3. Variations in the adsorbent are investigated in the cases of water and benzene.

4. Additional evidence is found that the adsorbed material exists as a liquid, even below the freezing point of the free liquid.

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[CONTRIBUTION FROM THE COLOR LABORATORY, BUREAU OF CHEMISTRY, UNITED STATES DEPARTMENT OF AGRICULTURE, NO. 88]

THE SPECTROPHOTOMETRIC DETERMINATION OF HYDROGEN-ION CONCENTRATIONS AND OF THE APPARENT DISSOCIATION CONSTANTS OF INDICATORS. I. THE METHODS

BY WALTER C. HOLMES

RECEIVED NOVEMBER 30, 1923

The degree of transformation of any indicator within the range of its utility is dependent upon the hydrogen-ion concentration of its solution. It may be measured with relative accuracy with the aid of the spectrophotometer and given numerical expression in terms of definite spectrophotometric ratios.

In the instance of an indicator which is colored in only one of its forms the suitable ratio (R_1) for defining the degree of transition at any point within the zone of color change is that of the intensity of the absorption at that point to that of an equal quantity of indicator under conditions insuring maximum intensity. With indicators which exhibit the essential behavior of monobasic acids (or bases), and with which complete transformation may be obtained, the numerical value of R_1 is that of the percentage color transformation. It may be determined by means of comparative absorption measurements carried out at a single wave length selected at or near the maximum of the absorption band of the colored form.

With two-color indicators it is possible to employ either or both of two ratios of this type, or to adopt a second type of ratio (R_2), that of the intensities of absorption at two wave lengths selected at or near the respective maxima of the two absorption bands in question. A ratio of this latter type affords a maximum degree of alteration per unit change in indicator transformation, since both the increase in one absorption form and the simultaneous decrease in the other contribute to that end. Its employment may prove further advantageous in other respects. Its value is unaffected by minor variation in the concentration of the indicator and the accuracy with which it may be determined, accordingly, is not impaired by any failure to insure complete uniformity in the quantity of indicator employed.

Inasmuch as this second type of ratio (R_2) referred to has not hitherto been utilized, to the author's knowledge, in the connection proposed, it will be well to illustrate its character further by means of absorption curves obtained in preliminary measurements with two indicators.

With 1-napthol-2-sodium sulfonate indophenol (prepared and supplied by W. M. Clark of the Hygienic Laboratory, United States Public Health Service), if the ratio of the intensity of absorption at 550 $\mu\mu$ to that at 625 $\mu\mu$ is adopted as R_2 its value will be seen to undergo extensive progressive variation over the range in hydrogen-ion concentration employed.

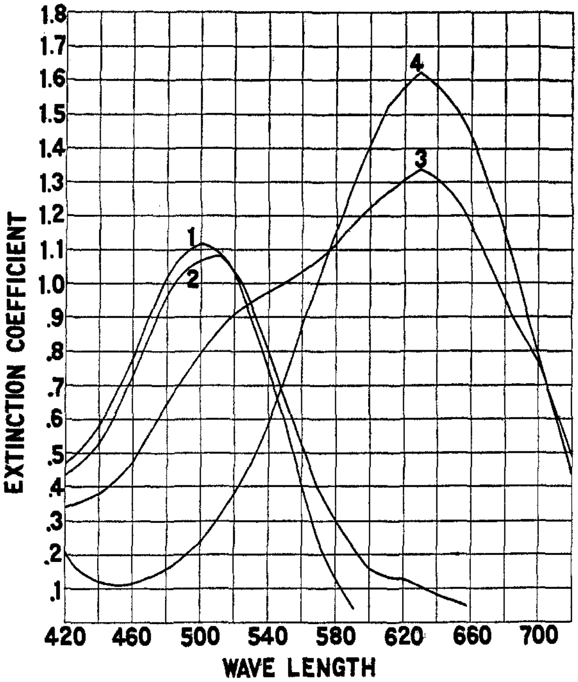

Fig. 1.

1-Naphthol-2-sodium sulfonate indophenol. 1: 75/m[a], PH 5.82; 2: 75/m, PH 7.74; 3: 70/m, PH 8.69; 4: 37.5/m, PH 10.19.

[a] Parts of dye per million parts of solvent.

PH	10.19	8.69	7.74	5.82
R_2	0.146	0.60	10.40	—

With phenolsulfonephthalein the ratio of the intensity of absorption at 460 $\mu\mu$ to that at 560 $\mu\mu$ may be employed. (The former wave length is selected in preference to one situated nearer to the maximum of the band of the indicator in mid-range in consideration of the advantage obtained thereby in visual sensitivity.) The following variation in R_2 may be noted.

*P*H	10.19	7.52	6.29
R_2	0.10	0.51	7.24

With phenolsulfonephthalein (and its various derivatives) a second ratio of the same type may be utilized in the acid range of the indicator.

Spectrophotometric ratios of either or both the general types referred to may be employed to advantage in the development and application of a spectrophotometric method for the evaluation of hydrogen-ion concentrations. For this purpose it is necessary merely to determine the ratios with suitable indicators in buffered solutions affording small intervals in Sörensen (*P*H) value over their effective ranges. Curves may be drawn defining the dependence of the ratios upon hydrogen-ion concentration, with the aid of which it will then be possible to base determinations of the hydrogen-ion concentrations of solutions of unknown Sörensen values upon spectrophotometric measurements.

