brown	9
Pr (III)	1:1	530		brown	9
Sm (III)	1:1	530		brown	9
U (VI)	1:2	540	1.87		10

Purification of the indicator (Ref. 3) has been carried out by dissolving the acidic form of the indicator in ethanol, and adding hydrochloric acid (1+20). After slow evaporation of the solvent on a warm steam bath the dye precipitates.

Purity check: -

The indicator is normally used as 0.5% solution in methanol or ethanol, also as Zn - salt (Zinchrome R) (Ref. 11).

Typical application of the indicator. Direct titration of Ca (pH 11.5), Mg (pH 10), Mn (pH 10), Zn (pH 10).

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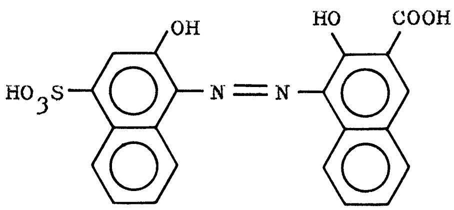
16. KALCES

Synonyms: Dye of Patton and Reeder; Calconcarboxylic acid; Cal-Red; HSN; HHSNN; NN-Indicator

Chemical names:
1-(2-Hydroxy-4-sulpho-1-naphthylazo)-2-hydroxy-3-naphthoic acid
2-Hydroxy-1-(2-hydroxy-4-sulphonaphthylazo)-3-naphthoic acid

Colour Index: -



$\cdot H_4L$

Protonation constants of the indicator

$\log K_1$ -OH	$\log K_2$ -OH (in sulphonated ring)	$\log K_3$ -COOH	$\log K_4$ $-SO_3H$	Conditions	Ref.
13.67	9.26			0.1M KCl	1
13-14	9.4	3.8	1-2	I=0.1	2
		4.4	2.7	0.1M KCl, 50% MeOH	3
14.4	7.6			0.1M KCl, 25% MeOH	3

Stability constants of metal-indicator complexes

Metal ion	Reaction	log K	Conditions	Ref.
Ca^{2+}	$Ca^{2+}+L^{4-} = CaL^{2-}$	5.0	I=0.1	2
	$Ca^{2+}+L^{4-} = CaL^{2-}$	5.85	0.1M KCl	1
	$Ca^{2+}+L^{4-} = CaL^{2-}$	6.3	0.1M KCl, 25% MeOH	3
Mg^{2+}	$Mg^{2+}+L^{4-} = MgL^{2-}$	7.6	0.1M KCl, 25% MeOH	3

Spectral characteristics of the indicator

Ion	λ_{max}, nm	$\epsilon_{max} x10^{-4}$	Colour	Ref.
H_2L^{2-}	~540		red-violet	1
HL^{3-}	620		blue	1
L^{4-}			pale-pink	1

Spectral characteristics of metal-indicator complexes

Metal ion	Metal:Reagent ratio	λ_{max}, nm	$\epsilon_{max}x10^{-4}$	Ref.
Ca(II)	1:1	620		1
U(VI)	1:2	570		4

Purification of the indicator has been carried out by washing of the indicator with 10 per cent hydrochloric acid (Ref. 5).

Purity check: -

The indicator is normally used as solid mixture with Na_2SO_4 (1:100).

Typical application of the indicator. Direct titration of Ca (pH 12-12.5).

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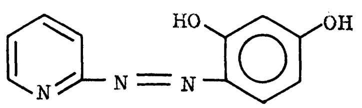
17. PAR

Synonyms: -

Chemical names:
4-(2-Pyridylazo)-1,3-dihydroxybenzene
Pyridyl-(2-azo-4)-resorcin
4-(2-Pyridylazo)resorcinol
1-(2,4-Dihydroxyphenylazo)-pyridine

Colour Index: -



H_2L

Protonation constants of the indicator

log K_1 o-OH	log K_2 p-OH	log K_3 $\equiv NH^+$	Conditions	Ref.
12.5	5.83	2.7	0.1M KNO_3	1
12.31	5.48	2.66	0.1M $NaClO_4$	2
11.9	5.6	3.1	I=0.1	3
11.5	6.20	2.57		4
11.95	5.57	3.03	I=0.1	5
11.98	5.56	3.02	0.1M KNO_3	6
12.4	6.9	2.3	I<0.01, 50% dioxan	7
13.00	7.01	2.35	I=0.1, 50% dioxan	2

Protonation constants of the indicator. (Cont.)

log K_1 o-OH	log K_2 p-OH	log K_3 $\equiv NH^+$	Conditions	Ref.
13.42	6.87	2.31	I 0.01, 50% dioxan	8
12.36	6.54	2.49	50% dioxan	9
12.12	6.81	2.93	I=0.06, 50% EtOH	10
	5.9	2.64	30% DMF	11

Stability constants of metal-indicator complexes

Metal ion	Reaction	log K	Conditions	Ref.
Al^{3+}	$Al^{3+}+L^{2-}=AlL^+$	11.5	0.1M $NaClO_4$	12
	$AlOH^{2+}+2HL^-=AlOH(HL)_2$	23.52	I=1.0, 50% EtOH	13
	$Al^{3+}+H_3L^+=AlHL^{2+}+2H^+$	-1.35	I=0.06, 50% EtOH	10
Bi^{3+}	$Bi^{3+}+HL^- = BiHL^{2+}$	17.2	0.1M $NaClO_4$	14
	$Bi^{3+}+HL^- = BiHL^{2+}$	18.2	I=0.1	15
Cd^{2+}	$Cd^{2+}+HL^- = CdHL^+$	10.5	0.1M $NaClO_4$	14
	$Cd^{2+}+HL^- = CdHL^+$	11.5	I=0.1	15
	$Cd^{2+}+2L^{2-} = CdL_2^{2-}$	19.6		
Co^{2+}	$Co^{2+}+2L^{2-} = CoL_2^{2-}$	21.1	0.1M $NaClO_4$	16
	$Co^{2+}+2L^{2-} = CoL_2^{2-}$	21.5	0.1M $NaClO_4$	17
	$Co^{2+}+HL^- = CoHL^+$	10.0	I=0.1	18
	$CoHL^++HL^- = Co(HL)_2$	7.1		
	$Co^{2+}+HL^- = CoHL^+$	14.8	I=0.1, 50% dioxan	18
	$CoHL^++HL^- = Co(HL)_2$	8.2		
	$Co^{2+}+HL^-+L^{2-}=Co(HL)L^-$	18.6	0.1M $NaNO_3$	19
	$CoL+H^+ = CoHL^+$	4.7	I~0.005,50% dioxan	20
	$CoOHL^-+H^+ = CoL$	6.0		
Cu^{2+}	$Cu^{2+}+HL^- = CuHL^+$	14.8	I=0.1	18
	$CuHL^++HL^- = Cu(HL)_2$	9.1		
	$Cu^{2+}+HL^- = CuHL^+$	16.4	I=0.1, 50% dioxan	18
	$CuHL^++HL^- = Cu(HL)_2$	8.9		
	$Cu^{2+}+HL^- = CuHL^+$	15.44	I<0.01, 50% dioxan	8
	$Cu^{2+}+HL^- = CuHL^+$	17.5	I=0.1	15
	$Cu^{2+}+2L^{2-} = CuL_2^{2+}$	38.2		
	$Cu^{2+}+HL^- = CuHL^+$	16.5	I=0.1	11
	$Cu^{2+}+2L^{2-} = CuL_2^{2-}$	36.1		

Stability constants of metal-indicator complexes. (Cont.)

Metal ion	Reaction	log K	Conditions	Ref.
	$CuL+H^+ = CuHL^+$	5.56	I<0.01, 50% dioxan	8
	$CuOHL^-+H^+ = CuL$	10.09		
Dy^{3+}	$Dy^{3+}+L^{2-} = DyL^+$	10.6	0.1M $NaClO_4$	12
	$Dy^{3+}+HL^- = DyHL^{2+}$	11.2		
Er^{3+}	$Er^{3+}+L^{2-} = ErL^+$	10.1	0.1M $NaClO_4$	12
	$Er^{3+}+HL^- = ErHL^{2+}$	11.0		
Fe^{3+}	$Fe^{3+}+H_2L=FeHL^{2+}+H^+$	0.8	0.1M KNO_3	6
	$FeL^++H^+ = FeHL^{2+}$	4.37		
Ga^{3+}	$Ga^{3+}+HL^- = GaHL^{2+}$	14.6	0.2M $NaClO_4$	21
	$Ga^{3+}+2L^{2-} = GaL_2^-$	30.3		
	$GaOH^{2+}+HL^- = GaL^+$	~18.8	I=0.1	22
	$Ga^{3+}+H_3L^+=GaHL^{2+}+2H^+$	2.90	I=0.06, 50% EtOH	10
In^{3+}	$In^{3+}+HL^- = InHL^{2+}$	13.6	I=0.1	3
	$In^{3+}+2L^{2-} = InL_2^-$	27.0		
	$In^{3+}+L^{2-} = InL^+$	12.54	I=0.2, 50% dioxan	9
	$InL^++L^{2-} = InL_2^-$	11.46		
	$In^{3+}+H_3L^+=InHL^{2+}+2H^+$	1.79	I=0.06, 50% EtOH	10
La^{3+}	$La^{3+}+L^{2-} = LaL^+$	9.2	0.1M $NaClO_4$	12
Mn^{2+}	$Mn^{2+}+2L^{2-} = MnL_2^{2-}$	15.6	0.1M $NaNO_3$	23
	$Mn^{2+}+HL^- = MnHL^+$	9.7	I~0.005,50% dioxan	7
	$MnHL^++HL^- = Mn(HL)_2$	9.2		
	$MnL+H^+ = MnHL^+$	8.8	I~0.005,50% dioxan	20
	$MnOHL^-+H^+ = MnL$	10.3		
	$Mn^{2+}+HL^- = MnHL^+$	9.79	I<0.01, 50% dioxan	8
	$MnHL^++HL^- = Mn(HL)_2$	9.13		
Nd^{3+}	$Nd^{3+}+L^{2-} = NdL^+$	9.8	0.1M $NaClO_4$	12
	$Nd^{3+}+HL^- = NdHL^{2+}$	11.1		
Ni^{2+}	$Ni^{2+}+HL^- = NiHL^+$	13.2	I~0.005,50% dioxan	7
	$NiHL^++HL^- = Ni(HL)_2$	12.8		
	$NiL+H^+ = NiHL^+$	7.7	I~0.005,50% dioxan	20
	$NiOHL^-+H^+ = NiL$	9.2		

Stability constants of metal-indicator complexes. (Cont.)

