METHYL RED AS AN INDICATOR.

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(Read at the Meeting, November 4, 1914.)

IN 1908 this indicator was introduced by Rupp and Loose (*ANALYST*, 1909, **34**, 29), who advocated its use because of its delicacy, and especially its value in the titration of ammonia and other comparatively weak bases, such as quinine. H. F. Tizard (*J. Chem. Soc.*, 1910, **97**, 2477) concluded that "as an indicator methyl red is greatly superior to methyl orange, as the colour curves show. The end-point is very much sharper than with methyl orange. Methyl red is, in fact, an extremely sensitive indicator, and should come into extensive use." However valuable this investigation may be in its special line, such sweeping conclusions on the data collected are very apt to be misleading to the analyst, and as a matter of fact they have been so. It is quite true that the end-point with methyl red is sharper than with methyl orange when these indicators are simply tested in water with acid or alkali. The difference is greater in solutions of neutral salts, such as chloride and sodium sulphate, in which case the sensitiveness of methyl red is not much affected, whereas that of methyl orange, as I pointed out in 1883, is considerably lessened. So far there is agreement, but the subsequent portions of the quotation given would naturally lead one to suppose that methyl red could be substituted for methyl orange, and naturally it has been concluded that it would act similarly to the latter in every particular, but with greater delicacy. Finding, as stated by Rupp and Loose, that methyl red was much superior to methyl orange for the titration of ammonia, a few tests were made to determine its value for other substances. The following figures show the percentages of alkali or acid, calculated on 100 parts of the actual substance tested, when methyl red was employed as indicator, the titration being made in the cold with standard sulphuric acid and sodium hydroxide respectively.

	Per Cent. found.					
Carbonate of soda	...	...	...	...	...	about 90·0
Boric acid ...	...	...	...	...	...	" 0·2
Acetic acid	...	...	...	...	...	" 94·0
Lactic acid	...	...	...	...	...	98·0

The end-point of the reaction in the case of lactic acid was fairly good, but the others, and especially sodium carbonate, showed such gradual change in colour that the result was of no value. The same is the case with sulphurous, phosphoric and tartaric acids. If quinine be dissolved in a slight excess of sulphuric acid and titrated with sodium hydroxide, using methyl orange as indicator, the end-point is about where the normal sulphate is produced, but the change in colour is obscure. With methyl red this occurs also when the normal sulphate is formed, the end-point being good in a hot solution, which is required to keep the salt in solution. The compound referred to is the quinine sulphate of the British Pharmacopœia, which is also neutral to litmus.

The above result with sodium carbonate is very low owing to the influence of the carbonic acid which is liberated, but if the solution is boiled off after each addition an excellent end-reaction is obtained. As free carbonic acid has practically no influence on methyl orange, it is apparent that methyl red belongs to a different category, and is, in fact, similar to litmus. This difference and similarity are also observable in the case of various acids, as well as the quinine, referred to above, so the assumption that methyl red can be used as a substitute for methyl orange has no foundation in fact. As a general rule it may be taken to resemble litmus in its indications, but rare instances may occur, as has been the case with other indicators, in which it may give a different result. It is thus imperative that, before any indicator is used for a special purpose, its general similarity to another indicator should not be depended upon, but its property in the particular circumstances should be carefully tested. In one of my previous papers (*J. Soc. Chem. Ind.*, 1887, 6, 195) I divided indicators into three classes: (1) The methyl orange group, (2) the litmus group, and (3) the phenolphthalein group; but I should now place methyl red as the one most resembling litmus, since, on the whole, including the more decisive change in colour and smallness of quantity of material required, it is to be preferred to the latter.

DISCUSSION.

Mr. F. W. F. ARNAUD said that he had found methyl red to be very useful, taking the place, in most instances, of methyl orange. While it could not be used in the presence of large quantities of carbonic acid, it was perfectly easy to titrate solutions of sodium carbonate with acid, using methyl red, provided that the solution was kept practically at boiling-point. It was a particularly useful indicator at night, as the colour-change was then very marked and easily discernible, whereas in the case of methyl orange the colour-change was sometimes difficult to see by artificial light. Methyl red was a very good indicator for use in the Kjeldahl process.

Mr. E. HINKS said that he used methyl red exclusively in the Kjeldahl process, but not much for other purposes, because of its liability to failure through the presence of carbonic acid.