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Evaluation of Screened Indicators by Tristimulus Colorimetry

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Three acid-base indicators methyl red, ethyl red and dimethyl yellow are screened with appropriate inert dyes to improve the quality of colour change. The trichromatic parameters for the screened indicators are determined by weighted ordinate method and the colour transition curves are drawn in accordance with RUCS system and CIE Lab 1976 system. Of the studied combination, the screened indicator Methyl red + Methylene blue (3 : 1) is found to be more superior due to its rapidity of colour change and achievement of grey colour at the end point.

INTRODUCTION

Improvement of colour changes of chemical indicators at the end point is a subject of investigation since a long time[1,2]. The basis of exact screening is the addition of selected inert colorants so as to obtain a grey end point. The ideal situation is achieved when the solution at the end point contains no colour at all. Calatayud *et al.*[3] stated that the classical colour transition at the end point represented by

Colour A–Colour (A + B)–Colour B

is less subjective and must be rejected in favour of the transition represented by

Colour A–Grey–Colour B

They further stated that the equivalence point must be coincident with the chromatic 'grey point'. The trichromatic study provides the basis for the necessary inert dye which must be added to the indicator for the above mentioned colour transition at the end point. Bosch *et al.*[4] carried out detailed investigation on the screening of several thiocarbazones and thiosemicarbazones to improve the quality of colour change (from yellow shade to red) in presence of various inert colorants. They developed an expression for the ratio of the indicators to concentrations of different inert dyes in order to obtain a colour transition of two complimentary colours through grey colour.

Eriochrome black-T and bromopyrogallol red, two indicators in chelatometric titration[5] of lead(II), are screened by mixing with inert dyes in the powder state since no previous solution is advisable. In the complexometric titrations[6] of iron(III), a mixture of sulphosalicylic acid and methyl blue is recommended as the best screened indicator. Arsenazo(III) in presence of mixture of naphthol green and methyl orange is proposed as a very good screened indicator in the titration of lead(II) with EDTA and the replicate titrations showed very low 'rsd' value while using the screened indicator than indicator alone.[3] Erichrome blue SE in combination with tartrazine and phenosafranine is found to be a better screened indicator in titration[7] of zinc(II) with EDTA. In this investigation the quality of colour changes in the acid-base indicators methyl red, dimethyl yellow and ethyl red are improved by screening with appropriate inert dyes. The trichromatic values (x, y), complimentary coordinates (Q_x, Q_y), the parameters of RUCS, UV and CIE lab values are determined for pure indicators and screened indicators using a computer program written in FORTAN-77 and run on OMC Omega Computer.

EXPERIMENTAL

A Milton Roy spectrophotometer with 1 cm path cell, a Toshniwal pH meter and a computer OMC Omega 58000 are used. Generally BDH indicators are used.

3.363×10^{-3} M conc. indicator solutions of methyl red, ethyl red and dimethyl yellow are prepared in 50% ethanol solution. Buffer solutions are prepared in triple distilled water as described by Clark-Lubbs procedure. The indicator solutions are diluted to 3.363×10^{-5} M. 10 ml of indicator solution is taken and diluted with about 20 ml distilled water. The solution is maintained at the desired pH by adding the appropriate buffer and the volume is made up to 50 ml with distilled water.

Absorption spectra of each of the solutions with 10 nm interval are taken at varying pHs with a difference of pH 0.2 unit and also in inert dye.

RESULTS AND DISCUSSION

From the chromaticity diagrams (Fig. 1), it has been observed that the line joining the true colour coordinates for the colours before and after the end point, indicating that the colour transition at the equivalent point needs improvement by screening with appropriate inert dyes. Methylene blue, indigocarmine and malachite green for methyl red, methylene blue, indigocarmine for ethyl red and methylene blue, indigocarmine for dimethyl yellow are used as inert dyes. The transition curves drawn with the screening indicators has shown marked improvement in colour change, since these curves are passing through grey point when the indicators and inert dyes are mixed in specific ratio (Fig. 2).

