

Selection of Suitable Indicators from Comparison of Colour Transformation in Terms of Index of Molar Colour Discrimination

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The concept of index of molar colour discrimination for acid-base and metallochromic indicators has been introduced. Its superiority over the specific colour discrimination (SCD) value is explained. The preference of xylenol orange analogue (XOA) for complexometric titration of lead and not that of mercury has been explained on the basis of molar colour discrimination index. The molar absorptivity of the latter complex is nearly twice as much as that of the former but the colour discrimination of the latter is only one-sixth that of the former.

In an earlier paper¹, we proposed the specific colour discrimination (SCD) value as a measure of sensitivity of the colour change of acid-base indicators. The SCD value of an indicator represents the calculated average number of colour discrimination steps over one pH unit at the rate of discrimination found experimentally over a small pH interval of about 0.1 pH unit (accurately measured). From the plot of SCD versus pH, the pH of maximum colour change (pH_{mcc}), and the half band width of colour change ($\Delta pH_{1/2SCD}$) were determined. The last parameter gives a measure of the rapidity of colour change; the smaller the $\Delta pH_{1/2SCD}$, the more rapid is the colour change. Such characterisations have been reported for phthalein and sulphonephthalein indicators². In highly alkaline or acidic medium, where the pH meter serves no useful purpose, the alkalinity or acidity is judged from colour changes of Hammett indicators. Bhaskare *et al.*³ employed SCD values for characterisation of indicators such as (*o*-hydroxyphenylazo)-*p*-nitrobenzyl cyanides (OHPNBC), its isomers and analogues in highly alkaline solutions. Clark *et al.*⁴ used the SCD values for characterising 2-cyano-3,3'-bis(*p*-nitroaniline)acrylonitrile (CPNA) and Gulati *et al.*⁵ used these for 2-(2'-lepidylazo)-1-naphthol-4-ammonium sulphionate (LANAS). More recently, we have reported similar characterisation of sulphamphthalein indicators⁶.

The SCD values in the case of acid-base as well metallochromic indicators change linearly with change in concentration of the indicator⁶ before attaining a maximum value. In chemical analysis the concentration of the indicator corresponding to the linear

portion of this curve is more useful. However, for comparison of the sensitivity, an SCD value conforming to a common concentration would be appropriate. Such a concentration could be a molar concentration, and the corresponding SCD can be designated as index of molar specific colour discrimination (MSCD). The MSCD values for the already reported²⁻⁶ indicators have now been calculated (see Table 1) and the results show that in case of *o*-cresol sulphamphthalein, thymol blue and cresol red in the alkaline range, and in case of *o*-cresol sulphamphthalein and thymol blue in the acidic range, the pH_{mcc} and the $pH_{1/2trf}$ fall close to each other and therefore these are most suitable indicators^{6,7}.

In the case of metallochromic indicators the colour change of interest is from zero transformation to complete transformation, and therefore easier to evaluate as compared with the gradual change of colour of an acid-base indicator. We describe here the colour transformation of XOA {3,3'-bis[bis(carboxymethyl)nitrilo]methyl-*o*-cresol sulphamphthalein} or xylenol orange analogue in its Pb(II) and Hg(II) complexes. XOA is related to *o*-cresol sulphamphthalein in the same manner as xylenol orange is related to cresol red.

XOA was synthesised⁸ by reacting *o*-cresol sulphamphthalein with formaldehyde and iminodiacetic acid in the presence of glacial acetic acid at $<60^\circ\text{C}$. The synthesised product was purified by partition extraction of its solution in 10% acetic acid saturated with butanol in a multipurpose solvent extractor⁹ at $<60^\circ$ using an equal volume of butanol saturated with 10% acetic acid.

XOA forms 1:1 complex with Pb(II) at pH 5-6 showing maximum absorption at 583 nm. It forms a 2:1 complex with Hg(II) at pH 10 showing maximum absorption at 600 nm. The molar absorptivities of Pb(II) and Hg(II) complexes are 41,000 and 74,500 litre mol⁻¹cm⁻¹ respectively (unpublished results). However, the visual colour transformation of the XOA in these complexes is not sensitive to the same extent. The close similarity of the absorption spectra of XOA and its Hg(II) complex at pH 10 could cause such an abnormality. The absorption spectra of XOA and its Pb(II) complex at the optimum pH of 5.5, however, are different from each other. It was, therefore, of interest to evaluate their colour transformation from tristimulus colourimetry.

