THE ANALYST.

AUGUST, 1903.

PROCEEDINGS OF THE SOCIETY OF PUBLIC ANALYSTS.

THE DETECTION AND ESTIMATION OF MINERAL ACID IN ACETIC ACID AND VINEGAR.

BY PHILIP SCHIDROWITZ, Ph.D.

(*Read at the Meeting, June 17, 1903.*)

THE fact that methyl orange cannot be used in the titration of acetic acid is well known. It is also a matter of common knowledge that aqueous solutions of acetic acid do react with methyl orange solution sufficiently to prevent the practical use of this indicator for the estimation of free mineral acid in acetic acid or vinegar under ordinary conditions. It does not appear to be generally known, however, that the addition of a sufficiency of ethylic alcohol to a solution of acetic acid entirely prevents the reaction of the latter with the indicator, or that the addition of alcohol to a solution of acetic acid, coloured pink or pinkish-brown with methyl orange solution, causes a reversion of colour to a pure yellow. This phenomenon is probably due to a repression of dissociation by the alcohol.* It is also not generally known that whereas (in aqueous solutions) methyl orange cannot be used for titrating mineral acids in weak organic acids (such as acetic acid) if the indicator be used in the liquid itself or in the shape of droplets tested with small portions of the liquid under titration, yet it is perfectly feasible to make practical estimations if methyl orange paper be used.† I may say that the latter fact was observed by me independently, and that it was only after much subsequent searching in literature that I found a passing reference in the work referred to in the footnote. I have not, however, been able to find any mention of an actual practical application of either of the processes indicated in the text-books or literature dealing with this subject.

With regard to the use of alcohol, I find that if the quantity of the latter is kept within certain limits very good results are obtained by direct titration. The experiments described below were all carried out with solutions covering the practical range of acetic acid strengths likely to occur in commercial vinegars, and using sulphuric acid as the mineral acid. Briefly, I have found that the best results are

* *Glaser*, "Indikatoren der Acidimetrie u. Alkalimetrie," p. 23.

† *Loc. cit.*, p. 116.

obtained by adding an equal volume of alcohol to the solution to be titrated, and subsequently 1 c.c. of alcohol for every 3 c.c. of decinormal alkali run in.

The methyl orange used in these experiments was recrystallized, made up to 0.5 gramme per litre, and one drop of this used throughout. In making the estimation, if fairly accurate results are desired, it is necessary to make use of a control. The control consists of a volume of distilled water (without alcohol) equal in volume to the total volume of the fluid titrated (at the end of the titration), and coloured with an equal quantity of methyl orange. It is not always possible to obtain exactly the same depth of colour in the liquid as in the control, but all that is necessary is to obtain the same colour and approximately the same depth of shade. With a little practice this is much simpler to carry out than to describe, as the following example will show. Result A was obtained by myself, result B by an independent worker, to whom I had briefly described but not shown the process :

Strength of acetic acid, 4 per cent. ; sulphuric acid actually contained, 1 per cent.

Sulphuric acid found— A : 1.015 per cent.

B : 1.037 per cent.

The following tables will show how the general conclusions recorded above were arrived at :

TABLE I.

Strength of acetic acid, 4 per cent. ; strength of sulphuric acid contained, 0.093 per cent. ; volume titrated, 10 c.c. ; alcohol used, 10 c.c.

		N. of c.c. $\frac{N}{10}$ Alkali = H_2SO_4 Per Cent. found.	
(a)	Without control ...	1.63	0.080
(b)	Controlled ...	2.12	0.104
(c)	„ ...	2.18	0.107
(d)	„ ...	1.96	0.096

TABLE II.

Strength of acetic acid, 4 per cent. ; sulphuric acid contained, 0.2 per cent. ; volume of solution as before.

		N. of c.c. Alcohol (in all). N. of c.c. $\frac{N}{10}$ Alkali = H_2SO_4 Per Cent. found.	
(a) }	10	...	{ 4.53 0.220
(b) }			{ 4.58 0.224
(c) }	14	...	{ 3.16 0.155
(d) }			{ 3.11 0.152
(e) }	12	...	{ 3.60 0.176
(f) }			{ 3.44 0.169
(h)	11.3	...	4.09 0.200

TABLE III.

Acetic acid, as before ; sulphuric acid contained, 0.5 per cent. ; volume titrated as before.

