[CONTRIBUTION FROM THE LABORATORY OF THE HIGHLAND PARK WATER DEPARTMENT]

A MODIFICATION OF GILLESPIE'S METHOD FOR THE DETERMINATION OF HYDROGEN-ION CONCENTRATIONS

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L. J. Gillespie[1] proposed a method for the colorimetric determination of hydrogen-ion concentration in terms of Sörensen values, P_H, of solutions without the use of buffer solutions, which is based on the modern theory of indicators and is very simple in technique and very accurate. It requires about 10 minutes to prepare a set of color standards by this method, and only such materials as a few pipets, test-tubes of uniform diameter, distilled water, dil. acid and alkali. The author has found these standards so reliable that he has used them to check standard buffer solutions. The drawback to the method is that the standards last for only a few hours.

The rapid fading of these standards is due largely to a change of hydrogen-ion concentration in the dil. acid and alkali solutions because of carbon dioxide from the laboratory air or the action of the solutions on the test-tubes (and when bromophenol blue is used as indicator, to the use of too strong sodium hydroxide solution). Buffer solutions resist slight changes due to these causes. Since color standards made with buffer solutions may be kept fairly well for a month by adding a few drops of toluene to the tubes and stoppering with paraffined corks, it occurred to the author to modify Gillespie's method by substituting roughly prepared buffer solutions for the production of the acid and alkaline colors instead of dil. acid and alkali.

Two or three drops of toluene added to standards prepared with such buffers will satisfactorily preserve all the indicators recommended by Clark[2] except methyl red. In the acid tubes containing methyl red the yellow or alkaline form of the indicator is extracted by toluene, thereby shifting the equilibrium and lowering the amount of acid color in the standards. However, when the methyl red standards are loosely stoppered for the first few days before paraffining the stoppers, the excess of toluene will evaporate and the standards will remain sufficiently accurate so that readings may be made to within ± 0.1 of a Sörensen unit. With the exception of methyl red, all the color standards prepared according to the method given below have been kept without change in shade for from 4 to 8 weeks in both winter and summer weather, the standards being kept in a dark closet when not in use.

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

[2] Clark, "The Determination of Hydrogen-ion Concentration," Williams and Wilkins, **1920**.

Modification of Gillespie's Method

Indicator Concentration.—It is best to use indicator concentrations as recommended by Gillespie (see Table I) wherever possible. Often, different indicator powders do not give the same color concentration or intensity and it is frequently necessary to double or triple the concentrations recommended in order to obtain good color differentiation. In analyses of the Great Lakes water, higher concentrations than triple that recommended give high results. The original concentrations recommended by Gillespie give the same final concentration of indicator in the unknown as the "four drops per 10 ml." of the indicator solutions recommended by Clark.[2]

Approximate Buffer Solutions.—The following buffer solutions, made from ordinary C. P. salts commonly found in the laboratory, may be used to produce the acid or alkaline colors instead of the dil. acid and alkali solutions used by Gillespie. In Table I these buffer solutions are indicated by the Roman numerals given below.

I. *N* Acetic acid (57.7 ml. of glacial acetic acid diluted to 1000 ml. with distilled water) for the acid colors of bromophenol blue and methyl red.

II. 7.0 g. of potassium dihydrogen phosphate per 1000 ml. of distilled water (C. P. "Analyzed") for the acid colors of bromocresol purple, bromothymol blue, phenol red, cresol red and thymol blue (alkaline range).

III. 18.0 g. of disodium phosphate dodecahydrate per 1000 ml. of distilled water (C. P. "Analyzed") for the alkaline colors of bromophenol blue and methyl red, and also for bromocresol purple and bromothymol blue, if desired.

IV. 1.0 g. of anhydrous sodium carbonate per 1000 ml. of distilled water (C. P. "Analyzed") for the alkaline colors of bromocresol purple, bromothymol blue, phenol red, cresol red, and thymol blue (alkaline range).

A very convenient color comparator may be made after the plan outlined in Gillespie's original article except that it should be 60 × 7.5 × 7.5 cm. and should contain 23 sets of 3 holes instead of 3 sets. This allows a complete set-up of the 11 color standards of any indicator in alternate sets of holes and facilitates the comparisons of unknowns with the standards.

Table I gives complete data for making up the indicator solutions and standards. It is essentially the same as Gillespie's[1] table except that he uses 1 drop of 0.2% sodium hydroxide solution in 5 ml. of distilled water to form the alkaline color of all indicators, and to form the acid colors he uses 1 ml. of 0.05 *N* hydrochloric acid and 4 ml. of distilled water for bromophenol blue, 1 drop of the dil. hydrochloric acid in 5 ml. of distilled water for methyl red, bromocresol purple, bromothymol blue and phenol red, and 1 drop of 2% potassium dihydrogen phosphate for cresol red and thymol blue.

The indicators, both the stock and dil. solutions, should be kept in dark colored bottles and the bottles containing the dil. indicator solutions should be fitted with stoppers through which are inserted 1 ml.

pipets. It is essential that the same pipet be used for both standards and unknown solutions, in order to obtain the same drop volume.