Aliquots containing 10 and 20 ml of $1.564 \times 10^{-4} M$ XOA solution were mixed with slightly more than half the molar concentration *viz.* 3.5 and 6.5 ml of 2.5

Table 1—Index of Molar Specific Colour Discrimination (MSCD) of Colour Transformation of Acid-Base and MCD of Metal Complexes of Metallochromic Indicators

Indicator	pH_{mcc}	$10^{-4} \times (MSCD/MCD)$	λ_{max} (nm)	$10^{-4} \times A_M$ (litremol ⁻¹ cm ⁻¹)	at (pH)
<i>Acidic range</i>					
Cresol red	0.55	35	522	2.30	(0.3)
Thymol blue	1.55	50	545	1.80	(0.70)
Phenol sulphamphthalein	1.35	47	500	4.40	(0.13)
<i>o</i> -Cresol sulphamphthalein	1.30	62	525	5.60	(0.25)
Congo red	5.05	42	490	2.19	(5.80)
LANAS	3.65	32	—	—	—
<i>Alkaline range</i>					
Phenolphthalein	10.26	112	550	2.15	(12.20)
Cresolphthalein	9.00	177	570	5.58	(11.00)
Thymolphthalein	10.50	87	590	3.10	(11.6)
Phenol red	7.68	87	560	4.00	(9.00)
Cresol red	7.90	57	570	4.63	(7.60)
Thymol blue	8.90	67	595	1.76	(9.40)
Phenol sulphamphthalein	8.15	136	560	2.30	(8.00)
<i>o</i> -Cresol sulphamphthalein	8.20	141	575	1.76	(9.70)
LANAS	8.00	67	595	0.85	(8.80)
<i>Transformation of XOA* indicator to equivalent complex</i>					
Lead-XOA complex	—	78	560	4.20	(9.80)
Mercury-(XOA) ₂ complex	—	14	575	3.30	(8.10)
			583	6.00	(10.10)
			600	3.28	(8.15)

* Xylenol Orange Analogue

$\times 10^{-4} M$ solution of mercury perchlorate. The solution was made to 100 ml after adjusting the pH to 10 with 0.1 M sodium bicarbonate and 0.1 M sodium hydroxide to get Hg(XOA)₂ complex free from interference from absorption of the ligand.

Similarly 0.65, 2.0, 10.0, 20.0 ml of $1.564 \times 10^{-4} M$ solution of XOA were mixed with slightly more than equimolar concentration *viz.* 0.5, 1.5, 7 and 13 ml of $2.5 \times 10^{-4} M$ lead nitrate solution. The solution was made to 100 ml after adjusting the pH to 5.5 with 10% hexamine solution and dil. HCl to give Pb(XOA) complex.

From the absorption spectra of the indicator and the complex, the tristimuli X, Y, Z of the transmitted light were calculated using CIE (commission Internationale de L'Eclairage) distribution for illuminant 'C' as described earlier^{1,2,6}. These tristimuli were transfor-

med to uniform colour spacing, L*, a*, b* coordinates of the CIE's 1976 recommendations by the formulae given therein⁶.

The tristimuli values of the complexant and the respective complexes are plotted in chromaticity triangle in Fig. 1. The length of the change in this representation is not uniform and does not directly measure the extension of colour change. The corresponding CIELAB's coordinates a* and b* are plotted in Fig. 2. In Fig. 2 the colour change is represented uniformly by the length of the change. The number of standard deviations ΔE_{ab}^* were also calculated.