Since the distances in the different regions of the chromaticity diagram have non-equivalent physical meanings, the colour distribution on this diagram is not uniform. The more uniform coordinates U, V on the RUCS[6] system are calculated from the following relations.

$$U = 0.075 - \frac{0.823(x + y - 1)}{1x - 7.05336y - 1.64023}$$

$$V = \frac{3.667x - 5.07713y - 1.36896}{1x - 7.05336y - 1.64023} - 0.5$$

The colour extension curves of the screened indicators in the RUCS system are shown in Fig. 3. Bucher *et al.* proposed the parameter[6] specific

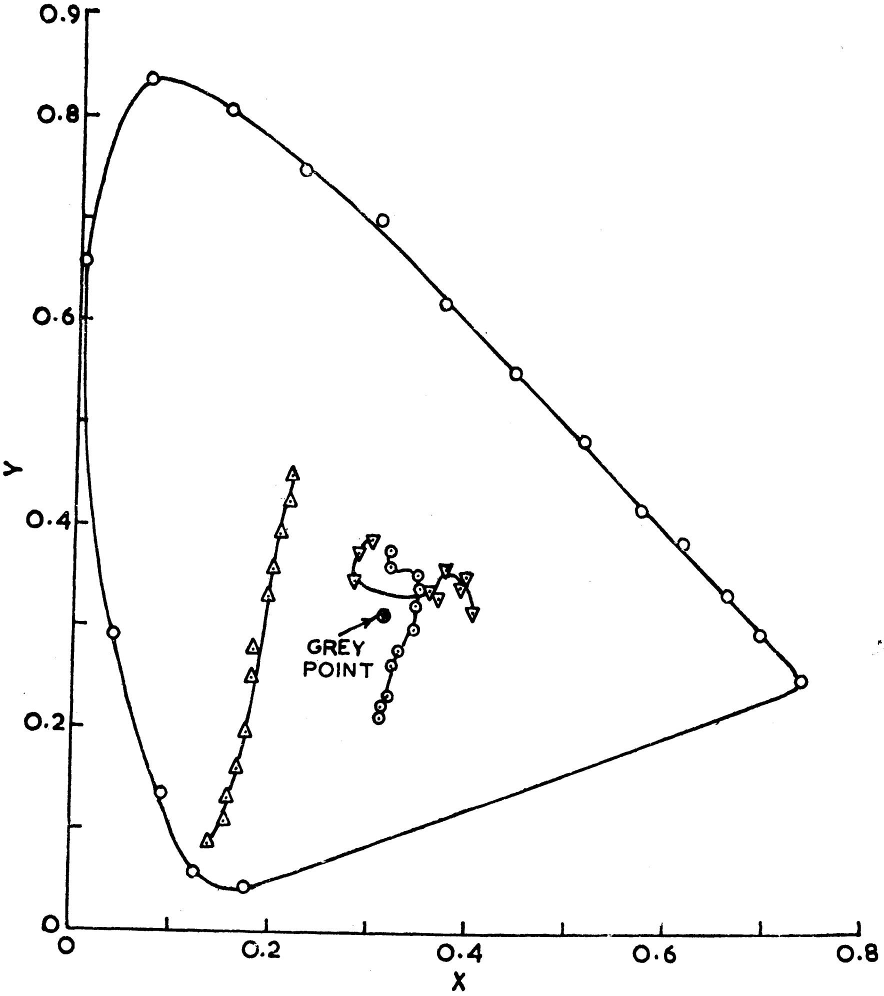

Fig. 1 Colour transition curves (x, y plots) of

⊙—⊙ Methyl red △—△ Ethyl red ▽—▽ Dimethyl yellow

colour discrimination which is equal to the number of colour discrimination steps for a small constant pH difference, pH 0.1 unit. The expression for colour discrimination ($\Delta C/\Delta pH$) is given by

$$\Delta C/\Delta pH = \frac{1}{2}\left(1000 \frac{\Delta\sigma}{\Delta pH}\right)$$

where

$$\sigma = \sqrt{(U_2 - U_1)^2 + (V_2 - V_1)^2}$$

The curves (Fig. 4) drawn between SCD and pH for various indicators showed peaks indicating the pH at which maximum colour change was

