THE USE OF MIXED INDICATORS

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The use of mixed indicators does not appear to have received sufficient attention in the fields of chemical analysis and of process control. Since, in the light of the ionic theory, indicators are classified not by the old fashioned idea of more or less sensitivity to acids and alkalies, but by their hydrogen-ion functional range of utility, it becomes possible to search for an *a priori* rational basis for certain valuable requirements in practice. These may be, (1) to prepare a mixture of indicators which as an apparently new indicator will work within any special range desired; (2) to effect an apparent displacement of the color changes of an indicator in either half of its working range to the other; (3) to obtain a better color indication for a given colored medium.

The above three requirements are carried out with especial ease with the series of brilliant sulfone-phthaleins listed in Table I. Table II includes the well-known simple phthaleins, neutral point indicators, and the basic indicators such as methyl orange and methyl red, but neither table is exhaustive.

Consider the case of bromothymol blue, the best of all true neutrality point indicators.

The mean working color change occurs at $P_H \frac{(6.0 + 7.6)}{2} = 6.8$, showing here pure green, neither yellowish nor bluish. When working with a medium, showing a reaction of P_H 6.8 and colored yellow, a common enough experience, it is obvious that the indicator will show a yellowish-green that may be difficult to see; this is a difficulty that is not eliminated entirely by Walpole's compensation principle. If, however, we had an indicator showing a blue color at P_H 6.8, a green effect would result with the medium. No indicator is known that shows a blue with its working range at P_H 6.8, but there is no need to discover an entirely new one which shall fulfil this condition. Bromocresol purple shows violet at this hydrogen-ion concentration, and as violet and green produce blue, all we need to do is to use a mixture of equal volumes of bromothymol blue and bromocresol purple. The result in practice is a blue at P_H 6.8. Thus while we have satisfied Requirement 3 we have also fulfilled Requirement 2 by apparently displacing the blue color change given by bromothymol blue at P_H 7.6 towards the acid half of the range. Also the blue color at P_H 6.8 is not so pronounced at P_H 6.6; and at P_H 6.0 it is found to be greenish-yellow, like bromocresol purple alone at P_H 5.9. Thus we have attained a third advantage; namely, starting from the neutral color of bromocresol purple we have to pass through 0.8 Sörensen units to

reach blue, while it takes 1.6 units to go from yellow to blue using bromothymol blue alone.

TABLE I

SULFONE-PHTHALEINS

Trade Name	Range of utility or working range in Sörensen units	Color change acid → alkaline (or less acid)
1. Thymol blue (acid range)	1.2–2.8	Red-yellow
2. Bromophenol blue	2.8–4.6	Yellow-blue
3. Bromocresol purple	5.2–6.8	Yellow-purple
4. Bromothymol blue	6.0–7.6	Yellow-blue
5. Phenol red	6.8–8.4	Yellow-red
6. Cresol red	7.2–8.8	Yellow-red
7. Thymol blue (alkaline range)	8.0–9.6	Yellow-blue

TABLE II

SIMPLE PHTHALEINS, NEUTRAL POINT AND BASIC INDICATORS

Trade Name	Range of utility or working range in Sörensen units	Color change acid → alkaline (or less acid)
1. Methyl violet	0.1–3.2	Green-blue
2. Toepfer's reagent	2.9–4.2	Red-yellow
3. Methyl orange	3.1–4.4	Pink-yellow
4. Methyl red	4.4–6.0	Rose red-yellow
5. Congo red	3.0–4.5	Blue-red
6. Lacmoid	4.0–6.0	Pink-violet-blue
7. Litmus (azolitmin)	5.4–7.8	Red-blue
8. Neutral red	6.8–8.0	Red-yellow
9. Phenolphthalein	8.3–10.0	Colorless-red
10. Thymolphthalein	8.3–10.5	Colorless-blue
11. *o*-Cresolphthalein	8.2–9.8	Yellow-purple
12. α-Naphtholphthalein	7.9–9.0	Red-green-blue

These three points are experimentally substantiated by titrating primary potassium phosphate with alkali. It is seen from the following data that although different types of blue colors are given by the indicators, the blue alkaline color of the mixed indicator occurs earlier than that of bromothymol blue when alkali is run into the phosphate under duplicating conditions. This fact alone of the earlier appearance of the alkaline color in the case of the mixed indicator is sufficient to show the latter's superior sharpness; a buffer action, be it noted, is used here to slow down the extremely rapid color changes that would otherwise result with both indicators, single and mixed, in using highly dissociated acids alone or bases alone even in low concentration, for a drop of a highly dissociated acid or base alone can be sufficient to change the hydrion concentration for the indicator by several powers of ten. Thus, using 50 cc. of monopotassium phosphate, (about 0.1 N), 1 cc. of 0.04% mixed indicator I gave a distinct blue color with 26 cc. of 0.1 N alkali, while the same quantity of bromothymol blue required 42 cc.