The plots of Figs. 1 and 2 show that the colour transformation of XOA to Hg(XOA)₂ complex at pH 10 is not conspicuous while that of XOA to Pb(XOA) complex of the same concentration at pH 5.5

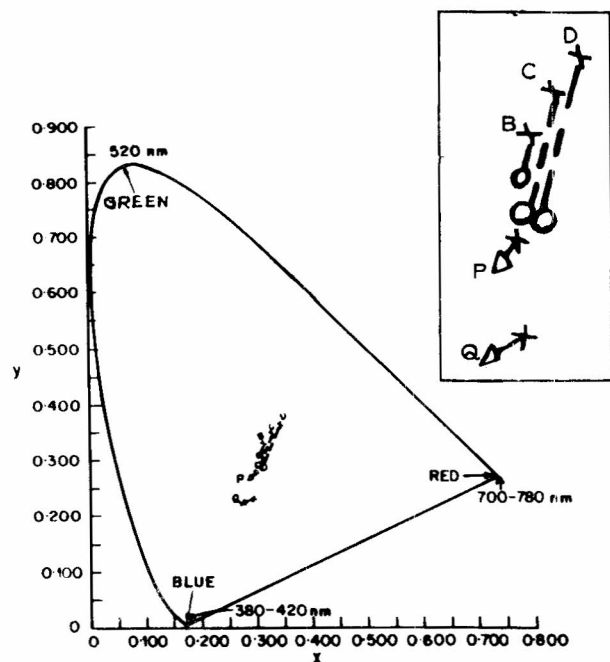


Fig. 1—Plots of x, y coordinates of the complex and XOA [X—○ change of colour from indicator to equivalent Pb(XOA) complex at pH 5.5; and X—○ that equivalent to Hg(XOA)₂ complex at pH 10.0 A: 1.02, B: 3.13, C: 15.64, D: 31.28 ($\times 10^{-6}$ M) Pb(XOA) complex P: 7.82, Q: 15.64 ($\times 10^{-6}$ M) Hg(XOA)₂ complex. Inset shows the plots on an enlarged scale (four times)].

is much more discriminatory. The former colour change occurs in the region of violet showing a change only in chromaticity. The change in the case of Pb(XOA) is from yellow to violet. These are complimentary colours, and therefore the colour change is more conspicuous.

For 31.28×10^{-6} M solution of XOA, its change to equivalent 15.64×10^{-6} M Hg(XOA)₂ complex involves a ΔE^* value of 6.7 while the change of XOA to equivalent 15.64×10^{-6} M Pb(XOA) complex involves a ΔE^* value of 36.6. The latter change is, therefore, about 6 times more sensitive. These evaluations show quantitatively why XOA is commonly recommended in the case of lead-EDTA titrations¹¹, but less so in mercury-EDTA determinations¹⁰.

The plot of colour change in terms of the number of standard deviations versus concentration of lead-XOA on its transformation from equimolar complexant XOA is sigmoid. The incremental number of colour

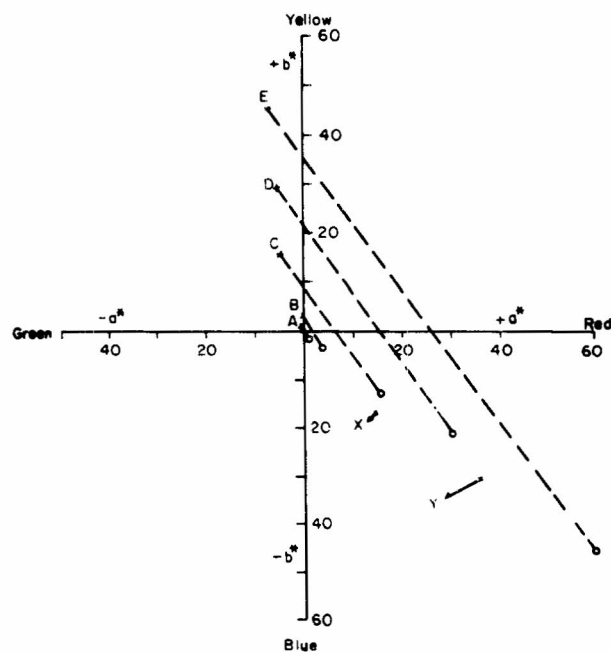


Fig. 2—Plots of a^*, b^* coordinates of the complex and XOA (notations same as in Fig. 1)

steps involved in the transformation of a molar solution of the complex from an equivalent amount of the complexant calculated from the limiting value, designated as index of molar colour discrimination (MCD), has been calculated and its values for Pb(XOA) and Hg(XOA)₂ are 78×10^4 and 16×10^4 respectively.

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