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THE ACIDIMETRY OF COLORED SOLUTIONS: AN APPLICATION OF THE POCKET SPECTROSCOPE.

BY ALFRED TINGLE.

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Introduction.

In the course of certain work carried on at this laboratory, it was necessary to titrate alkaloidal solutions containing much coloring matter. The latter, as frequently happens in such cases, could not be removed without vitiating the quantitative results. The method of overcoming this trouble, proposed by A. H. Allen, could not be applied. Allen dissolved the base and impurities in a solvent immiscible with water, then added standard acid until methyl orange in the aqueous layer showed an acid reaction. The natural coloring matters with which the writer had to deal passed into the aqueous layer to an extent sufficient to mask any available indicator. This does not appear to be a novel experience.

The spectroscope seemed to offer a means of differentiating the color produced by an indicator from that produced by colored resins. It also appeared probable that the change of color of an indicator at the neutral point could be as readily determined by the spectroscope as by the naked eye.

On the whole, the results have justified this belief, though it has been found that certain precautions are necessary which were not foreseen at the outset of the work. The conditions of success have been worked out for 5 indicators. There seems no reason to suppose that the same cannot be done for all. In this work a large spectroscope is neither necessary nor desirable. The results here recorded were obtained with a small "Beck-Thorp" Direct Vision Diffraction instrument, which can be carried in the pocket. Very likely an instrument of the older-fashioned direct vision prism type would have been just as serviceable.

Method of Conducting Titrations.

A blank experiment is necessary to fix the end-point of most indicators. It was found that, as a general rule, where the breadth of an absorption band is changed by the solution becoming alkaline, the change is progressive and increases with the alkalinity. Thus the position of the edge of the band will be determined by the concentration of the indicator, the thickness of liquid through which the light passes, and the degree of alkalinity of the solution.

The titrations may be made in any convenient vessel. Its shape is unimportant so long as it and the spectroscope are so placed that the same thickness of liquid is viewed after each addition of alkali. The writer has often used conical flasks for the purpose. Most of the experiments recorded here were made in flat-sided tincture bottles.

Two similar titration vessels must be provided. The first contains the liquid to be titrated, brought to such dilution that a sufficient amount of light can pass through it.[1] In the second vessel, used for the "blank," is placed nearly the same volume of water (some excess being allowed for the standard solution which will be added), made alkaline by one drop of decinormal sodium hydroxide solution. The indicator which is to be used is added slowly from a buret or a Mohr's pipet to this faintly alkaline solution till it is seen that the edges of the absorption bands are sufficiently well defined. The position of the most characteristic edge of the most characteristic band is registered on the scale (or by the luminous pointer in the Beck-Thorp instrument). This defines the end-point of the titration. The volume of indicator solution used must also be noted. The same volume of indicator solution is next added to the acid liquid to be titrated, and standard alkali is then run in as usual until the position of the characteristic absorption band is seen to be that registered from the "blank" as the end-point. The only difference from an ordinary titration lies in the fact that between every two additions of alkali the liquid should be examined spectroscopically instead of by the naked eye.

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[1] If, for any reason, dilution is not permissible and the liquid is very dark, special vessels must be employed so that only a very thin layer of solution is under examination.

Should the end-point be overrun, back titration can always be employed, so long as the end is eventually obtained by adding alkali to an acid solution and not *vice versa.*

It may be here noted that, in general, very much larger quantities of indicator are needed in this method than would be desirable in ordinary titrations.

The Degree of Accuracy Obtained.

This point was tested after taking every precaution to eliminate the effects of unconscious personal bias from the experimental results.

Separate portions of decinormal sulfuric acid were measured carefully, diluted, and colored with a carefully neutralized vegetable extract to such extent that an "end-point" could not be distinguished by the unaided eye. They were then handed to the experimenter, who was not aware of the amount of acid present until the titrations had been completed.[1] The coloring matter used was in some cases prepared from tea and in others from stick licorice. It seems unnecessary to give details of the means used to insure neutrality. The solutions were titrated against an approximately decinormal solution of sodium hydroxide which had been standardized in the usual manner. The titrations were made in flat-

TABLE I.—TITRATIONS WITH DIFFERENT INDICATORS.