In order to estimate accurately the primary phosphate according to the equation $2KH_2PO_4 + NaOH = KNaHPO_4 + KH_2PO_4 + H_2O$ the Sörensen value at the end-point must be 6.85 in 0.05 N concentration; and as this corresponds to the middle portion of the gradual slope of the titration curve it is necessary to supplement the titration by color matching. The standard consists of 50 cc. of 0.2 N monopotassium phosphate solution, 25 cc. of 0.2 N sodium hydroxide solution, 10 cc. of mixed indicator and 115 cc. of water; this shows a blue color (P_H 6.85) when observed in a test-tube; in a flask, dichroism may become evident by the appearance of a reddish tint in thick layers; this can be avoided if desired by using less indicator, but dichroism is not necessarily an objection.

If the phosphate to be titrated is also colored, the standard color is a combination of the two colors viewed through equal depths of the pure standard alone and of the phosphate.

TABLE III

TITRATION OF PHOSPHORIC ACID SOLUTION COLORED AN INTENSE YELLOW WITH METANIL YELLOW

Volume of phosphate used	0.1 N NaOH added	Strength of phosphate used
Cc.	Cc.	N
25	26	0.208
20	21	0.210
25	25.2	0.202

The standard color appeared greenish.

It must be emphasized that the yellow-to-blue changes with bromothymol blue and with the mixed indicator are not of the same type, but the advantage remains that the working range of a similar kind of color change as that given by bromothymol blue is halved by the addition of bromocresol purple and so the mixed indicator is sharper for the purpose of titration.

That similar kinds of color changes are not of the same type, will be understood from the following comparison table.

MIXED INDICATOR EQUIVALENT TO			
P_H value		P_H value	Color
6.0	Bromocresol purple	5.9	Green-yellow
6.2	Bromophenol blue	3.6	More greenish
6.4	Bromophenol blue	3.8	Green
6.6	Bromophenol blue	4.0	Blue-green
6.8	Bromophenol blue	4.2	Blue

The above comparisons were made in uniformly bored, unflanged test-tubes of hard white glass, using the same concentration of indicator, single or mixed, per cubic centimeter of solution. The standards were those of Clark and Lubs, and the concentration actually used was 0.05 cc. per cubic centimeter or 10 to 11 drops (as delivered from a Dreyer pipet) per 10 cc.

It is of course remarkable that bromophenol blue brings out the type of colors with the mixed indicator bromocresol purple and bromothymol blue. But it must be noted that the color at P_H 6.4 is greenish only with regard to the type of yellow and blue at P_H 6.0 and 6.8 respectively: the same color change given at P_H 3.8 by bromophenol blue is really a bluish-green as compared to the full blue given at P_H 4.6 by this simple indicator; yet for all this the advantage mentioned above remains. With a higher Sörensen value than 6.8 the mixed indicator keeps blue, the maximum depth being reached at P_H 7.6 and appears like thymol blue at P_H 9.2 with regard to type. Thus it will be seen from this example that mixed sulfone-phthaleins can be made to give almost any characteristic type of color given by any single sulfone-phthalein at a Sörensen value other than that required by the single indicator. This is of enormous advantage in process control when one deals with colored or turbid liquors.

Mixed Indicator II.—A 0.04% solution of bromocresol purple as the aqueous monosodium salt was combined in equal volumes with a 0.04% solution of bromophenol blue as the aqueous monosodium salt.