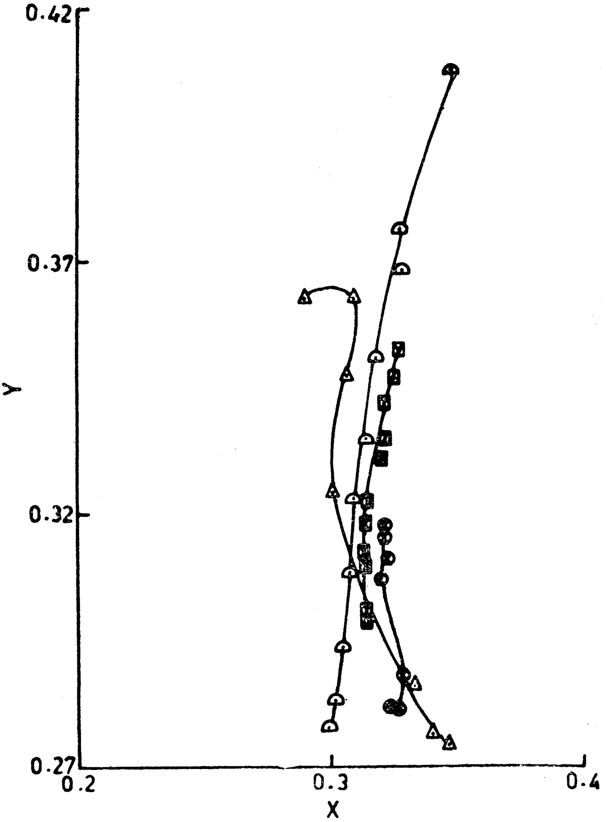

Fig. 2 Colour transition curves of

⌓ —⌓ Ethyl red + Methylene blue (6 : 1)
⊠ —⊠ Ethyl red + Indigo carmine (3 : 2)
△ —△ Dimethyl yellow + Methylene blue (3 : 1)
⊗ —⊗ Dimethyl yellow + Indigo carmine (2 : 1)

occurring. The half band width is a measure of rapidity of colour change. From measured values of SCD and half band width (Table 1) it is evident

TABLE 1

Indicator	pH mcc	SCD at max. colour change	Half band width in pH units
Methyl red + Methylene blue	5.2	39	0.130
	5.8	33	0.297
Methyl red + Indigocarmine	5.2	34	0.165
	5.8	31	0.198
Methyl red + Malachite green	4.7	33	0.198
	5.8	30	0.165
Ethyl red + Methylene blue	6.6	58	0.198
	6.2	43	0.396
Ethyl red + Indigocarmine	6.0	36	0.264
	6.7	28	0.330
Dimethyl yellow + Methylene blue	3.0	128	0.200
Dimethyl yellow + Indigocarmine	3.0	141	0.140

that the colour change for the screened indicator Methyl red-Methylene blue is more desirable than under the condition that indigocarmine is the