Expt. No.	Volume of 0.1 N H_2SO_4 by direct measurement. Cc.	Volume of 0.1 N H_2SO_4 calculated from titration results. Cc.	Difference. Cc.	Indicator.	Volume of indicator solution used in titration. Cc.	Strength of indicator solution.
1.......	15.0	15.21	+0.21	Cochineal	2.5	Saturated in 50% alcohol
2.......	26.0	25.98	—0.02	Cochineal	2.5	
3.......	20.0	19.96	—0.04	Cochineal	2.5	
4.......	21.0	21.04	+0.04	Methyl orange	1.0	0.1%
5.......	17.5	17.49	—0.01	Methyl orange	1.0	0.1%
6.......	18.5	19.16	+0.66	Methyl orange	1.0	0.1%
7.......	14.0	14.11	+0.11	Methyl orange	1.0	0.1%
8.......	22.5	22.43	—0.07	Methyl orange	1.0	0.1%
9.......	20.3	20.15	—0.15	Lacmoid	0.4	0.2%
10.......	21.5	21.73	+0.23	Lacmoid	0.4	0.2%
11.......	18.7	18.97	+0.27	Lacmoid	0.4	0.2%
12.......	15.0	14.90	—0.10	Phenolphthalein	0.2	1.0%
13.......	20.3	20.28	—0.02	Phenolphthalein	0.2	1.0%
14.......	16.5	16.34	—0.16	Phenolphthalein	0.2	1.0%
15.......	21.8	21.73	—0.07	Rosolic acid	0.2	1.0%
16.......	15.1	15.13	+0.03	Rosolic acid	0.2	1.0%
17.......	15.4	15.51	+0.11	Rosolic acid	0.2	1.0%

The bad result obtained in Expt. 6 is attributed to a sudden irregularity which developed in the artificial light used as a source of the bright spectrum.

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[1] The author's thanks are due to Mr. F. W. Babington, Chief Analyst in this laboratory, who very kindly measured out these acids for him and who helped in many other ways to bring this work to a speedy and successful issue. His kindly help and encouragement in this as in other cases has been invaluable.

sided tincture bottles. All solutions were diluted to approximately 50 cc. at the outset, the thickness of liquid through which the observations were made being nearly 45 mm. Some of the experiments were made by daylight, and others at night under such conditions that the "end-point" could not have been seen, even had no coloring matter been present.

Lacmoid is, from the nature of its absorption spectrum, the most difficult indicator to use in this fashion.

In judging the above results it must be remembered that the method is intended for use in cases where the liquid to be titrated is so colored that no other means can be used for detecting the end-point, or where the operation must be performed under adverse conditions as to light. Apart from such conditions it is only in connection with methyl orange that the writer would suggest the use of the spectroscope instead of the unaided eye. The work involved in the new method is greater, because even the most handy instrument is not as quick in action as the eye itself.

In all the foregoing experiments on colored solutions the coloring matter used was such that absorption due to it was confined to the blue end of the spectrum. The method can be equally well applied when absorption is at the red end.

An example of the latter sort is supplied by solutions of copper salts. The determination of sulfuric acid in the presence of copper sulfate is an operation of technical importance, *e. g.*, in control of electro-deposition baths. As commonly carried out, it is very difficult to determine the correct end-point. Spectroscopic determination of this point is very easy.

To a solution of 2.5 g. of pure crystallized copper sulfate in 40 cc. of water, 25 cc. of decinormal sulfuric acid was added. The mixture was then titrated against sodium hydroxide solutions, using methyl orange as an indicator. The spectroscope showed that neutrality was reached on adding 26.2 cc. of alkali.

A subsequent titration of 25 cc. of the same acid alone, using lacmoid as indicator, showed that 26.2 cc. of the same alkali solution was needed for neutrality.

With the spectroscope there was no difficulty in finding the end-point, which was almost, or quite, indistinguishable without it.

A saturated solution of copper sulfate diluted 6 times is sufficiently transparent to be used in this method in a layer 45 mm. thick, the illumination being only moderate.

Characteristics of the Indicators.

Before using this method of titration the analyst should acquaint himself by experience with the peculiarities of the selected indicator.

The following remarks may guide him and save waste of time, but each person must decide for himself the working conditions which best suit his circumstances. No attempt has been made in this work to characterize the absorption bands in any numerical way, for their breadth varies with several factors. In the experiments on which these remarks are based, the volume of liquid to which the indicators were added was approximately 70 cc. and the thickness through which the spectra were observed was 40–45 mm. Little attention has been paid to the changes in the edges of the absorption bands nearest the violet end of the spectrum for two reasons: (1) This edge, in the case of most of the bands examined, is not so sharply defined as the other. (2) Much of the violet and blue is absorbed by the brown and yellow natural coloring matters which are usually responsible for obscuring the end-point in this class of titration.

Cochineal.—The indicator solution was of such strength as could be obtained by allowing 50% alcohol to extract as much pigment as possible from an excess of cochineal powder.

When 2.5 cc. of such a solution is added to the standard volume of acidified liquid, absorption does not extend much beyond the blue region of the spectrum, but on neutralization the band extends over almost the whole of the green region and acquires a sharper edge. The neutral point must be determined in a carefully made blank experiment, for the change in color is progressive with increasing alkalinity. It is well known that an excess of alkali changes the color of cochineal; spectroscopically observed, this change is marked by an extension of the absorption towards the red. In a properly managed titration, taking the precautions mentioned, the end-point can be readily detected.