TABLE I

DATA FOR THE DETERMINATION OF SÖRENSEN VALUES OF HYDROGEN-ION CONCENTRATION

Drops of indicator in		Drops of buffer to equalize level in tubes		P_H values of each pair of tubes						
Acid tube	Alk. tube	Acid	Alk.	Bromophenol blue	Methyl red	Bromocresol purple	Bromothymol blue	Phenol red	Cresol red	Thymol blue
1	9	9	1	3.1	4.05	5.3	6.15	6.75	7.15	7.85
3[a]	17[a]	17[a]	3[a]	3.3	4.25	5.5	6.35	6.95	7.35	8.05
2	8	8	2	3.5	4.4	5.7	6.5	7.1	7.5	8.2
3	7	7	3	3.7	4.6	5.9	6.7	7.3	7.7	8.4
4	6	6	4	3.9	4.8	6.1	6.9	7.5	7.9	8.6
5	5	5	5	4.1	5.0	6.3	7.1	7.7	8.1	8.8
6	4	4	6	4.3	5.2	6.5	7.3	7.9	8.3	9.0
7	3	3	7	4.5	5.4	6.7	7.5	8.1	8.5	9.2
8	2	2	8	4.7	5.6	6.9	7.7	8.3	8.7	9.4
17[a]	3[a]	3[a]	17[a]	4.8	5.75	7.0	7.85	8.45	8.85	9.55
9	1	1	9	5.0	5.95	7.2	8.05	8.65	9.05	9.75
% Indicator soln. used by Gillespie				0.008	0.008	0.012	0.008	0.004	0.008	0.008
Ml. of 0.1 N NaOH per 0.1 g. of indicator for stock soln.				1.64	..	2.78	1.77	3.10	2.88	2.38
Produce acid color with 5 ml. (10 ml. for 3–17 ratio) of Buffer No.				I	I	II	II	II	II	II
Produce alk. color with same amount of Buffer No.				III	III	IV	IV	IV	IV	IV

[a] The 3/17 and 17/3 ratio pairs require 10 ml. of buffer to each tube instead of 5.

Procedure: (1) Place eleven pairs of test-tubes of uniform diameter in the comparator; (2) add the correct number of drops of indicator to each tube; (3) add the correct number of drops of buffer solution to total 10 drops to each tube; (4) add 5 ml. of the buffer to each tube from a buret; (5) add 2 or 3 drops of toluene to each tube; (6) stopper with paraffined cork stoppers. To 5 ml. of the unknown add 10 drops of indicator and compare with the standards, compensating for color and turbidity in the usual way in the comparator.

The author has found the drop method very accurate and more convenient than measuring the indicator in 0.1 ml. If it is preferred to measure the indicator in 0.1 ml. instead of by drops, Table I may still be used except that in the columns marked "drops of indicator" and "drops of buffer," 0.1 ml. should be used as equivalent to 1 drop, and 10 ml. of buffer used instead of 5 to produce the acid or alkaline colors. For the 3/17 and 17/3 drop-ratio pairs, 0.15/0.85 and 0.85/0.15 ml. ratios may be used with 10 ml. of buffer solutions.

Summary

1. A modification of Gillespie's method for the determination of hydrogen-ion concentrations in terms of Sörensen values, P_H, is given in which

the color standards have been preserved for from 4 to 8 weeks or more.

2. The method is particularly suited to the average technical laboratory because of its accuracy, simplicity of technique, and the use of ordinary C. P. "Analyzed" salts instead of the highly purified buffer salts recommended by Clark.[1]

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[CONTRIBUTION FROM THE LABORATORY OF PHYSICAL CHEMISTRY OF THE UNIVERSITY OF UPSALA]

THE DETERMINATION OF THE DISTRIBUTION OF SIZE OF PARTICLES IN DISPERSE SYSTEMS[1]

BY THE SVEDBERG AND HERMAN RINDE

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Some years ago one of us[2] pointed out the eminent importance of determinations of the distribution of size of particles in disperse systems and suggested two experimental methods founded on the resistance law,

$$f = 6\pi\eta r v \tag{1}$$

where f is the friction developed when a sphere of radius r is moving with the velocity v in a liquid possessing the viscosity η.

The force applied to keep the particle in constant motion was, as suggested in the paper referred to, (1) the force of gravitation, (2) the shocks from the surrounding molecules of the liquid. In other words, the first method applies Stokes' law,

$$r = \sqrt{\frac{9\,h\eta}{2(s_p - s_d)gt}} \tag{2}$$

where h is the height of fall, s_p and s_d the density of the particles and the dispersion medium, respectively, g the gravitational constant and t the time of fall. The second method applies the Einstein law for the Brownian movements

$$r = \frac{RT}{N} \cdot \frac{1}{3\pi\eta\,\overline{(x_2 - x_1)^2}} \cdot t \tag{3}$$

where R is the gas constant, T the absolute temperature and $\overline{(x_2 - x_1)^2}$ the average square of the displacement of the particle in the time t.

Some series of measurement illustrating the use of the first method were given. The fall of a statistically sufficient number of particles was measured with the aid of a microscope provided with a dark-field condenser and the frequency curves of the size of particles were drawn. The particles studied in this investigation were all of spherical shape (mercury, gamboge, fats).

A preliminary attempt to utilize the second procedure was made by

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[1] Presented before the Physical Chemistry Symposium, Rochester Section, American Chemical Society, January 19 and 20, 1923.

[2] Svedberg and Estrup, *Kolloid-Z.*, **9**, 259 (1911).