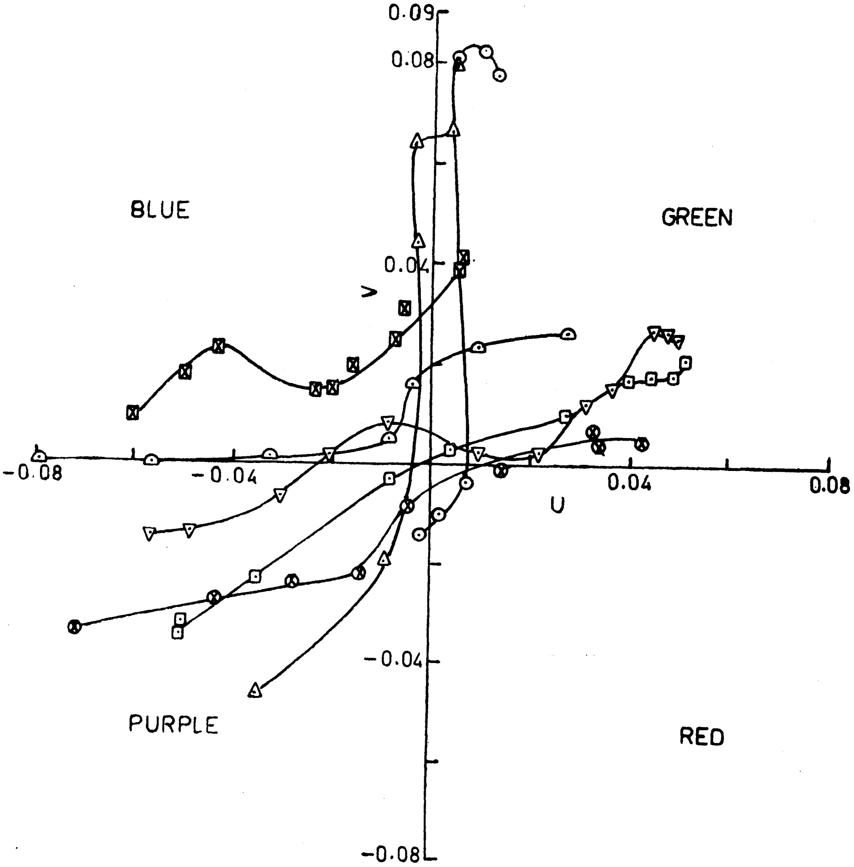

Fig. 3 U-V coordinates of the change of colour with pH for the screened indicators in RUCS system

⊡—⊡ Methyl red + Methylene blue (3 : 1)
▽—▽ Methyl red + Indigo carmine (3 : 2)
⊗ —⊗ Methyl red + Malachite green (2.5 : 2)
⌓ —⌓ Ethyl red + Methylene blue (6 : 1)
⊠—⊠ Ethyl red + Indigo carmine (3 : 2)
⊙ —⊙ Dimethyl yellow + Methylene blue (3 : 1)
△ —△ Dimethyl yellow + Indigo carmine (2 : 1)

inert dye used. Malachite green is also screening the colour change well for this indicator but with less success than the former two. Similar observations are made while studying the characteristics of the screening by inert dyes on ethyl red and dimethyl yellow.

