

A SYMPOSIUM ON INDICATORS¹

INTRODUCTION: A BRIEF HISTORICAL SKETCH

C. J. BROCKMAN

Department of Chemistry, University of Georgia, Athens, Georgia

Received December 10, 1934

As an introduction to this Symposium a very short historical sketch of the developments in the uses of indicators will be of interest. The first reference to the use of a color indicator, as we know it today, is in the work of Robert Boyle, who in 1660 wrote a treatise entitled "The Experimental History of Colours." He used a tincture of Lignum Nephriticum (2): "I drop into the infusion just as much distilled vinegar, or other acid liquor as will serve to deprive it of its blueness (which a few drops, if the sour liquid be strong, and the phial small, will suffice to do;), then without changing my posture, I drop and shake into the same phial a small portion of spirit of hartshorn or urine, and finding that upon this affusion the tincture immediately recovers its ceruleous color, And therefore I allow myself to guess at the strength of the liquors examined by this experiment, by the quantity of them which is sufficient to destroy or restore the ceruleous colour of our tincture."

Another quotation is interesting (3): "Take good syrup of violets, impregnated with the tincture of the flowers, drop a little of it upon a white paper (for by that means the change of colour will be more conspicuous, and the experiment may be practiced in smaller quantities), and on this liquor let fall two or three drops of spirit either of salt or vinegar, or almost any other eminently acid liquor, and upon the mixture of these you shall find the syrup immediately turned red: . . . if instead of spirit of salt, or that of vinegar, you drop upon the syrup of violets a little oil of tartar per deliquium, or the like quantity of a solution of potashes, and rub them together with your finger, you shall find the blue colour of the syrup turned in a moment into a perfect green."

Besides those already mentioned, Boyle used many other color indicators, among which were: the juice of the blue corn flower (Exp. XXI), coch-

¹ Presented before the Division of Physical and Inorganic Chemistry at the Eighty-eighth Meeting of the American Chemical Society held at Cleveland, Ohio, September, 1934.

ineal (Exp. XXIV), turnesol (Exp. XXXVI), infusion of Brazil Wood and Madder (Exp. XXXVII), logwood extract (Exp. XXXIX), turmeric (Exp. XLIX).

It is interesting that Frederic Hoffman considered mineral spirit (carbonic acid) to possess the nature of an acid because when dissolved in water it reddened tincture of turnesol (11).

Almost a century later the *Encyclopedie Methodique, Chimie et Metallurgie*, which was edited by M. Fourcroy at Paris in 1804, stated (7): "Vegetable colours are employed especially for distinguishing between acids and bases. The former redden, or change into a red, some vegetable colours, and one chooses for this purpose the aqueous sugary tincture of violets, or syrup of violets, or tincture of tournesol. The former is reddened only by the strong acids; the second, less blue at the start and tending toward violet, is changed to red by even the most weak acids; so these two coloured reagents are used in this manner as a means of measuring the energy of various acids. Towards alkalies these vegetable colours react differently and are employed for detecting the presence, the energy, concentration and quantity of alkali. In general, alkalies change the blue vegetable colours to green, especially in the case of violets, mauve, carnations, roses, bark of turnips and radishes. Curcuma is very much more sensitive to alkali than the other colours and indicates alkali in quantities which cannot be detected by other means."

A few years later Faraday (8) devotes an entire chapter to "Coloured Tests—Neutralization," in which he gives an intimate discussion of the production and uses of test solutions and test papers in the laboratory and suggests that all work should be done in the "daylight; artificial light not permitting that just estimation of the changes by which the presence of a small amount of acid or alkali is to be determined."

Following the work of Arrhenius (1887) came the concept of acidity resolved into two components, one of which is "normality," which, in the older sense, is the *quantity* factor of "acidity," while the other is the hydrogen-ion concentration, which is the *intensity* factor. In 1909 Sørensen (13) introduced the present mode of expressing hydrogen-ion concentration, namely, pH.

The study of oxidation-reduction indicators is a recent development, at least from the theoretical point of view. It is true that dyes of certain types were used as far back as the time of Pasteur (12), and even the time of Helmholtz (14), to indicate the exhaustion of oxygen from the bacterial culture media which they were using. However, it was not until 1920, when Gillespie (9) published some data on the electrode potentials which were induced by bacterial reduction, that the quantitative study of such oxidation-reduction systems began. Unfortunately, or perhaps fortunately, these

electrode potentials were in some cases uncertain. All of this led finally, in the hands of W. Mansfield Clark, to the development of a supplementary method which could be used to check the electrode measurements of oxidation-reduction intensity. This was the color indicator method, which is to oxidation-reduction systems what the acid-base indicators are in the study of hydrogen-ion equilibria.

W. Mansfield Clark (4) in 1920 reported on the system methylene blue-methylene white. He has now carried his investigations through some twenty papers on the development of color indicators for the study of oxidation-reduction systems in organic reactions. Today its theoretical basis is rather firmly established. A summary with pertinent diagrammatic charts has recently been published by Clark (5).

A great deal remains to be done, not only in providing indicators more closely or more evenly graded with respect to their characteristic potentials, but also indicators which, having the potentials required for particular purposes, also have other properties suited to those purposes.

REFERENCES

- (1) BILLMANN, E.: *Ann. chim.* **9**, 109 (1921).
- (2) *The Works of Robert Boyle*, Vol. II, p. 47. London (1744).
- (3) *Ibid*, p. 53, Experiment XX.
- (4) CLARK: *J. Wash. Acad. Sci.* **10**, 255 (1920).
- (5) CLARK: *Medicine* **13**, 207 (1934).
- (6) CONANT, KAHN, FIESER, AND KURTZ: *J. Am. Chem. Soc.* **44**, 1382 (1922).
- (7) *Encyclopedie Methodique, Chimie et Metallurgie*, Vol. IV, p. 66.
- (8) FARADAY, MICHAEL: *Chemical Manipulations*, 1st American edition, pp. 284-6. Philadelphia (1831).
- (9) GILLESPIE: *Soil Sci.* **9**, 199 (1920).
- (10) GRANGER, F. S., AND NELSON, J. M.: *J. Am. Chem. Soc.* **43**, 1401 (1921).
- (11) HOFFMAN, FREDERIC: *Dissertation physico-medic. select.*, p. 183. Leyden (1708).
- (12) PASTEUR, L.: *Compt. rend.* **87**, 33 (1878).
- (13) SØRENSEN, S. L. P.: *Biochem. Z.* **21**, 131, 201 (1909).
- (14) VON HELMHOLTZ, H.: *Arch. Anat. Physiol. Med.*, p. 453 (1843).