Metal ion	Reaction	log K	Conditions	Ref.
	$Ni(HL)L^{-}+L^{2-}=Ni(HL)L_2^{3-}$	12.4	0.1M $NaClO_4$	24
	$Ni^{2+}+2L^{2-} = NiL_2^{2-}$	22.1	0.1M $NaClO_4$	19
Pb^{2+}	$Pb^{2+}+HL^{-} = PbHL^{+}$	8.6	I=0.1	18
	$Pb^{2+}+HL^{-} = PbHL^{+}$	11.9	0.1M $NaClO_4$	11
	$Pb^{2+}+2L^{2-} = PbL_2^{2-}$	24.7		
	$Pb^{2+}+HL^{-} = PbHL^{+}$	12.9	I=0.1	15
	$Pb^{2+}+2L^{2-} = PbL_2^{2-}$	26.6		
	$Pb^{2+}+L^{2-} = PbL$	10.96	I=0.1	5
	$Pb^{2+}+HL^{-} = PbHL^{+}$	5.45^{x}		
Pd^{2+}	$PdHL^{+}+H^{+} = PdH_2L^{2+}$	4.35	I=0.1, 50% dioxan	25
	$PdL+H^{+} = PdHL^{+}$	5.38		
Pt^{2+}	$Pt^{2+}+L^{2-} = PtL$	15.7	I=0.1	26
	$Pt^{2+}+HL^{-} = PtHL^{+}$	20.1		
Pr^{3+}	$Pr^{3+}+L^{2-} = PrL^{+}$	9.3	0.1M $NaClO_4$	12
	$Pr^{3+}+HL^{-} = PrHL^{2+}$	10.5		
Sc^{3+}	$Sc^{3+}+HL^{-} = ScHL^{2+}$	12.8	I=0.4	27
Sm^{3+}	$Sm^{3+}+L^{2-} = SmL^{+}$	10.1	0.1M $NaClO_4$	12
	$Sm^{3+}+HL^{-} = SmHL^{2+}$	11.4		
Tl^{3+}	$Tl^{3+}+HL^{-} = TlHL^{2+}$	17.93	0.1M $NaClO_4$	28
	$Tl(OH)_2^{+}+HL^{-}=Tl(OH)_2HL$	24.17	0.1M $NaClO_4$	29
UO_2^{2+}	$UO_2^{2+}+L^{2-} = UO_2L$	12.5	I=0.1	6
	$UO_2L+L^{2-} = UO_2L_2^{2-}$	8.4		
	$UO_2^{2+}+L^{2-} = UO_2L$	16.2	I=0.1, 50% dioxan	18
	$UO_2L+L^{2-} = UO_2L_2^{2-}$	9.6		
	$UO_2^{2+}+L^{2-} = UO_2L$	11.9	I=0.1	8
	$UO_2^{2+}+L^{2-} = UO_2L$	11.9	I=0.1	30
	$UO_2^{2+}+HL^{-} = UO_2HL^{+}$	12.7		
VO_2^{+}	$VO_2^{+}+L^{2-} = VO_2L^{-}$	16.49	I=0.01	31
	$VO_2^{+}+L^{2-} = VO_2L^{-}$	18.81	I=0.01	32
	$VO_2^{+}+HL^{-} = VO_2HL$	17.16		
Y^{3+}	$Y^{3+}+L^{2-} = YL^{+}$	9.1	0.1M $NaClO_4$	12

Stability constants of metal-indicator complexes. (Cont.)

Metal ion	Reaction	log K	Conditions	Ref.
	$Y^{3+}+HL^{-} = YHL^{2+}$	10.2		
Yb^{3+}	$Yb^{3+}+L^{2-} = YbL^{+}$	10.2	0.1M $NaClO_4$	12
	$Yb^{3+}+HL^{-} = YbHL^{2+}$	11.1		
Zn^{2+}	$Zn^{2+}+HL^{-} = ZnHL^{+}$	10.5	I=0.1	18
	$ZnHL^{+}+HL^{-} = Zn(HL)_2$	6.6		
	$Zn^{2+}+HL^{-} = ZnHL^{+}$	11.2	I=0.1, 50% dioxan	18
	$ZnHL^{+}+HL^{-} = Zn(HL)_2$	7.8		
	$Zn^{2+}+HL^{-} = ZnHL^{+}$	12.6	I=0.1	15
	$Zn^{2+}+HL^{-} = ZnHL^{+}$	11.6	I=0.1	11
	$Zn^{2+}+2L^{2-} = ZnL_2^{2-}$	23.2		
	$Zn^{2+}+2L^{2-} = ZnL_2^{2-}$	20.5	I=0.1	33
Zr^{4+}	$Zr(OH)_3^{+}+HL^{-}=Zr(OH)_3HL$	16.5	I=0.1	34

x In the case when $M(HL)_n$ complexes are formed, the metal ion replaces proton in o-OH group, except the starred value which was calculated assuming dissociation of p-hydroxyl proton.

Conditional stability constamts of metal-indicator complexes

Metal ion	Metal:Reagent ratio	log K	Conditions	Ref.
Ag (I)	1:1	5.47	pH 10.5	35
Au (III)	1:1	5.7	~0.01M HNO_3	36
Cr (III)	1:2	11.5	pH 4	37
Ga (III)	1:2	10.0	pH 4	38
Gd (III)	1:2	9.9	pH 6.2	4
Hg (II)	1:1	5.7	pH 5.5-6.5[x]	39
	1:2	11.0	pH 3[x]	
Ho (III)	1:2	9.9	pH 6.2	4
In (III)	1:2	9.6	pH 4	38
Lu (III)	1:2	10.1	pH 6.2	4
Nd (III)	1:2	9.4	pH 6.2	4
Pr (III)	1:2	9.9	pH 6.2	4
Sm (III)	1:2	10.3	pH 6.2	4
Tl (III)	1:2	9.8	pH 4	38
Tm (III)	1:2	10.2	pH 6.2	4
Yb (III)	1:2	9.8	pH 6.2	4

x in H_2O+EtOH+MeOH+dioxan (34+4+31+31)

Spectral characteristics of the indicator

Ion	λ_{max}, nm	ϵ_{max}x10^{-4}	Colour	Remarks	Ref.
H_3L^+	395				30
	395				6
	395	1.55			2
	395		yellow		40
	420	1.48		50% dioxan	41
	430-444			30% DMF	30
	441-448			90% DMF	30
H_2L	385				30
	386				6
	383	1.57			2
	385		yellow		40
	392	1.52		50% dioxan	41
	388			30% DMF	30
	389			90% DMF	30
HL^-	413				30
	414				6
	413		yellow		40
	415	2.59		50% dioxan	2
	414	2.31		30% DMF	41
	413			90% DMF	30
L^{2-}	488				6
	485	1.73			2
	490		orange		40
	502	1.78		50% dioxan	41

Spectral characteristics of metal-indicator complexes

Metal ion	Metal:Reagent ratio	λ_{max},nm	ϵ_{max}x10^{-4}	Colour	Ref.
Ag(I)	1:1	510	2.03	orange	35
Al(III)	1:1 (AlL^+)		3.64(λ=510)		12
Bi(III)	1:1 ($BiHL^{2+}$)	515	1.07		15
Cd(II)	1:2 (CdL_2^{2-})	495	5.78		15
Co(II)	1:2	510	5.67		42
	1:2	510	6.00	red	17
Co(III)	1:1 (CoL_2^-)	510			43
	1:2 ($Co(HL)_2^+$)	558,430	1.85; 3.75		
Cr(III)	1:2	550	1.2		37
Cu(II)	1:1 ($CuHL^+$)	522	1.29		15
	1:2 (CuL_2^{2-})	505-510	5.89		
Dy(III)	1:1 ($DyHL^{2+}$)		1.12(λ=510)		12
	1:1 (DyL^+)		2.7 (λ=530)		
Er(III)	1:1 ($ErHL^{2+}$)		1.59(λ=510)		12
	1:1 (ErL^+)		4.1 (λ=530)		
Fe(II)	1:3	500	5.0	red	44
Fe(III)	1:2 (FeL_2^-)	535	6.1		
Ga(III)	1:1 ($GaHL^{2+}$)	490	2.12	orange	21
	1:2 (GaL_2^-)	500	9.9	orange	21
Gd(III)	1:3	576	8.89		45

Spectral characteristics of metal-indicator complexes. (Cont.)

