NOTE OF A NEW INDICATOR IN WATER ANALYSIS

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The selection of an indicator for use in the titration of the bicarbonate alkalinity of natural waters has always presented some difficulty. Probably the first indicator used for this purpose, of which we have any record, was the coloring matter of red wine, for we are told that the Romans titrated natural waters with sour wine the red coloring matter of the wine acting as a natural indicator. Since that time other and better indicators have been suggested, it is true however that the selection of those suggested has often been made with very little more regard to the needs that the indicator must fill than was the original red wine of the Romans.

An examination of some of the more recent textbooks and reference books shows the following recommendations. Thresh (1913), Mason (1912), and Stocks (1912) recommend Methyl Orange. Leffman (1909) and Chemiker Kalender (1917) recommend Alizarin with Methyl Orange as an alternate. The first two editions of Standard Methods of Water Analysis A. P. H. A. recommend the use of either Lacmoid in hot solution or Erythrosine cold and advise against the use of Methyl Orange due to the difficulty of getting supplies of that indicator of sat-

isfactory quality. The third or (1917) edition of Standard Methods of Water Analysis, A. P. H. A. allows the use of Methyl Orange.

It will be seen from the above that Methyl Orange is the more popular indicator for this titration. The disadvantages of the others are so marked that it is hardly necessary to refer to them. The necessity of shaking the Erythrosine with chloroform makes its use tedious and slow. Lacmoid must be used in a boiling solution. This is a decided disadvantage. Methyl Orange can be used in a cold solution, works very satisfactorily in all cases excepting in water with an excess of alum. Methyl Orange indicates a slight residual alkalinity in a water in which all of the bicarbonate alkalinity has been used up by the addition of alum and even where there is a slight excess of alum in the water. Larger excesses of alum give an acid reaction. If such a case is suspected it is absolutely necessary to use some other indicator, such as Erythrosine or Lacmoid, which reacts acid to a dilute solution of alum.

While the end point change of Methyl Orange is very sharp and satisfactory to most chemists, quite often one finds chemists to whom the color change is very indefinite and difficult to distinguish. This is probably due to a slight color blindness but is nevertheless a real disadvantage of this indicator.

In 1916 Clark and Lubs[1] described a new series of indicators which they studied with reference to their use in the colorimetric determination of the hydrogen ion concentration. Acree and co-workers have studied the chemical structure and mechanism of color change of these indicators. The entire series without exception are brilliant colors and show a very marked color change at their neutrality point. One of these indicators tetrabrom phenol-sulphonpthalein changes color at a hydrogen ion concentration almost identical with that of methyl orange. The color change is from blue in alkaline to yellow in acid solution. This color change is much different from that of Methyl Orange and we feel that many

[1] W. M. Clark and H. A. Lubs, J of Bact. 2, 1-3, 109-136, 191-236 (1917).

people will find it much more easily detected. We have found it to be very satisfactory for use in titration of the bicarbonate alkalinity of natural waters. Table 1 gives a typical series of results. 50 cc. of water were used and duplicate titrations made with Methyl Orange and the tetra-bromphenol-sulphonthalein. It will be noted that the variation between the results obtained with the two indicators is slight being practically no greater than would be found between duplicate determinations using the same indicator. The results tend to be somewhat higher since there is a constant difference, it could be eliminated by re-standardization of the standard acid using the new indicator. It was found that the titration could be carried out satisfactorily by ordinary electric light although the daylight was to be preferred.

TABLE I.

CUBIC CENTIMETERS OF N/50 SULFURIC ACID TO NEUTRALIZE 50 cc. OF WATER

	Observer No. 1			Observer No. 2*		Observer No. 3
Sample Number	M. O. Day	B.P.B. Day	B.P.B. Night	M. O. Night	B.P.B. Day	B.P.B. Night	M. O. Night
1	12.7	....	....	....	12.5	12.5	12.5
2	15.7	....	....	....	15.6	15.6	15.4
3	12.8	....	....	....	13.1	13.1	12.9
4	11.4	....	....	....	11.5	11.5	11.3
5	13.8	....	....	....	13.9	13.9	13.7
6	12.5	....	....	....	12.6	12.7	12.6
7	12.1	....	....	....	12.4	12.4	12.2
8	7.7	8.0	8.0	7.9	7.9	....	....
9	8.3	8.5	8.4	8.3	8.4	....	....
10	5.5	5.6	5.7	5.6	5.6	....	....
12	7.7	7.7	7.8	7.7	7.6	....	....
13	1.4	....	....	....	....	....	....
14	11.0	11.2	11.3	11.0	11.1	....	....
15	15.5	15.7	15.5	15.9	15.5	....	....
16	5.7	5.8	6.0	5.8	5.9	....	....
17	4.1	4.2	4.5	4.2	4.2	....	....
18	21.3	21.5	21.8	21.5	21.4	....	....

B. P. B.=Tetra-brom-phenol-sulfonphthalein.

M. O. =Methyl Orange

* No Methyl Orange results obtained by observer number two on account of color blindness.

Titration with electric light using this indicator was however much easier than when Methyl Orange was used. One or two experiments with the so-called daylight electric light indicated that the titration was a little more easily made with this light than when using ordinary electric light. Excess alum interfers in the same way as with Methyl Orange. Experiments have not been made in substituting this indicator for Methyl Orange in other titrations. We cannot say therefore whether it can be recommended as a general substitute for Methyl Orange but can recommend it as a substitute for Methyl Orange in the titration of bicarbonates with acid.