Methyl Orange. Neutral.—This is used in 0.1% solution. The commercial article is weighed, moistened with dil. hydrochloric acid and evaporated to dryness. The product is moistened with dil. ammonium hydroxide in excess and again evaporated until completely dry, dissolved in water and diluted to the required volume. In this way neutrality is secured. The directions usually given for preparing this indicator result in the presence of free acid. When 1 cc. of the above solutions is added to the standard volume of water a sharp enough edge is produced at the end of the absorption band nearest to the red. This band covers part of the green and much of the blue region of the spectrum. Addition of alkali produces no change, but acidification causes the band to move towards the red end until, when all the indicator has been converted into free acid, it covers practically the whole green region. At the same time the absorption becomes sharper.

Neutral methyl orange as thus prepared and used in this large quantity is only intended for use in titrations when an alkali is being added to an acid. Used *vice versa,* an error would be introduced to the amount of the standard acid required to acidify the indicator.

The fact that the spectrum of neutral methyl orange does not differ from that of an alkaline solution shows that the common practice of carrying titrations in which it is used to "the intermediate tint" is a mistaken one. The correct end-point has not been reached until no further color change is produced.

In a recent paper with F. W. Babington,[1] the present author made some comments on the discrepancy observed between the titers of alkali solutions as determined by different indicators. It has now been shown that, as far as methyl orange is concerned, the discrepancy arises from "the intermediate tint" being considered the sign of neutrality.

That the discrepancy does not occur when the spectroscopic end-point is taken is shown by the results tabulated below. In the experiments from which they are derived only the usual amount of indicator was added when the end-point was observed by the eye alone. The solutions used were not in any way colored except by the indicator.

TABLE II.—END POINTS.

Titration of 25.0 cc. of 0.1 N H_2SO_4 with NaOH.

Indicator.	Eye alone. Cc. required.	Using spectroscope. Cc. required.
Methyl orange	25.2	25.3
Cochineal	25.3	25.3
Lacmoid	25.3	..

Lacmoid.—The strength of the stock solution used in these experiments was 0.2%. Under the standard conditions it was found that 0.4 cc. was needed to produce the characteristic spectroscopic effect. At this concentration the visible spectrum transmitted consists only of red rays when the reaction is acid. When neutral these also are absorbed, blue being transmitted if the source of light is sufficiently powerful. Under normal conditions, however, neutrality is indicated by total suppression of the whole spectrum. The spectroscopic end-point with this reagent is not very sharp. Probably improvement could be effected by using a more dilute stock solution. This would make it possible to regulate more closely the depth of color suitable to each titration.

Phenolphthalein.—A 1% stock solution was used. For each experiment 0.2 cc. was taken, but the exact amount does not affect the position of the absorption bands to be observed, as is the case with most other indicators. This is because the change taking place when the end-point is reached consists in the development of a totally new band in the green, closely bordering upon the yellow region, one edge almost coinciding with the "D line."

Rosolic Acid.—The stock solution was 1%, and of this 0.2 cc. was a convenient amount to take for titrations made under these standard con-

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[1] *Chemical Industry in Canada during the War*, 10, 32; *J. Soc. Chem. Ind.*, 36, 1203–4 (1917) (abs.).

ditions. When the solution becomes very slightly alkaline the absorption band which is characteristic of the acid solution broadens abruptly, extending further into the green towards the red end of the spectrum, but leaving some of the green region still visible. The indications are very marked, so that rosolic acid lends itself well to this spectroscopic method. The neutral point as indicated by the spectroscope is the same as that found without its aid, so that the divergence of indications by rosolic acid from those by other indicators is not eliminated by the use of this new method.

Litmus and Hematoxylin have been examined only as to their suitability for use with the spectroscope in a very cursory manner, but the probabilities appear to be in their favor. Litmus must be used in considerably larger quantity than usual, as in the case of cochineal and methyl orange. When alkaline, it shows a well marked band. Hematoxylin gives a sharply defined edge to the absorption band seen in alkaline solution only when a considerable amount of it is present.

Summary.

1. The spectroscope is an efficient means of distinguishing the exact neutral point in many acidimetric titrations.

2. It can be used for this purpose in cases where the unaided eye would fail.

3. The necessary concentration of most indicators is greater when they are to be used in connection with the spectroscope.

4. The best conditions under which some of the commonest indicators can be used in connection with the spectroscope have been established.

OTTAWA, CANADA.

ON EQUILIBRIUM IN THE SYSTEM: FERROUS CARBONATE, CARBON DIOXIDE AND WATER.[1]

BY HERBERT J. SMITH.

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It has long been known that ferrous carbonate is more soluble in water containing carbon dioxide than in pure water.[2] The increase in solubility is due to the formation of the more soluble ferrous bicarbonate, which has, however, never been obtained in the solid state. It is shown in this paper that the solid salt, at a temperature of 25°, would have a decomposition tension of carbon dioxide greater than 25 atmospheres.

If we study the system: ferrous carbonate, carbon dioxide and water

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[1] From a dissertation submitted to the Faculty of the Ogden Graduate School of Science of the University of Chicago in candidacy for the Degree of Doctor of Philosophy.

[2] Wagner, *Z. anal. Chem.*, 6, 171 (1867); Hauer, *J. prakt. Chem.*, 81, 381 (1860).