Metal ion	Metal:Reagent ratio	λ_{max}, nm	$\epsilon_{max} x10^{-4}$	Colour	Ref.
Hf (III)	1:4	510	3.75[x1]	orange	46
Hg (II)	1:1	540	2.01	orange-red	47
	1:2	500	6.8		48
Ho (III)	1:2	515		red	4
In (III)	1:1 ($InHL^{2+}$)	505	1.71		3
	1:2 (InL_2^-)	500-510	9.67		
	1:1	500	3.28	orange	49
La (III)	1:1 (LaL^+)		1.85(λ=510)	orange-red	12
Lu (III)	1:2	515		red	4
Mn (II)	1:2	496	8.65		23
Nb (III)	1:1	540	2.33[x2]		50
	1:1	520	2.8[x3]		
	1:1	520	3.03[x4]		
Nd (III)	1:1 ($NdHL^{2+}$)		1.06(λ=510)		12
	1:1 (NdL^+)		4.0 (λ=530)		12
Ni (II)	1:3	490	1.75	red	51
	1:3	495	7.64	orange	24
Np (V)	1:1	510	4.29		52
Pb (II)	1:1 ($PbHL^+$)	512	1.08		15
	1:2 (PbL_2^{2-})	522	5.02		
Pd (II)	1:1 (PdH_2L^{2+})	580	0.86[x5]	green	25
	1:1 ($PdHL^+$)	515;525	2.68; 2.89[x5]	red	
	1:1 ($Pd(OH)L^-$)	520	3.25[x5]	red	
Pr (III)	1:1 ($PrHL^{2+}$)		1.09(λ=510)		12
	1:1 (PrL^+)		2.0 (λ=530)		
Pt (II)	1:1 ($PtHL^+$)	660	2.29		26
	1:1 (PtL)	520	5.95		
Rh (III)	1:2	510	0.7		53
Sb (III)	1:2	540	1.2[x6]	red	54
Sc (III)	1:1	530	1.47(λ=520)		27
Sm (III)	1:1 ($SmHL^{2+}$)		1.15(λ=510)		12
	1:1 (SmL^+)		4.1 (λ=530)		
Tm (III)	1:2	515			4
Tl (III)	1:1	520	2.0		28
U (VI)	1:1 (UO_2HL^+)	510	1.86		30
	1:1 (UO_2L)	530	3.85		
V (IV)	1:1 ($VOHL^+$)	525	1.65		55
	1:1 (VOL)	540	3.3		
V (V)	1:1 (VO_2HL)	525	1.7		55
	1:1 (VO_2L^-)	545	3.6		
Y (III)	1:1 (YHL^{2+})		1.44(λ=510)		12
	1:1 (YL^+)		4.7(λ=520)		
Yb (III)	1:1 ($YbHL^{2+}$)		1.3(λ=510)		12
	1:1 (YbL^+)		4.0(λ=530)		

Spectral characteristics of metal-indicator complexes. (Cont.)

Metal ion	Metal:Reagent ratio	λ_{max}, nm	ϵ_{max}x10^{-4}	Colour	Ref.
Zn (II)	1:1	560	0.22		15
	1:2	495	9.05		33
Zr (IV)	1:1	520	1.5		34

x1 - in i-PeOH, x2 - in oxalate, x3 - in tartrate, x4 - in fluoride, x5 - in 50% dioxane, x6 - in 60% acetone.

Purification of the indicator has been carried out by crystallization from methanol (Ref. 5).

Purity check by thin layer chromatography (Silufol R, EDTA) - solvents: benzene-acetone (9+2), benzene-methanol (9+1). (Ref. 5).

The indicator is normally used as 0.05 or 0.2% aqueous solution.

Typical application of the indicator. Direct titration of Bi (pH 1-2), Cd (pH 9-10), Cu (pH 5-11), Fe (III) (pH 2-3), Ga, In (pH 2-2.5), Mn (pH 9), Pb (pH 5-6, 9-10), Tl (pH 1.7), Zn (pH 5-6, 9-11), and lanthanides (pH 6-7); especially recommended for Bi (pH 1-2). Also in back-titration of Al (pH 7) with Pb(II) solution as titrant. In some titrations (e.g. Al, Sb) the indicator is used as the Cu-PAR complexes.

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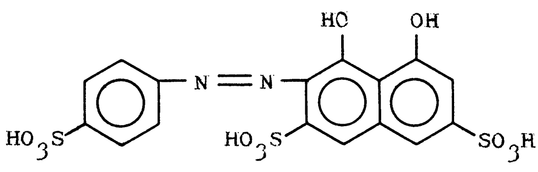
18. SPADNS

Synonyms: 2-(4-Sulphophenylazo)-chromotropic acid

Chemical names:
2-(4-Sulphophenylazo)-1,8-dihydroxynaphthalene-3,6-disulphonic acid
4,5-Dihydroxy-3-[(p-sulphophenyl)azo]-2,7-naphthalene-disulphonic acid
(the commercial product is a trisodium salt)

Colour Index: -



H_5L

Protonation constants of the indicator

log K_1 -OH	log K_2 -OH	Conditions	Ref.
	8.90		1
	8.52	I=0.1	2
15.1	9.26		3

Conditional stability constants of metal-indicator complexes

Metal ion	Metal:Reagent ratio	log K	Conditions	Ref.
Dy(III)	1:1	3.0	pH 6.06	4
		3.7	pH 7.07	
		4.0	pH 7.50	
	2:3	19.6	pH 7.86	4
Gd(III)	1:1	4.1	pH 6.0	5
		4.7	pH 7.02	
Ho(III)	1:1	2.8	pH 6.06	4
		3.5	pH 7.07	
		4.0	pH 7.50	
	2:3	19.3	pH 7.86	
La(III)	1:1	3.5	pH 6	5
		3.9	pH 6.53	
	2:3	19.6	pH 7.7	
		16.9	pH 8.8	
Nd(III)	1:1	3.9	pH 6.0	5
		4.4	pH 6.94	
	2:3	21.9	pH 7.7	
		16.2	pH 8.8	
Pd(II)	1:2	9.9	pH 3.5	6
	1:3	~15	pH 10.5	
Pr(III)	1:1	3.9	pH 6.0	5
		4.0	pH 6.65	
	2:3	19.2	pH 7.7	
		16.9	pH 8.8	
Sm(III)	1:1	4.0	pH 6.0	5
		4.7	pH 7.22	
	2:3	21.2	pH 7.7	
		16.2	pH 8.8	
Y(III)	1:1	4.4	pH 6.0	5
		4.8	pH 6.8	
	2:3	21.8	pH 7.7	
		17.4	pH 8.8	

Spectral characteristics of the indicator

Ion	λ_{max}, nm	$\epsilon_{max} x10^{-4}$	Colour	Ref.
H_2L^{3-}	510-520	~0.3	red	3
HL^{4-}	510-520	~0.2	red	3
L^{5-}	530	~0.25	red	3

Spectral characteristics of metal-indicator complexes

Metal ion	Metal:Reagent ratio	λ_{max}, nm	$\epsilon_{max} x10^{-4}$	Colour	Ref.
Al(III)	1:1	590			7
Ba(II)	1:1	570	1.3		8
Ca(II)	1:1	570		blue-violet	9
Dy(III)	1:1	600		violet	4
	2:3	600		violet	

Spectral characteristics of metal-indicator complexes

Metal ion	Metal:Reagent ratio	λ_{max}, nm	$\epsilon_{max} x 10^{-4}$	Colour	Ref.
Gd(III)	1:1 2:3	542 553			10
Ho(III)	1:1 2:3	600 600		violet violet	4
La(III)	1:1 2:3	528 538			10
Nd(III)	1:1 2:3	530 542			10
Pd(II)	1:2 1:3	550 580			6
Pr(III)	1:1 2:3	530 538			10
Sc(III)	1:1	560	1.07		2
Sm(III)	1:1 2:3	532 545			10
Sr(II)	1:1	560	0.4	blue-violet	8
Th(IV)	1:1	580	3.2	blue-violet	11
Y(III)	1:1 2:3	545 565			10
Zr(IV)	2:1	580	1.89		4

Purification of the indicator has been carried out by crystallization from ethanol (Ref. 3).

Purity check by paper chromatography (Whatman 3MM) using as solvent pyridine - 28% ammonia - 1-pentanol (2+2+1) (Ref. 12).

The indicator is normally used as 0.02-0.4% aqueous solution.

Typical application of the indicator: Direct titrations of Th (pH 2.5-3.5) Zr (pH 1.5-2.5).

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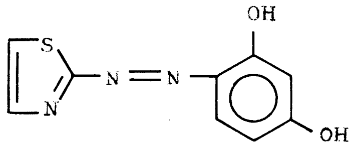
19. TAR

Synonyms: -

Chemical names:
4-(2'-Thiazolylazo)-1,3-dihydroxybenzene
4-(2-Thiazolylazo)-resorcinol

Colour Index: -



H_2L

Protonation constants of the indicator

log K_1 o-OH	log K_2 p-OH	log K_3 $\equiv NH^+$	Conditions	Ref.
9.3	6.0	1.25	0.1M $NaClO_4$	1
9.44	6.23	0.96	0.1M $NaClO_4$	2
9.59	6.16		I=0.2	3
9.68	6.15			4
		1.56	I=1.0	5
9.15			0.1M $NaClO_4$	6
10.3	5.9		aqueous solution (?)	7
10.52	6.40		20% MeOH	8
9.88	6.18	1.13	I=0.1, 2% dioxan	9
9.49	6.17	0.98	I=0.1, 2% dioxan	10
12.80	7.37	1.65	I<0.01, 50% dioxan	11
10.76	6.53	0.9	I=0.1, 50% MeOH	12
10.3	5.9		20% MeOH	13
10.7	6.5		50% MeOH	13
9.4	6.2		5% EtOH	13
10.67	6.51	0.75	0.1M KNO_3, 30% EtOH	14
10.54	6.56	0.75	I=0.1, 30% EtOH	15
10.42	6.56	0.84	1M $NaClO_4$, 30% DMF	16
11.52	7.25	1.06	1M $NaClO_4$, 50% DMF	16

Stability constants of metal-indicator complexes

Metal ion	Reaction	log K	Conditions	Ref.
Al^{3+}	$AlOH^{2+}+2HL^-=AlOH(HL)_2$	14.28	0.1M $NaClO_4$, 50% MeOH	17
Bi^{3+}	$Bi^{3+}+HL^- = BiHL^{2+}$	13.11	0.1M $NaClO_4$	2
Ca^{2+}	$Ca^{2+}+HL^- = CaHL^+$	3.5	0.1M $NaClO_4$, 50% MeOH	12
Cd^{2+}	$Cd^{2+}+HL^- = CdHL^+$	7.0	0.1M $NaClO_4$	4

Stability constants of metal-indicator complexes. (Cont.)