	Mixed Indicator Equivalent to		
P_H value		P_H value	Color
3.4	Bromocresol purple	5.3	Deep yellow
3.6	Bromocresol purple	5.4	Deep yellow
3.8	Bromophenol blue	3.5	Yellow-green
4.0	Bromophenol blue	3.5	Yellow-green
4.2	Bromophenol blue	3.7	
	or bromothymol blue	6.8	Green
5.0	Bromocresol purple	6.5	Pale purple
5.4	Bromophenol blue	4.2	
6.0	Bromocresol purple	6.8	Purple
6.2	Bromocresol purple	7.0	Violet

Beyond P_H 6.2 only a deepening of the violet color occurs. Between P_H 4.2 and 5.0 the color keeps about the same so that the mixed indicator has two ranges well marked out, the first, P_H 3.4 to 4.2 (0.8 unit interval); the second, P_H 5.0 to 6.2 (1.2 units interval); with a yellow medium, the second range shows the superiority of the mixed indicator over methyl red which works within this range but through orange to yellow. Bromophenol blue alone is also ruled out because its Sörensen value at the end of its working range is not more than P_H 4.6. Thus Requirement 1 is well fulfilled.

As an indicator, mixed indicator II is especially superior to methyl red, *p*-nitrophenol and bromocresol purple in its second range, particularly with colored liquids. Furthermore, it can replace bromophenol blue alone, where the end-point with acid titrants is desired as the acid limit of a useful range and not as the mean working color change; in this case, P_H 3.4–3.6 is the acid limit not given by any single indicator in Tables

I and II. The following titration experiments illustrate the utility of the mixed indicator.

Estimation of Formic Acid in the Presence of Phenol.—On the basis of the dissociation constant of phenol (1.3×10^{-10}) and of formic acid (2.4×10^{-4}), the conditions for a titration were adjusted for an end-point at P_H 6.2.

(1) A 200cc. stock solution was made from 2.59 g. pure phenol and 3.428 g. of formic acid of 80.5% quality as determined by titration to the ordinary phenolphthalein end-point, or the equivalent of 2.76 g. of pure formic acid. Of this solution, 5 cc. was diluted with about 100 cc. of water, 12.5 cc. of indicator added and the mixture titrated with 0.1 *N* sodium hydroxide solution, 14.91 cc. being required. The volume at the end-point was made up to 250 cc. and matched against a standard Clark and Lubs solution of P_H 6.2 containing 0.05 cc. of indicator per cubic centimeter. To eliminate completely the effect of the phenol acidity, 1.107 g. of original formic acid alone titrated to match the same color required 19.3 cc. of *N* sodium hydroxide solution, and on this basis the purity of the formic acid is 80.2% so that factor of degree of neutralization is the reciprocal of 802/805 or 1/0.996. The volume of 0.1 *N* sodium hydroxide solution added is thus increased to 14.97 cc. and the 200 cc. of stock solution therefore contained 2.75 g. of formic acid, a result agreeing with that based on the phenolphthalein end-point.

The above results were unaffected by the presence of as much as 50 cc. of 0.2% alcoholic methyl red in the stock solution, for the color match obtained by superimposing the colors due to methyl red and the mixed indicator at P_H 6.2 approximated to the useful color of bromocresol purple alone at P_H 6.4. It is, therefore, obvious that a yellow medium is better adapted for use with the mixed indicator than with methyl red alone or bromocresol purple alone in the region of P_H 6.0.

(2) The estimation was repeated with the conditions adjusted for an end-point (in the titration of the two acids) at P_H 5.5. At P_H 5.5 the color-match approximates to bromophenol blue alone at about P_H 4.2 and the mixed indicator is thus superior to bromocresol purple alone even for use in the colorless stock solution, for the color given by the latter indicator is dirty-looking.

Sixty cc. of stock solution, without dilution, treated with 4.2 cc. of mixed indicator required 18 cc. of *N* sodium hydroxide solution (allowing for the factor of degree of neutralization at P_H 5.5), the total volume at the end-point being 80 to 85 cc. The stock solution therefore contained 2.76 g. of formic acid.

Such concordant results are also rendered possible by molecular ratios of phenol to formic acid other than 0.46 of the stock solution considered.

Mixed Indicator III.—A 0.04% solution of bromophenol blue as the aqueous monosodium salt was combined in equal volumes with a 0.02% solution of cresol red as the aqueous monosodium salt.

P_H value	Mixed Indicator Equivalent to	P_H value	Color
4.6	Bromophenol blue	3.9	Green
6.8	Bromophenol blue or mixed indicator I at	4.2 6.8	Blue
7.6	Bromocresol purple	6.9	Purple
8.8	None	...	Intense violet

This combination forms a continuous triple range which is large; at P_H 4.6–6.8 the color is green-blue; at 6.8–7.6 it is blue-purple; at 7.6–8.8 it is purple-violet. These three color-change intervals are distinct and well marked.