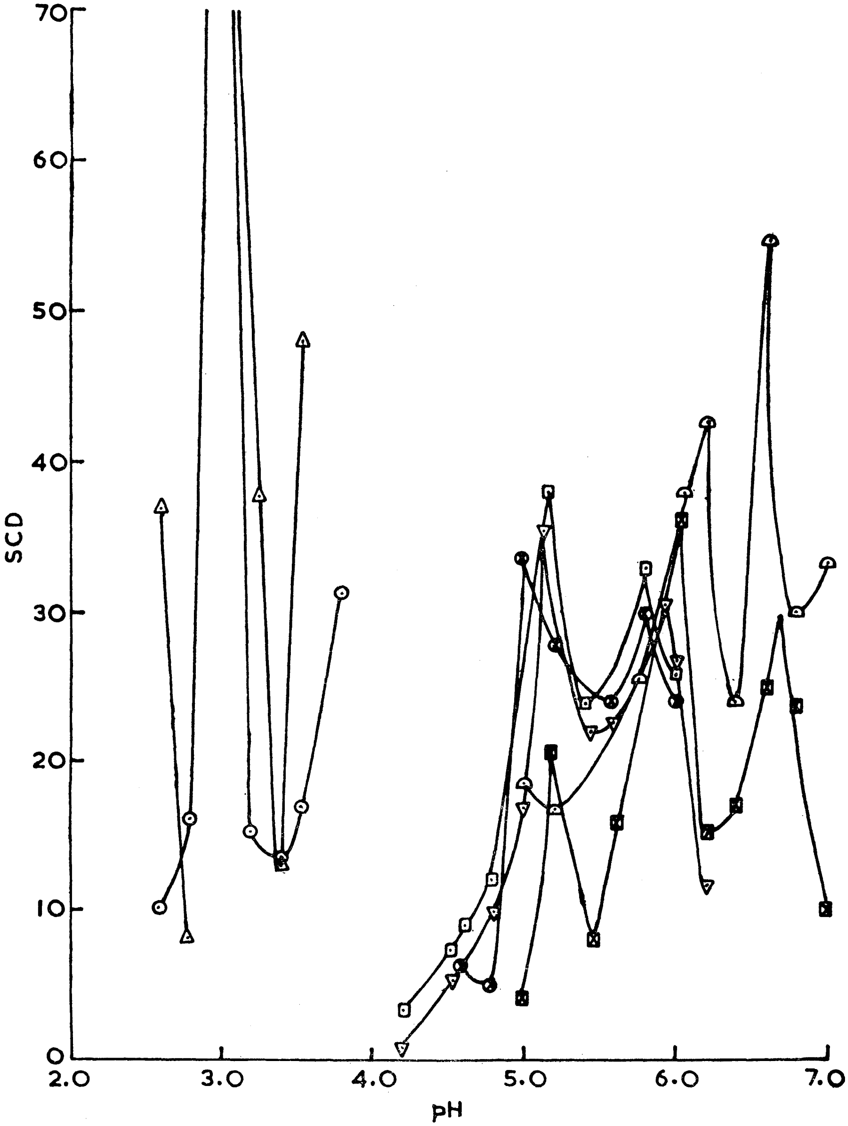

Fig. 4 Specific colour discrimination (SCD) in pH (Index as in Fig. 3)

CIE La*b* parameters defined in 1976 enable us to draw more uniform graphs between the coordinates a* and b* which give an account of transition curves during the course of the titration when the curve passes through the origin (grey point). The colour change is considered to be very sharp, since the transition between the complementary colours at the end point passes through colourlessness.

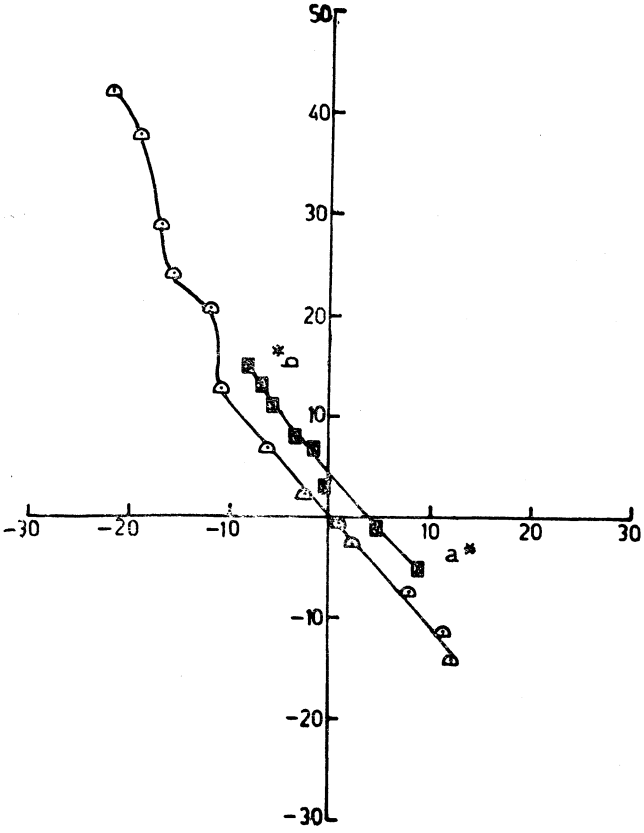

Fig. 5 CIE Lab 1976 parameters a* vs. b*

△—△ Ethyl red + Methylene blue (6 : 1)
☒—☒ Ethyl red + Indigo carmine (3 : 2)

From Figure 5 it has been observed that a mixture of methyl red and methylene blue in the ratio of 3 : 1 functions as good screened indicator, since the curve passes through origin. For the similar composition the rapidity of colour change is also very good as indicated by the low value of half band width of SCD curves. In this study the colour transition curves which passed through the origin of (a* vs. b*) graph are methyl red + methylene blue 3 : 1),

Methyl red + Methylene blue (3 : 1),
Methyl red + Indigocarmine (3 : 2),
Ethyl red + Methylene blue (6 : 1),

Ethyl red + Indigocarmine (3 : 2),

Dimethyl yellow + Methylene blue (3 : 1),

Dimethyl yellow + Indigocarmine (2 : 1).

This investigation based on trichromatic studies enables us to know the correct composition of inert dye to be added to three different acid-base indicators for improving the quality of colour change.

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