Metal ion	Reaction	log K	Conditions	Ref.
	$Cd^{2+}+2HL^{-} = Cd(HL)_2$	16.0	0.1M $NaClO_4$, 50% MeOH	12
Co^{2+}	$Co^{2+}+HL^{-} = CoHL^{+}$	12.05	I<0.01, 50% dioxan	11
	$CoHL^{+}+HL^{-} = Co(HL)_2$	11.23		
	$Co^{2+}+2L^{2-} = CoL_2^{2-}$	16.15	0.1M $NaClO_4$	18
Cr^{3+}	$Cr^{3+}+HL^{-} = CrHL^{2+}$	10	0.1M $NaClO_4$, 50% MeOH	12
Cu^{2+}	$Cu^{2+}+HL^{-} = CuHL^{+}$	8.34^x	I=0.1, 2% dioxan	10
	$Cu^{2+}+L^{2-} = CuL$	13.66		
	$Cu^{2+}+HL^{-} = CuHL^{+}$	11.56	0.1M $NaClO_4$	2
	$Cu^{2+}+L^{2-} = CuL$	13.55		
	$Cu^{2+}+HL^{-} = CuHL^{+}$	8.4^x	I=0.1	19
	$Cu^{2+}+L^{2-} = CuL$	13.9		
	$Cu^{2+}+HL^{-} = CuHL^{+}$	14.2	I<0.01, 50% dioxan	11
	$CuL+H^{+} = CuHL^{+}$	11.56		
	$CuOHL^{-}+H^{+} = CuL$	10.13		
	$Cu^{2+}+HL^{-} = CuHL^{+}$	12.3	0.1M $NaClO_4$, 50% MeOH	12
	$CuHL^{+}+HL^{-} = Cu(HL)_2$	9.9		
Fe^{2+}	$Fe^{2+}+HL^{-} = FeHL^{+}$	9.5	I=0.1	20
	$Fe^{2+}+2HL^{-} = Fe(HL)_2$	21.6	0.1M $NaClO_4$, 50% MeOH	12
Fe^{3+}	$Fe^{3+}+H_2L = FeHL^{2+}+H^{+}$	0.67	I=0.1, 30% EtOH	14
	$Fe^{3+}+2H_2L = Fe(HL)_2^{+}+2H^{+}$	0.73		
	$Fe^{3+}+HL^{-} = FeHL^{2+}$	10.4	I=0.1	20
Ga^{3+}	$Ga^{3+}+HL^{-} = GaHL^{2+}$	12.0	0.1M $NaClO_4$, 50% MeOH	12
	$Ga^{3+}+HL^{-} = GaHL^{2+}$	9.1	0.1M $NaClO_4$	21
	$Ga^{3+}+L^{2-} = GaL^{+}$	12.8		
In^{3+}	$In^{3+}+HL^{-} = InHL^{2+}$	10.06	0.1M $NaClO_4$	21
	$In^{3+}+L^{2-} = InL^{+}$	10.8		
	$In^{3+}+HL^{-} = InHL^{2+}$	10.8	0.1M $NaClO_4$, 50% MeOH	12
Ir^{3+}	$Ir^{3+}+HL^{-} = IrHL^{2+}$	9.46	I=0.1, 2% acetone, 50% DMF	22
Mn^{2+}	$Mn^{2+}+HL^{-} = MnHL^{+}$	9.43	I<0.01, 50% dioxan	11

Stability constants of metal-indicator complexes. (Cont.)

Metal ion	Reaction	log K	Conditions	Ref.
	$MnHL^{+}+HL^{-} = Mn(HL)_2$	8.6		
	$MnOHL^{-}+H^{+} = MnL$	9.4		
	$Mn^{2+}+HL^{-} = MnHL^{+}$	13.1	0.1M $NaClO_4$ 50% MeOH	12
Ni^{2+}	$Ni^{2+}+HL^{-} = NiHL^{+}$	12.94	I<0.01, 50% dioxan	11
	$NiHL^{+}+HL^{-} = Ni(HL)_2$	11.82		
	$NiL+H^{+} = NiHL^{+}$	6.84		
	$NiOHL^{-}+H^{+} = NiL$	8.55		
	$Ni^{2+}+L^{2-} = NiL$	10.0	I=0.1, 30% EtOH	15
	$Ni^{2+}+2L^{2-} = NiL_2^{2-}$	17.1		
	$Ni^{2+}+HL^{-} = NiHL^{+}$	9.2		
	$Ni^{2+}+HL^{-} = NiHL^{+}$	6.06^{x}	I=0.1	10
	$Ni^{2+}+L^{2-} = NiL$	10.23		
Os^{4+}	$Os^{4+}+H_2L = OsHL^{3+}+H^{+}$	~-3	I=0.1	23
Os^{8+}	$Os^{8+}+HL^{-} = OsL^{6+}+H^{+}$	~-0.9	I=0.1	23
Pb^{2+}	$Pb^{2+}+HL^{-} = PbHL^{+}$	8.34	0.1M $NaClO_4$	2
	$Pb^{2+}+HL^{-} = PbHL^{+}$	9.7	0.1M $NaClO_4$, 50%MeOH	12
Pt^{2+}	$Pt^{2+}+HL^{-} = PtHL^{+}$	~12	0.1M $NaClO_4$, 50% MeOH	12
Rh^{3+}	$Rh^{3+}+HL^{-} = RhHL^{2+}$	~12	0.1M $NaClO_4$, 50% MeOH	12
Sc^{3+}	$Sc^{3+}+HL^{-} = ScHL^{2+}$	10.4	0.1M $NaClO_4$, 50% MeOH	12
	$ScHL^{2+}+HL^{-}=Sc(HL)_2^{+}$	9.9		
	$Sc^{3+}+HL^{-} = ScHL^{2+}$	9.4	I=0.1	24
TiO^{2+}	$TiO^{2+}+HL^{-} = (TiO)HL^{+}$	13	0.1M $NaClO_4$, 50% MeOH	12
Tl^{3+}	$Tl^{3+}+HL^{-} = TlHL^{2+}$	12	0.1M $NaClO_4$, 50% MeOH	12
	$Tl^{3+}+HL^{-} = TlHL^{2+}$	13.41	0.1M $NaClO_4$	25
UO_2^{2+}	$UO_2^{2+}+L^{2-} = UO_2L$	11.35	0.1M $NaClO_4$	26
	$UO_2^{2+}+HL^{-} = UO_2HL^{+}$	9.8		
	$UO_2^{2+}+HL^{-} = UO_2HL^{+}$	10.7	0.1M $NaClO_4$, 50% MeOH	12
	$UO_2HL^{+}+HL^{-}=UO_2(HL)_2$	9.7		

Stability constants of metal-indicator complexes. (Cont.)

Metal ion	Reaction	log K	Conditions	Ref.
	$UO_2^{2+}+HL^- = UO_2HL^+$	9.5	I=0.1	13
VO^+	$VO^++HL^- = VOL+H^+$	1.9	I=0.1	27
VO^{2+}	$VO^{2+}+HL^- = VOHL^+$	11.2	0.1M $NaClO_4$ 50% MeOH	12
	$VOHL^++HL^- = VO(HL)_2$	9.8		
VO_2^+	$VO_2^++HL^- = VO_2HL$	12.1	I=0.1, 30% DMF	28
	$VO_2^++HL^- = VO_2HL$	10.2	I=0.1, 30% EtOH	
Zn^{2+}	$Zn^{2+}+HL^- = ZnHL^+$	7.19	0.1M $NaClO_4$	2
	$Zn^{2+}+HL^- = ZnHL^+$	11.08	I<0.01, 50% dioxan	11
	$ZnHL^++HL^- = Zn(HL)_2$	10.11		
	$ZnL+H^+ = ZnHL^+$	7.12		
	$ZnOHL^- + H^+ = ZnL$	8.74		
	$Zn(OH)_2L^{2-}+H^+=ZnOHL^-$	8.98		
	$Zn^{2+}+2HL^- = Zn(HL)_2$	17.2	0.1M $NaClO_4$, 50% MeOH	12
ZrO^{2+}	$ZrO^{2+}+HL^- =(ZrO)HL^+$	13	0.1M $NaClO_4$, 50% MeOH	12

x These values differ from those in which the dissociation of - o-hydroxyl group has been assumed as preceding the dissociation of p-hydroxyl proton. The difference is equal to $\log K_1 - \log K_2$.

Spectral characteristics of the indicator (in aqueous solution)

Ion	λ_{max}, nm	$\epsilon_{max} \times 10^{-4}$	Colour	Ref.
H_3L^+	488	2.48(λ=510)	orange	2
	484			8
	481			14
H_2L	410-440	0.17(λ=510)	yellow	2
	410-440	~1.9	yellow	3
	446			8
	415,438			14
HL^-	470	1.55(λ=510)		2
	481			8
	476			3
	400,480			14
L^{2-}	510	3.45	red	2
	515			8
	516	~3.4	red	3
	513			14