As an indicator it is often superior to phenol-, thymol- and thymolsulfone-phthaleins, in the color shown at P_H 8.8; this being the alkaline limit of the useful range, it may sometimes be preferred to the mean working color change of thymol blue. It may here be stated that in acidimetric and alkalimetric titrations it is open to one in working to a given hydrogen-ion concentration, either to add the titrant (whether acid or alkali) to the point of the mean working color change of the indicator which indicated the desired Sörensen value, or so to choose the indicator that the acid titrant is added until the desired hydrogen-ion concentration is reached as the lower limit of the working range, or that the base titrant is added until the given hydrogen-ion concentration is reached as the higher or end limit of the working range. For Sörensen values between either limit and the mean working color change, color matching in addition would have to be resorted to, owing to the poor resolving power of the eye over the varying high intensities of the acid or alkaline colors, whichever the eye fixes on instinctively.

Twenty-five cc. of pure 0.2 *N* monopotassium phosphate was titrated to P_H 8.8 in 0.1 *M* concentration; using the mixed indicator, 49.6 cc. of 0.1 *N* sodium hydroxide solution was required instead of 50 cc. calculated. Titrating to P_H 6.8 in 0.05 *N* concentration and matching the color, the blue end-point was obtained when 25 cc. of 0.1 *N* solution was added, corresponding to the calculated amount.

It is interesting to note that in the range P_H 4.6 to 8.8, green-violet, the mean working color change is $(4.6 + 8.8) \div 2 = 6.7$, and in practice, the blue resulting from the blending of the green and violet appears at P_H 6.8 within the limit of experimental error ± 0.1 Sörensen units.

A mixture of phenol- and thymolphthaleins in equal volumes of 0.04% strength in 50% alcohol would be advantageous for some work, for instead of titrating phosphoric acid to P_H 9 in 0.1 *M* concentration using phenolphthalein alone to a decided pink color and thus probably reaching the exponent 10.0, it is necessary only to reach a pale purple at P_H 9.0, for beyond this the color deepens and tends toward the blue.

When a mixed indicator is found to give a very characteristic color at a certain Sörensen value as in the case of mixed indicator III the property can sometimes be applied to detecting qualitatively the purity of a substance. All pure substances capable of dissolving in water or aqueous alcohol or of forming salts with acids or bases will yield definite Sörensen values at definite concentrations which may be found by careful colorimetric comparison with the Clark and Lubs standards. The presence of small amounts of impurities will be shown by different or abnormal

Sörensen values which will be the more distinct, the less the impurities function as a buffer with the pure substance. Not all single indicators providing the necessary Sörensen value can be used for this purpose; some will probably react chemically with the substance tested and some may not give a color that is satisfactory. Mixed indicators would here be an advantage.

In the above examples of mixed indicators, the properties given are true when their preparation is carried out as described; different results may be obtained by having a greater proportion of one or the other component. In the case of mixed indicator I it was found, however, that the deviation from the range P_H 5.9–6.8 is less marked when bromothymol blue is made the larger constituent, that is, in proportion greater than 50%. Thus the optimum suitability of a double or mixed indicator will depend not only on the individual indicators mixed but also on their relative proportions chosen for simultaneous use.

A spectroscopic study of the examples of mixed indicators given should provide a fuller insight into the exact nature of the equilibria involved in attempting to correlate ionization, tautomerization and light absorption phenomena.

Summary

1. Differences of subjective color are enhanced when two indicators are partially transformed at the same hydrogen-ion concentration.

2. The colorimetric determination of hydrogen-ion concentration can, therefore, be rendered more precise where necessary and in certain titrations sharper end-points obtained. These advantages apply especially to colored liquids.

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ELASTICITY OF PURIFIED GELATIN JELLIES AS A FUNCTION OF HYDROGEN-ION CONCENTRATION

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In a previous communication entitled "The Elastic Properties of Gelatin Jellies"[1] two of the present writers have given the results on the measurements of the rigidity of gelatin jellies from commercial gelatins, at various concentrations and under different conditions of preparation. Certain rather anomalous effects were observed when the rigidity was determined for jellies containing different concentrations of acid and alkali, the Sörensen values of which had been determined electrometrically in solutions.

[1] Sheppard and Sweet, THIS JOURNAL, **43**, 539 (1921).