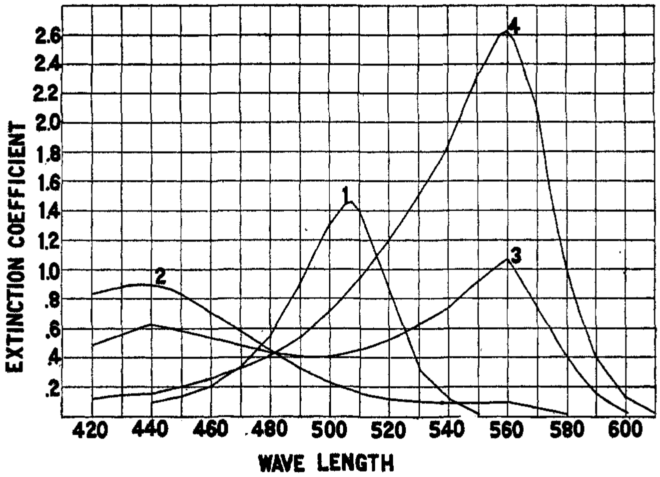

Fig. 2.—Phenolsulfonepthalein.
1: 10% H_2SO_4; 2: *P*H 6.29; 3: *P*H 7.52; 4: *P*H 10.19.

The ease and rapidity with which such methods may be standardized and applied may be emphasized. Any type of spectrophotometer may be employed; one with which intensity values (extinction coefficients) may be read directly from the photometer scale, and of which the manipulation necessitates only ordinary care and skill, is a convenient instrument for the purpose. The determination of a spectrophotometric ratio may be made in a very few minutes.

The accuracy of the method is dependent upon an advantageous selection of indicators and upon the restriction of their employment within the zones of Sörensen values in which the variation in their ratios is appreciable. The sulfonephthalein series of indicators, adopted by Clark and Lubs and recently extended by Cohen,[1] is reasonably suitable for spectrophotometric application but is not adapted to afford optimum accuracy with the method. The ideal indicators for the purpose are such as give two bands of which both occur in spectral regions in which the eye is relatively sensitive to variations in intensity, whereby accuracy in the determination of ratios of the R_2 type is favored. Such indicators are found among the indophenols and should be preferred provided their other qualifications for employment prove satisfactory.

With a judicious selection of indicators and technique the spectrophotometric method affords the maximum accuracy possible in indicator methods. The evaluations are based upon a matching of the intensity of light of the same color in contiguous fields. The phenomena of dichromatism encountered with many indicators, introduce no interference. The presence of such degrees of color and turbidity as are ordinarily met in solutions to be evaluated does not affect the accuracy with which the ratios may be measured, since the technique of spectrophotometric practice is, or may be made, such that an exact compensation for their effects is obtained automatically. The difficulties introduced by excessive color or turbidity may be overcome by increasing the concentration of the indicator and decreasing the thickness of the layer of solution employed in the measurements. The resort to thin layers of solution should also render it possible to determine the ratio of a solution when only a few drops of material may be available for examination.

In the instance of indicators which behave like monobasic acids the data obtained in the empirical calibration of their spectrophotometric ratios against Sörensen value may be utilized in determining their approximate apparent dissociation constants and the approximate form of their dissociation curves. The fundamental principles upon which these determinations may be based are those of the "drop-ratio" methods employed by Clark and Lubs[2] and by Gillespie[3] and do not require specification in detail. The spectrophotometric method affords greater accuracy than is possible in visual methods, however, and is convenient in application. With a minimum amount of experimental data it is possible to calculate the ratios (of either type) which the indicators will have at any transition point in their transformation or, conversely, to calculate the degrees of dissociation which correspond to any given values in ratios. The experimental data may be employed in checking the dissociation equilibrium, and the theoretical dissociation in checking the accuracy of the experimental method.

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[1] Cohen, "Public Health Reports," **38**, No. 5, Feb. 2, **1923**, p. 199.

[2] Clark and Lubs, *J. Bact.*, **2**, 1, 109, 191 (1917).

[3] Gillespie, *Soil Science*, **9**, 115 (1920); THIS JOURNAL, **42**, 742 (1920).

The spectrophotometer has rendered important service in the investigation of indicators.[4] The methods outlined in the present paper provide a simple, convenient and relatively accurate means of utilizing the spectrophotometer to advantage in the employment of indicators, and are useful adjuncts to established methods for the determination of hydrogen ions. Data will be supplied in subsequent communications bearing upon the practical application and limitations of the methods in the instances of representative indicators.

The author wishes to take this opportunity to express his appreciation to W. Mansfield Clark of the Hygienic Laboratory, United States Public Health Service, for valuable suggestions and for criticisms of these methods.

Summary

Simple, convenient and relatively accurate methods are outlined for the determination of the hydrogen-ion concentrations of solutions by spectrophotometric means. They are based upon empirical calibration of spectrophotometric ratios with suitable indicators against known hydrogen-electrode values.

The data of such calibrations afford an advantageous means for the calculation of the approximate apparent dissociation curves of indicators and their approximate apparent dissociation constants.

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[CONTRIBUTION FROM THE COLOR LABORATORY, BUREAU OF CHEMISTRY, UNITED STATES DEPARTMENT OF AGRICULTURE, No. 89]

THE ABSORPTION SPECTRA OF CERTAIN DERIVATIVES OF PARA-CYMENE

BY WALTER C. HOLMES

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Spectrophotometric data obtained with six mono-azo dyes prepared from *p*-cymene at this Laboratory by M. Phillips are recorded in the following table. For comparison, corresponding absorption measurements on five commercial dyes derived from benzene, of which the former are homologs, are also included. The *p*-cymene derivatives were made from intermediates of good purity and compared favorably with commercial dyes of the best grade in respect to freedom from subsidiary coloring matters.

All values recorded are the averages of ten or more measurements made with a standard spectrometer, provided with a Nutting photometer. Since both the laboratory and the commercial products examined contained various amounts of inorganic salts the absolute value of the measurements is without significance. The data obtained, however, afford a reliable

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[4] See THIS JOURNAL, **41**, 1031 (1919).