Spectral characteristics of metal-indicator complexes

Metal ion	Metal:Reagent ratio	λ_{max}, nm	$\epsilon_{max} \times 10^{-4}$	Remarks	Ref.
Bi(III)	1:1 ($BiHL^{2+}$)	540	2.24		2
	1:1 (BiL^{+})	530	3.08		2
Cd(II)	1:1 ($CdHL^{+}$)	500	3.06		2
	1:2	530		50% MeOH	12
Co(II)	1:2	510	5.6		18
Co(III)	1:2	500		50% MeOH	12
Cr(III)	1:2	525[x1]	4.98	t-BuOH - H_2O	
Cu(II)	1:1 ($CuHL^{+}$)	560	2.09		2
	1:1 (CuL)	505-510	3.11		2
	1:1 (CuL)	515	2.92		1
	1:1	555		50% MeOH	12
	1:2	510		50% MeOH	12
	1:1 ($CuHL^{+}$)	560		2% dioxan	9,10
	1:1 (CuL)	520		2% dioxan	9,10
Fe(III)	1:2	480,540	2.26 (λ=540 nm)		1
	1:2	495	3.3	30% EtOH	14
Ga(III)	1:1	530	~5.7		21
Hf(III)	1:4	540	5.8	20% MeOH	29
Hg(II)	1:1	525		50% MeOH	12
In(III)	1:1	530	2.24		24
	1:2	530	5.22		
Ir(III)	1:1	520	2.14	2% acetone+ 50% DMF	22
	1:1	530	2.35		1
La(III)	1:3	520	3.52		1
Mn(II)	1:1	527		50% MeOH	13
Ni(II)	1:1 ($NiHL^{+}$)	540	2.04	30% EtOH	15
	1:1 (NiL)	505	3.1		
	1:2 ($Ni(HL)_2$)	540	3.7		
	1:2 (NiL_2^{2-})	505	6.6		
	1:2	500	3.15		1
Os(IV)	1:1	550	1.55		23
Os(VIII)	1:1	550	2,22		23
Pb(II)	1:1 ($PbHL^{+}$)	540	1.99		2
	1:1 (PbL)	530	3.04		
	1:1 (PbL)	530[x2]	3.22		30
Rh(III)	1:1	540	2.28	water+DMF	31
Sc(III)	1:3	540	5.06	10% dioxan	32
Th(IV)	1:2	520	1.9		1
Ti(III)	1:1	540	1.5		1
Tl(III)	1:1 ($TlHL^{2+}$)	520	2.28		25
	1:1 (TlL^{+})	540	3.26		
U(VI)	1:1 (UO_2HL^{+})	530	2.33		26
	1:1 (UO_2L)	540-545	3.25		

Spectral characteristics of metal-indicator complexes. Cont.

Metal ion	Metal:Reagent ratio		$_{max}$, nm	$_{max}$ x10^{-4}	Remarks	Ref.
	1:1		534			7
V(III)	1:1		550	2.82		27
V(V)	1:1		545^{x3}	2.65		1
Zn(II)	1:1	$ZnHL^{+}$	520	2.35		2
	1:1	ZnL	500	3.55		2
Zr(IV)	1:1		515		50% MeOH	12

The following colours are given: x1 - red, x2 - red-violet, x3 - violet.

Purification of the indicator has been carried out by recrystallization from methanol, ethanol or by fractional precipitation with diethyl ether or hydrochloric acid (Ref. 33).

Purity check by paper chromatography using as solvent: isobutanol - ammonia - water (15+4+1).(Ref. 33). An alternative is thin layer chromatography on silica gel with various solvent compositions: n-butanol - ethanol - 2M ammonia (3+1+1) (Ref. 34), benzene - acetic acid (4+1)(Ref. 35), benzene - chloroform - acetic acid (25+5+6.2)(Ref. 35) or carbon tetrachloride - acetic acid (15+4) (Ref. 35). On silica gel in presence of 0.05M EDTA, following solvent compositions can be used (Ref. 36) : benzene - methanol (4+1), benzene - acetone (4+1), or chloroform - methanol (9+1).

The indicator is normally used as 0.1% solution in ethanol or methanol. A few drops of such solution are added to titrated solution

Typical application of the indicator. Direct titration of Co (pH 4-7), Cu (pH 4-7), Ni (pH 4-7), Tl (pH 1,2-5.5,) lanthanides; especially recommended for Cu (pH 4-7). In some titrations Cd, Fe, Hg, In, Mn, Ni, Pb, Sc, Zn, it is recommended to use the indicator as the Cu-TAR complex.

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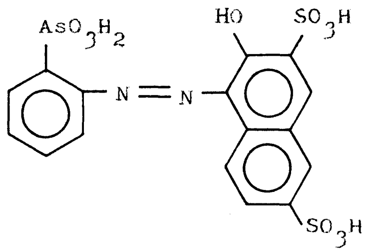
20. THORIN

Synonyms: Thoron, Thoronol, APNS, APANS, Naphtharson, Naphthazarin

Chemical names:

4-[(o-Arsonophenyl)azo]-3-hydroxy-2,7-naphthalene disulphonic acid
1-(2'-Arsonophenylazo)-2-hydroxy-naphthalene-3,6 disulphonic acid
(the commercial product is disodium salt)

Colour Index:



H_5L

Protonation constants of the indicator

log K_1 -OH	log K_2 $-AsO_3H^-$	log K_3 $-AsO_3H_2$	log K_4 $-SO_3H$	Conditions	Ref.
	11.9	8.3	3.7	I=0.5	1
	10	7.2	3.6		2
~14	~11.5	~ 8	~4	I=0.1-1	3

Conditional stability constants of metal-indicator complexes

Metal ion	Metal:Reagent ratio	log K	Conditions	Ref.
Be(II)	1:1	6.9	pH 12	4
Ce(IV)	1:2	8.5	pH 4	5
Cr(III)	1:2	15.4	pH 2.5	6
Eu(III)	1:2	8.4	pH 4	7
Hf(IV)	1:2	8.4	pH 0.75-2.5	8
La(III)	1:2	10.1	pH 5.5	9,10
Lu(III)	1:2	9.6	pH 4	7
Pd(II)	1:1	4.38	pH 3	10
Sc(III)	1:2	~9	pH 5.5	11
Tb(III)	1:2	8.8	pH 4	7
Th(IV)	1:2	9.6	pH 5	11
	1:2	10.2	pH 1	12
U(VI)	1:1	4.4	pH 3	10
Y(III)	1:2	8.6	pH 4	13
Yb(III)	1:2	9.5	pH 4	7

Spectral characteristics of the indicator

Ion	λ_{max}, nm	$\epsilon_{max}x10^{-4}$	Colour	Ref.
H_5L	510	1.4	red	3
H_4L^-	480		orange	3
H_3L^{2-}	490		rose	3
H_2L^{3-}	490	1.4	rose	3
HL^{4-}	460		yellow	3
L^{5-}			red	3

Spectral characteristics of metal-indicator complexes

Metal ion	Metal:Reagent ratio	λ_{max}, nm	$\epsilon_{max}x10^{-4}$	Colour	Ref.
Be(II)	1:1	470			4
Ce(IV)	1:2	500		rose	5
Cr(III)	1:2	500	0.7	red	6
Eu(III)	1:2	500			7
Hf(IV)	1:2	500			8
La(III)	1:2	515		red	9
Lu(III)	1:2	500			7
Pd(II)	1:1	525			10
Tb(III)	1:2	500			7
Th(IV)	1:2	545		red	12
U(VI)	1:1	545		red	10
	1:1	545	0.3		3

Spectral characteristics of metal-indicator complexes. (Cont.)

Metal ion	Metal:Reagent ratio	λ_{max}, nm	$\epsilon_{max}x10^{-4}$	Colour	Ref.
Y(III)	1:2	500		pink	13
Yb(III)	1:2	500			7
Zr(IV)	1:1	540	0.34		14

Purification of the indicator has been carried out by crystallization from water (Ref. 1) or precipitation from hydrochloric solutions with successive recrystallization from ethanol (Ref. 15).

Purity check by paper electrophoresis (380 V, 4 mA, t=2-6 h), electrolyte: 30% CH_3COOH (Ref. 15).

The indicator is normally used as 0.5% aqueous solution.

Typical application of the indicator. Direct titrations of: Bi (pH 2-3), Th (pH 1-3), Sc (pH 4.5-6.5). Especially recommended for Th (pH 1-3). Also in back-titrations with La(III) as titrant in determination of Bi, Co, Cu, Ni, Pb, Zn at pH about 6, or additionally in the presence of 50% methanol in determination of Al (pH 4-5), Cd, Zn.

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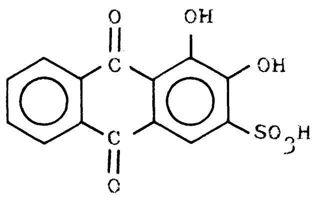
III. OTHER INDICATORS

21. ALIZARIN RED S

Synonyms: Alizarin Carmine
Alizarin S

Chemical name: 1,2-Dihydroxyanthraquinone-3-sulphonic acid

Colour index: C.I. 58005, Mordant Red 3



H_3L

Protonation constants of the indicator

log K_1 α-OH	log K_2 β-OH	Conditions	Ref.
10.85	5.49	I=0.5	1
11.20	4.60	I=0.05	2
11.02	5.55		3
	5.53	0.1M KCl	4
11.03		0.1M KCl	5
10.72	5.39	I=0.5, 25°C	6

Stability constants of metal-indicator complexes

Metal ion	Reaction	log K	Conditions	Ref.
Al^{3+}	$Al^{3+}+2HL^{2-} = Al(HL)_2^-$	12.1	I=0.1	7
	$Al^{3+}+2H_2L^- = Al(H_2L)_2^+$	11.5	0.1M $NaClO_4$	8
	$Al^{3+}+L^{3-} = AlL$	11.31	I=0.1	9
	$Al^{3+}+2L^{3-} = AlL_2^{3-}$	17.37		
Be^{2+}	$Be^{2+}+L^{3-} = BeL^-$	9.77	0.1M $NaClO_4$	10
	$BeL^-+L^{3-} = BeL_2^{4-}$	6.92		
Ce^{4+}	$Ce^{4+}+L^{3-} = CeL^+$	10.52	I=0.1	9
	$Ce^{4+}+2L^{3-} = CeL_2^{2-}$	15.13		
Co^{2+}	$Co^{2+}+L^{3-} = CoL^-$	9.02	0.1M $NaClO_4$	10
	$CoL^-+L^{3-} = CoL_2^{4-}$	6.61		
Cu^{2+}	$Cu^{2+}+L^{3-} = CuL^-$	10.61	I=0.2^x	11
	$CuL^-+L^{3-} = CuL_2^{4-}$	8.30		
Ga^{3+}	$Ga^{3+}+2HL^{2-} = Ga(HL)_2^-$	9.57	I=0.1	7
	$Ga^{3+}+2H_2L^- = Ga(H_2L)_2^+$	11.6	0.1M $NaClO_4$	8
Hg^{2+}	$Hg^{2+}+L^{3-} = HgL^-$	8.04	I=0.2^x	11
	$HgL^- + L^{3-} = HgL_2^{4-}$	6.10		
In^{3+}	$In^{3+}+2H_2L^- = In(H_2L)_2^+$	11.5	0.1M $NaClO_4$	8

Stability constants of metal-indicator complexes. (Cont.)

Metal ion	Reaction	log K	Conditions	Ref.
Ni^{2+}	$Ni^{2+}+L^{3-} = NiL^-$	9.43	0.1M $NaClO_4$	10
	$NiL^-+L^{3-} = NiL_2^{4-}$	6.02		
Pb^{2+}	$Pb^{2+}+L^{3-} = PbL^-$	11.36	I=0.2[x]	11
	$PbL^-+L^{3-} = PbL_2^{4-}$	5.60		
Th^{4+}	$Th^{4+}+L^{3-} = ThL^+$	11.52	I=0.1	9
	$ThL^++L^{3-} = ThL_2^{2-}$	6.63		
UO_2^{2+}	$UO_2^{2+}+L^{3-} = UO_2L^-$	11.95	0.1M $NaClO_4$	10
	$UO_2L^-+L^{3-} = UO_2L_2^{4-}$	5.71		
Zn^{2+}	$Zn^{2+}+L^{3-} = ZnL^-$	8.72	I=0.2[x]	11
	$ZnL^-+ L^{3-} = ZnL_2^{4-}$	6.32		
Zr^{4+}	$Zr^{4+}+2OH^-+L^{3-}= Zr(OH)_2L^-$	49.0	I=1.6	1

[x] Values for other ionic strengths in the range 0-0.20 were also given.

Conditional stability constants of metal-indicator complexes

Metal ion	Metal:Reagent ratio	log K	Conditions	Ref.
Al(III)	1:2	7.2-7.5	pH 2.5-4.5	12
Co(II)	1:1 1:2	5.6 10.3	pH 6-10 pH 11.5	13
Cu(II)	1:1	5.5		14
Gd(III)	1:2	8.6-8.7	pH 4	15
Ge(IV)	1:3	52.8(β_3)	0.1M acetate	16
Hf(IV)	1:2	10.2	pH 1.5	17
In(III)	1:2	9.0-9.4	pH 4	18
La(III)	1:2	8.3-8.6	pH 3.5-6.5	19
Lu(III)	1:2	9.1-9.2	pH 4	15
Mo(VI)	1:2	9.6	pH 4	20
Nb(III)	1:2	8.3	pH 3.5-5.5	21
Nd(III)	1:1 1:2	12.73 8.90	I=0.05 I=0.05	2
Ni(II)	1:1	4.35	pH 7	22
Pr(III)	1:1 1:2	12.56 8.90	I=0.05	2
Sc(II)	1:2	9.2	pH 4.0	23
Tb(III)	1:2	8.0-9.2	pH 4	15
Th(IV)	1:2	8.2	pH 3.2-8.0 (?)	24
V(IV)	1:2	8.4-9.2	pH 4	25
W(VI)	1:2	7.83	pH 4-6	26

Conditional stability constants of metal-indicator complexes.(Cont.)

Metal ion	Metal:Reagent ratio	log K	Conditions	Ref.
Y(III)	1:2	9.5-9.6	pH 4.0	23
Yb(III)	1:2	8.6-8.7	pH 4	14

Spectral characteristics of the indicator

Ion	λ_{max}, nm	ϵ_{max}	Colour	Ref.
H_2L^-	420			27
HL^{2-}	525		red	27
L^{3-}	555		red-violet	27

Spectral characteristics of metal-indicator complexes

Metal ion	Metal:Reagent ratio	λ_{max}, nm	$\epsilon_{max}x10^{-4}$	Colour	Ref.
Al(III)	1:2	480		yellow	7
Cd(II)	2:2	490	1.5	yellow	28
Co(II)	1:1	570	0.97	red-violet	13
Ga(III)	1:2	470		yellow	7
Gd(III)	1:2	520		red	15
Hf(IV)	1:2	520		red	17
In(III)	1:2	530		violet	18
La(III)	1:2	520	0.89	red	19,29
Lu(III)	1:2	530		violet	4
Mo(VI)	1:2	470		yellow	20
Ni(II)	1:1	590	0.55	violet	22
Pr(III)	1:2	530		violet	2
Sc(II)	1:2	500		red	23
Tb(III)	1:2	530		violet	15
Th(IV)	1:2	520		red	24

Purification of the indicator(Ref. 1) has been carried out by crystallization from 50% ethanol.

Purity check (Ref. 1) was carried out by pH titration with sodium hydroxide.

The indicator is used as 0.05-0.2% aqueous solution.

Typical applications of the indicator. Direct titration of lanthanides (pH 4-4.5) and Th (pH 1.5-6.5). Also in back-titration of Al (pH 3-5), Bi (pH 2-2.8), Th (pH 4) with Th(IV) solution as titrant.

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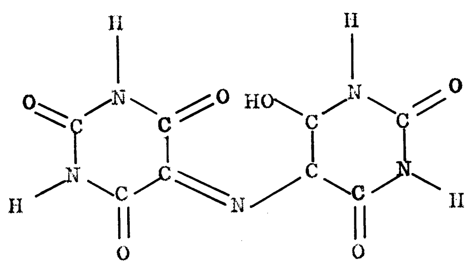
22. MUREXIDE

Synonyms: Ammonium purpurate
(some authors and producers use the name Murexide for ammonium salt)

Chemical name: 5,5-Nitrilodibarbituric acid

Colour index: 56086



H_5L

Protonation constants of the indicator

log K_1 -NH	log K_2 -NH	log K_3 -NH	log K_4 -NH	log K_5 -OH	Conditions	Ref.
		10.9	9.2	0	I=0.1	1
				1.6	I=0 (corr)	2
14-14.5	13.5	10.3	8.7		?	3

Stability constants of metal-indicator complexes

Metal ion	Reaction	log K	Conditions	Ref.
Ca^{2+}	$Ca^{2+}+H_2L^{3-} = CaH_2L^-$	5.0	I=0.1	1[x]
	$Ca^{2+}+H_3L^{2-} = CaH_3L$	3.6		
	$Ca^{2+}+H_4L^- = CaH_4L^+$	2.6		
		2.68	I=0.1	4
Cd^{2+}	$Cd^{2+}+H_4L^- = CdH_4L^+$	4.2	I=0.1	1[x]
Ce^{3+}	$Ce^{3+}+H_4L^- = CeH_4L^{2+}$	3.65	0.1M KNO_3, 12°C	5
Co^{2+}	$Co^{2+}+H_4L^- = CoH_4L^+$	2.46	0.1M KNO_3, 12°C	5
Cu^{2+}	$Cu^{2+}+H_2L^{3-} = CuH_2L^-$	15	I=0.1	1[x]
	$Cu^{2+}+H_2L^{3-} = CuH_2L^-$	14.4	I=0.1	6
Dy^{3+}	$Dy^{3+}+H_4L^- = DyH_4L^{2+}$	3.78	0.1M KNO_3, 12°C	5
Er^{3+}	$Er^{3+}+H_4L^- = ErH_4L^{2+}$	3.48	0.1M KNO_3, 12°C	5
Eu^{3+}	$Eu^{3+}+H_4L^- = EuH_4L^{2+}$	4.17	0.1M KNO_3, 12°C	5
Gd^{3+}	$Gd^{3+}+H_4L^- = GdH_4L^{2+}$	4.08	0.1M KNO_3, 12°C	5
Ho^{3+}	$Ho^{3+}+H_4L^- = HoH_4L^{2+}$	3.71	0.1M KNO_3, 12°C	5
In^{3+}	$In^{3+}+H_4L^- = InH_4L^{2+}$	4.61	0.1M KNO_3, 12°C	5
La^{3+}	$La^{3+}+H_4L^- = LaH_4L^{2+}$	3.43	0.1M KNO_3, 12°C	5
Lu^{3+}	$Lu^{3+}+H_4L^- = LuH_4L^{2+}$	3.45	0.1M KNO_3, 12°C	5
Nd^{3+}	$Nd^{3+}+H_4L^- = NdH_4L^{2+}$	4.04	0.1M KNO_3, 12°C	5
Ni^{2+}	$Ni^{2+}+H_4L^- = NiH_4L^+$	3.36	0.1M KNO_3, 12°C	5
Pr^{3+}	$Pr^{3+}+H_4L^- = PrH_4L^{2+}$	3.78	0.1M KNO_3, 12°C	5
Sc^{3+}	$Sc^{3+}+H_4L^- = ScH_4L^{2+}$	4.50	0.1M KNO_3, 12°C	5
Sm^{3+}	$Sm^{3+}+H_4L^- = SmH_4L^{2+}$	4.20	0.1M KNO_3, 12°C	5
Tb^{3+}	$Tb^{3+}+H_4L^- = TbH_4L^{2+}$	3.95	0.1M KNO_3, 12°C	5
Tm^{3+}	$Tm^{3+}+H_4L^- = TmH_4L^{2+}$	3.36	0.1M KNO_3, 12°C	5
Y^{3+}	$Y^{3+}+H_4L^- = YH_4L^{2+}$	3.36	0.1M KNO_3, 12°C	5
Yb^{3+}	$Yb^{3+}+H_4L^- = YbH_4L^{2+}$	3.41	0.1M KNO_3, 12°C	5
Zn^{2+}	$Zn^{2+}+H_4L^- = ZnH_4L^+$	3.1	I=0.1	1[x]
	$Zn^{2+}+2H_3L^{2-}=Zn(H_3L)_2^{2-}$	9.3	I=0.1	7

x Side reactions of metal cations were not taken into account, which may explain some d fferences for Ca with data in Ref. 8.

Conditional stability constants of metal-indicator complexes

Metal ion	Metal:Reagent ratio	log K	Conditions	Ref.
Ca (II)	1:1	2.72-2.75-2.81-2.92-3.38-3.46-3.56-3.80-4.13	pH 4.0-4.5-5.0 - 5.5-6.0-6.5 - 7.0-7.5-8.0 x	8
Ce (III)	1:1	6.2	pH 6.5-7.5	9
	1:1	4.2	pH 6.0	10
Dy (III)	1:1	4.7	pH 6.0	10
Er (III)	1:1	4.7	pH 6.0	10
Eu (III)	1:1	5.34-5.38-5.42-5.55	pH 4.0-4.5 - 5.0-5.5	8
	1:1	4.8	pH 6.0	10
Gd (III)	1:1	4.90-4.96-5.00-5.13	pH 4.0-4.5 - 5.0-5.5 x	8
	1:1	4.6	pH 6.0	10
Ho (III)	1:1	4.6	pH 6.0	10
La (III)	1:1	4.49-4.52-4.55-4.68	pH 4.0-4.5 - 5.0-5.5 x	8
	1:1	4.4	pH 6.0	10
Lu (III)	1:1	5.3	pH 6.0	10
Nd (III)	1:1	4.6	pH 6.0	10
Pr (III)	1:1	4.4	pH 6.0	10
Sc (III)	1:1	4.2	pH 6.0	10
Sm (III)	1:1	4.7	pH 6.0	10
Tb (III)	1:1	4.89-4.94-4.98-5.13	pH 4.0-4.5 - 5.0-5.5 x	8
	1:1	4.4	pH 6.0	10
Th (IV)	1:1	6.9	pH 8-9	9
Tm (III)	1:1	4.9	pH 6.0	10
V (IV)	1:1	5.2	pH 6.0-7.2	9
Y (III)	1:1	4.2	pH 6.0	10
Yb (III)	1:1	5.1	pH 6.0	10

x pH values for respective log K which take into account side reactions of metal ions.

Spectral characteristics of metal-indicator complexes

Metal ion	Metal:Reagent ratio	λ_{max}, nm	$\epsilon_{max} \times 10^{-4}$	Colour	Ref.
Ca (II)	1:1 (CaH_4L^+)	475	2.1	yellow-orange	1
		484			5
	(CaH_3L)			red-orange	1
	(CaH_2L^-)	515	1.8	red	11
Cd (II)	1:1	485		orange	1

Spectral characteristics of metal-indicator complexes. (Cont.)

Metal ion	Metal:Reagent ratio	λ_{max}, nm	$\epsilon_{max} x10^{-4}$	Colour	Ref.
Cu(II)	1:1	460	2.1	yellow	11
Sc(III)	1:1 (ScH_4L^{2+})	460			5

Purification of the indicator (Ref. 12) has been carried out by dissolving 1g of indicator in 900 cm^3 water at 30°, salting out the filtered solution with 60 g ammonium chloride, filtering, washing the precipitate with 60% and with absolute methanol and drying at 110°. The results are rather unsatisfactory and rather a new synthesis from alloxantine is recommended.

Purity check was carried out by titration with sodium hydrosulphite solution (Ref. 12) or with titanium(III) (Ref. 13).

The indicator is normally used: a solid diluted with NaCl or K_2SO_4 (1:100 till 1:500). 1% aqueous solution is unstable and better results are obtained with 0.1% solution in anhydrous ethyleneglycol (Ref. 14).

Typical applications of the indicator. Direct titration of Ca (pH>10), Co (pH 8-10), Cu (pH 4 or 7-8), Ni (pH 8,5-11.5,) Sc (pH 2.6), Th (pH 2.5), Zn (pH 8-9); especially recommended for Ca (pH>10). Also in back-titration of Cr, Ga (pH 10) using nickel(II) and copper(II) solution as titrants, respectively.

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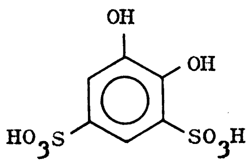
23. TIRON

Synonyms: Catecholdisulphonic acid

Chemical name: 1,2-Dihydroxybenzene-3,5-disulphonic acid (mainly available as disodium salt)

Colour index: -



H_4L

Protonation constants of the indicator

log K_1 -OH (m- to SO_3H)	log K_2 -OH	Conditions	Ref.
11.85	7.29	I=0.5	1
11.83	7.25	I=1.0	2
12.60	7.60	I=0.1	3
12.6	7.66	I=0.1	4,5
12.48	7.59	I=0.1	6
12.6	7.68	I=0.1	7
11.72	7.46	I=0.1	8
12.55	7.66	I=0.1	9

Stability constants of metal-indicator complexes

Metal ion	Reaction	log K	Conditions	Ref.
Al^{3+}	$Al^{3+}+L^{4-} = AlL^-$	16.7	I=0.1	10
		17.2		11
		16.65	I=0.2	12
		19.02*	I=0	13
		16.79*	I=0.1	14
	$AlL^-+L^{4-} = AlL_2^{5-}$	13.6	I=0.1	10
		13.3		11
		13.6	I=0.2	12
		12.08*	I=0	13
		16.58*	I=0.1	14
	$AlL_2^{5-}+L^{4-} = AlL_3^{9-}$	9.7	I=0.1	10
		2.4*	I=0	13
		14.34*	I=0.1	14
As^{3+}	$H_3AsO_3+2H_2L^{2-} = AsL_2^{5-}+H^++3H_2O$	-3.90[a]	I=1.0	15
$B(OH)_3$	$B(OH)_3+H_2L^{2-} = BL(OH)_2^{3-}+H^++H_2O$	-3.72	I=0.1	16
		-3.18[b]	I=1.0	17
Ba^{2+}	$Ba^{2+}+L^{4-} = BaL^{2-}$	4.1	I=0.1	18
	$Ba^{2+}+HL^{3-} = BaHL^-$	2.0		
Be^{2+}	$Be^{2+}+L^{4-} = BeL^{2-}$	12.88	I=0.1	19
	$BeL^{2-}+L^{4-} = BeL_2^{6-}$	9.37		
	$Be^{2+}+HL^{3-} = BeHL^-$	4.02		

Stability constants of metal-indicator complexes. (Cont.)

Metal ion	Reaction	log K	Conditions	Ref.
Cd^{2+}	$Cd^{2+}+L^{4-} = CdL^{2-}$	7.7	I=0.1	20
	$CdL^{2-}+L^{4-} = CdL_2^{6-}$	5.6		
Co^{2+}	$Co^{2+}+L^{4-} = CoL^{2-}$	8.2	I=0.1	20
		9.49	I=0.1	18
	$CoL^{2-}+L^{4-} = CoL_2^{6-}$	6.2	I=0.1	20
	$Co^{2+}+HL^{3-} = CoHL^-$	3.08	I=0.1	18
Cu^{2+}	$Cu^{2+}+L^{4-} = CuL^{2-}$	12.8	I=0.1	20
		14.28	I=0.1	9
		14.23	I=0.1	6
		13.99	I=0.1	21
		14.43	I=0.1	22
		14.53	I=0.1	18
	$CuL^{2-}+L^{4-} = CuL_2^{6-}$	11.0	I=0.1	20
		11.14	I=0.1	9
		11.26	I=0.1	6
		11.17	I=0.1	21
		10.93	I=0.1	22
	$Cu^{2+}+HL^{3-} = CuHL^-$	5.14	I=0.1	22
		5.48	I=0.1	18
Dy^{3+}	$Dy^{3+}+L^{4-} = DyL^-$	14.36	I=0.1	23
	$Dy^{3+}+HL^{3-} = DyHL$	5.59		
Er^{3+}	$Er^{3+}+L^{4-} = ErL^-$	14.48	I=0.1	23
	$Er^{3+}+HL^{3-} = ErHL$	5.45		
Fe^{3+}	$Fe^{3+}+L^{4-} = FeL^-$	18.74	I=0.5	24
		20.7	I=0.1	5
		20.4	I=0.1	25
	$FeL^-+L^{4-} = FeL_2^{5-}$	14.23	I=0.5	24
		15.2	I=0.1	5
		15.0	I=0.1	25
		15.03		26
	$FeL_2^{5-}+L^{4-} = FeL_3^{9-}$	10.28	I=0.5	24
		11.0	I=0.1	5
		10.4	I=0.1	25
		10.7		26
	$FeL^-+H^+ = FeHL$	1.8	I=0.1	5
		2.12	I=0.5	24
Ga^{3+}	$Ga^{3+}+L^{4-} = GaL^-$	~18.4	I=0.2	12
		19.26	I=0.1	27
	$GaL^-+L^{4-} = GaL_2^{5-}$	15.50	I=0.2	12
Gd^{3+}	$Gd^{3+}+L^{4-} = GdL^-$	14.10	I=0.1	23
	$Gd^{3+}+HL^{3-} = GdHL$	5.92		
Ge^{4+}	$H_2GeO_3+3H_2L^{2-} =$			
	$= GeL_3^{8-}+2H^++3H_2O$	2.74[c]	I=0.1	28
		2.30	I=0.11	29
		3.50	I=0.50	
		3.70	I=1.0	

Stability constants of metal-indicator complexes. (Cont.)

Metal ion	Reaction	log K	Conditions	Ref.
	$GeO_2+2H_2L^{2-}=GeL_2^{4-}+2H_2O$	3.89	I=1.0	
Hf^{4+}	$Hf^{4+}+L^{4-} = HfL$	24.66	I=0.2	30
	$Hf^{4+}+3L^{4-} = HfL_3^{8-}$	66.92		
Hg^{2+}	$Hg^{2+}+L^{4-} = HgL^{2-}$	19.86	I=0.1	27
Ho^{3+}	$Ho^{3+}+L^{4-} = HoL^-$	14.39	I=0.2	23
	$Ho^{3+}+HL^{3-} = HoHL$	5.42		
In^{3+}	$In^{3+}+L^{4-} = InL^-$	17.00 16.34	I=0.2 I=0.1	12 27
	$InL^-+L^{4-} = InL_2^{5-}$	13.85	I=0.2	12
La^{3+}	$La^{3+}+L^{4-} = LaL^-$	12.87	I=0.1	23
Mg^{2+}	$Mg^{2+}+L^{4-} = MgL^{2-}$	6.86	I=0.1	18
	$Mg^{2+}+HL^{3-} = MgHL^-$	1.98		
Mn^{2+}	$Mn^{2+}+L^{4-} = MnL^{2-}$	7.20 8.6	I=1 I=0.1	31 32
	$MnL^{2-}+L^{4-} = MnL_2^{6-}$	5.50	I=1	31
	$MnL_2^{6-}+L^{4-} = MnL_3^{10-}$	3.53		
	$MnL^{2-}+H^+ = MnHL^-$	6.68		
MoO_4^{2-}	$MoO_4^{2-}+2H_2L^{2-} =$			
	$= MoO_2L_2^{2-}+2H_2O$	6.59	I=0.1	33
Nd^{3+}	$Nd^{3+}+L^{4-} = NdL^-$	13.69	I=0.1	23
	$Nd^{3+}+HL^{3-} = NdHL$	5.61		
Ni^{2+}	$Ni^{2+}+L^{4-} = NiL^{2-}$	9.4 9.96 8.56	I=0.1 I=0.1 I=1	34 18 20
	$Ni^{2+}+HL^{3-} = NiHL^-$	3.00	I=0.1	18
	$NiL^{2-}+L^{4-} = NiL_2^{6-}$	6.34	I=1	20
	$NiL^{2-}+H^+ = NiHL^-$	5.3	I=1	
Pb^{2+}	$Pb^{2+}+L^{4-} = PbL^{2-}$	11.95	I=1	20
	$PbL^{2-}+L^{4-} = PbL_2^{6-}$	6.33		
Pr^{3+}	$Pr^{3+}+L^{4-} = PrL^-$	13.47	I=0.1	23
Sb^{3+}	$Sb(OH)_3+2HL^{3-} =$			
	$=SbL_2^{5-}+OH^-+2H_2O$	3.95	I=0.1	35
	$SbL(OH)^{2-}+H_2L^{2-} =$			
	$= SbL_2^{5-}+H^++H_2O$	-1.23		
	$SbL_2^{5-}+H^+ = SbHL_2^{4-}$	2.0	I=0.1	36

Stability constants of metal-indicator complexes. (Cont.)

Metal ion	Reaction	log K	Conditions	Ref.
	$SbL^{-}+H_2L^{2-} = SbL_2^{5-}+2H^+$	-5.73 -6.01	 I=1.0	
Sc^{3+}	$Sc^{3+}+L^{4-} = ScL^-$	18.07 18.96	I=0.1 I=0.1	8 27
	$Sc^{3+}+HL^{3-} = ScHL$	8.94	I=0.1	
	$ScL^-+H_2O=ScL(OH)^{2-}+H^+$	-6.10	I=0.1	8
Sm^{3+}	$Sm^{3+}+L^{4-} = SmL^-$	13.92	I=0.1	23
	$Sm^{3+}+HL^{3-} = SmHL$	5.72		
Sr^{2+}	$Sr^{2+}+L^{4-} = SrL^{2-}$	4.55	I=0.1	18
	$Sr^{2+}+HL^{3-} = SrHL^-$	1.88		
Tb^{3+}	$Tb^{3+}+L^{4-} = TbL^-$	14.14	I=0.1	23
	$Tb^{3+}+HL^{3-} = TbHL$	5.71		
TiO^{2+}	$TiO^{2+}+2H_2L^{2-} =$ $= TiO(HL)_2^{4-}+2H^+$	-0.3	I=0.1	37
	$TiO^{2+}+3HL^{3-} =$ $= TiL_3^{8-}+H^++H_2O$	19.8		
Tm^{3+}	$Tm^{3+}+L^{4-} = TmL^-$	14.36	I=0.1	23
	$Tm^{3+}+HL^{3-} = TmHL$	5.67		
UO_2^{2+}	$UO_2^{2+}+HL^{3-} = UO_2HL^-$	6.2	I=0.1	4
VO^{2+}	$VO^{2+}+L^{4-} = VOL^{2-}$	16.74 16.8	I=0.1 I=0.1	3 38
	$VOL^{2-}+L^{4-} = VOL_2^{6-}$	14.20 14.4	I=0.1 I=0.1	3 38
Y^{3+}	$Y^{3+}+L^{4-} = YL^-$	13.72	I=0.1	23
	$Y^{3+}+HL^{3-} = YHL$	5.13		
Yb^{3+}	$Yb^{3+}+L^{4-} = YbL^-$	14.43	I=0.1	23
	$Yb^{3+}+HL^{3-} = YbHL$	5.65		
Zn^{2+}	$Zn^{2+}+L^{4-} = ZnL^{2-}$	10.19	I=0.1	39
	$ZnL^{2-}+L^{4-} = ZnL_2^{6-}$	8.33		
Zr^{4+}	$Zr^{4+}+L^{4-} = ZrL$	24.15	I=1.0	40

[a] Ionic strength dependance: $\log K = -8.186+9.162\sqrt{I}\,(1+0.553\sqrt{I})^{-1} - 1.61I$.

[b] Ionic strength dependance: $\log K = -4.34+3.05\sqrt{I}\,(1+1.3\sqrt{I})^{-1} - 0.16I$.

[c] Ionic strength dependance (Ref. 4): $\log K = -2.307+27.49\sqrt{I}\,(1+2.85\sqrt{I})^{-1} - 0.370I$.

[x] Large differences in stability constants cannot be probably explained on the basis of ionic strength effect only.

Conditional stability constants of metal-indicator complexes

Metal ion	Metal:Reagent ratio	log K	Conditions	Ref.
Ce (IV)	1:3	3.75	pH 7-10.5	4
VO_2^+	1:1	1.15	pH 1, I=0.1	4

Spectral characteristics of the indicator
Solutions of the indicator do not absorb in VIS.

Spectral characteristics of metal-indicator complexes

Metal ion	Metal:Reagent ratio	λ_{max}.nm	ϵ_{max}x10^{-4}	Colour	Ref.
Ce (IV)	1:3	500	0.44	red	42
Fe (III)	1:1	660	0.18	blue	26
	1:2	560	0.5	violet	26
	1:3	480	0.6	pink	26

Purity of the indicator. Commercial product appears to be of sufficient purity for use as an indicator.

Purity check by absorbance measurement at λ=260 nm, pH=10.8, where ϵ= 7.699 (Ref. 44).

The indicator is used as 2% aqueous solution.

Typical application of the indicator. Direct titration of Fe(III) at pH 2-3. Also in back-titration of Zr, Hf using iron(III) solution as titrant.

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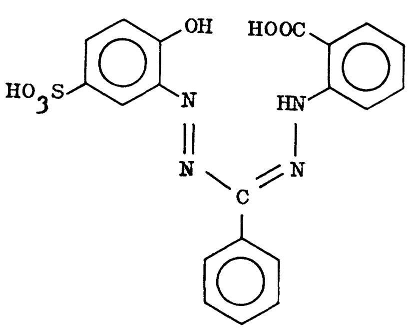
24. ZINCON

Synonyms: -

Chemical names:
o-[1-(2-Hydroxy-5-sulphophenyl)-3-phenyl-5-formazano]benzoic acid
5-(o-Carboxyphenyl)-1-(2-hydroxy-5-sulphophenyl)-3-phenylformazane
2-{2-[α-(2-Hydroxy-5-sulphophenylazo)-benzylidene]-hydrazino}-benzoic acid

Colour index: -



H_4L

Protonation constants of the indicator

log K_1 ≡NH$^+$	log K_2 -OH	log K_3 -COOH	Conditions	Ref.
>14	8.25	4.5		1
13	7.9	4	I=0.1	2

Stability constants of metal-indicator complexes

Metal ion	Reaction	log K	Conditions	Ref.
Zn^{2+}	$Zn^{2+}+HL^{3-} = ZnL^{2-}+H^+$	-1(-1.8)	I=0.1	1.2

Conditional stability constants of metal-indicator complexes

Metal ion	Metal:Reagent ratio	log K	Conditions	Ref.
Ga(III)	1:1	5.7	pH 6	3
Ni(II)	1:1	6.7	pH 6	4

Spectral characteristics of the indicator

Ion	λ_{max}	ϵ_{max}	Colour	Ref.
H_4L			red	1,6
H_3L^-			red-violet	1,6
H_2L^{2-}			yellow	1,6
HL^{3-}	490		red-orange	1,6

Spectral characteristics of metal-indicator complexes

Metal ion	Metal:Reagent ratio	λ_{max},nm	$\epsilon_{max}x10^{-4}$	Colour	Ref.
Cu(II)	1:1	600	1.9		5
Ga(III)	1:1	630	2.2	blue	3
Ni(II)	1:1	520,665	1.09, 0.97^x	violet	4
Zn(II)	1:1	620	1.9	blue	6
	1:1	625	2.4	blue	7

^{x} respectively for two maxima

Purification of the indicator was not described in the literature. Similar compounds have been purified by crystallization from anhydrous ethanol (Ref. 8).

Purity check. -

The indicator is used as 0.1% ethanolic solution.

Application of the indicator. Direct titration of Cd (pH 6), Hg (pH 6), Pb (pH 6), Zn (pH 9-10). Also in back-titration at pH about 10 of Al, Ca, Cd, Co, Cr, Cu, Fe(III), In, Mn, Ni, Pb and Lanthanides using zinc(II) solution as titrant.

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SUBJECT INDEX

The numbers refer to the sequence of indicators in this report.

Names and synonyms

According to metals, for which stability constants of complexes are given

According to metals for which conditional stability constants of complexes are given