		N. of c.c. Alcohol (in all). N. of c.c. $\frac{N}{10}$ Alkali = H_2SO_4 Per Cent. found.	
(a) }	10	...	{ 14.51 0.711
(b) }			{ 14.73 0.721
(c) }	13	...	{ 10.25 0.502
(d) }			{ 10.25 0.502
(e) }	14	...	{ 9.82 0.481
(f) }			{ 9.82 0.481

The results for a solution containing 1 per cent. H_2SO_4 have already been given above. The volume (total) of alcohol used in this series was 10 c.c. + $\frac{1}{3}$ volume of alkali run in—i.e., 16.9 c.c. alcohol in all.

I next thought it desirable to apply the process to different strengths of acetic acid, the percentage of mineral acid remaining constant. (N.B.—For the above tables the strength of the acetic acid remained constant, the mineral acid being varied.)

TABLE IV.

Strength of acetic acid, 3 per cent.; sulphuric acid contained, 0.5 per cent.; alcohol, etc., as above.

N. of c.c. $\frac{N}{10}$ Alkali = H_2SO_4 Per Cent. found.			
(a)	...	10.25	0.502
(b)	...	10.14	0.497

The results for an acetic acid of 4 per cent. strength have already been given (Tables I. to III.).

TABLE V.

Strength of acetic acid, 5 per cent.; sulphuric acid contained, 0.5 per cent.

N. of c.c. $\frac{N}{10}$ Alkali = H_2SO_4 Per Cent. found.			
(a)	...	10.14	0.497
(b)	...	10.25	0.502

The Limits of the Process.—The process gives results sufficiently accurate for all ordinary purposes up to a limit of 0.01 per cent. I base this statement on the following figures:

Strength of acetic acid in all titrations, 4 per cent.; 10 c.c. solution + 10 c.c. alcohol used in each case.

N. of c.c. $\frac{N}{10}$ Alkali = H_2SO_4 Per Cent. contained.				H_2SO_4 actually present Per Cent.
(a)	...	0.982	0.048	0.053
(b)	...	0.545	0.027	0.026
(c)	...	0.218	0.011	0.013

The process described above cannot, unfortunately, be applied to ordinary coloured vinegars, owing to the fact that the only decolorizing agent which is of practical value in other respects—namely, animal charcoal—obstinately retains a considerable proportion of the mineral acid. It is, however, applicable to distilled (white) vinegars, acetic acid, and similar solutions.

In the case of coloured vinegars, a simple titration, using methyl orange *paper* as an indicator, gives very good results. The paper I used was prepared by passing good filter-paper through a solution of the indicator (prepared as described above), and then drying and cutting up into strips in the usual manner. In this case also it is well to use a control consisting of a genuine vinegar or a solution of acetic acid of approximately equal strength to the sample under examination. Genuine vinegars give a light brownish spot on the paper, which is easily differentiated from a vinegar containing 0.05 to 0.1 per cent. of free mineral acid. I have found little difficulty in practice in distinguishing up to the former limit.

The following results were obtained, working on a genuine vinegar to which a certain proportion of mineral acid was added by me, and analysed (a) according to Hehner's method;* (b) by the above method, carried out by myself; and (c) by the above method, carried out by an independent worker, to whom I had described but not demonstrated the process.

Method.					Per Cent. H_2SO_4 found.
(a)	Hehner's method	...	...	...	0.448
(b)	...	...	...	...	0.454
(c)	...	...	...	...	0.437

In all the above tables I give the third place of decimals for purely arithmetical reasons.

A titration of a 4 per cent. solution (colourless) of acetic acid containing 0.5 per cent. H_2SO_4 by this method gave as a result 0.48 per cent.

Obviously, both the alcohol and the (methyl orange) paper processes may be applied as qualitative as well as quantitative tests.

DISCUSSION.

Mr. ALLEN said that those who had been concerned in the determination of mineral acid in vinegar would appreciate the importance of the author's observation that the determination could be satisfactorily made by simple titration. The process appeared to be to some extent comparable with the titration of boric acid in the presence of glycerin; and probably the behaviour of some other acids with indicators would be materially modified by the presence of a notable amount of alcohol. In some cases with which he had to deal some years previously, in which a number of samples of so-called vinegar, all from the same source, were found to be adulterated with sulphuric acid, the excuse of the defence was that the acetic acid used in the concoction of the vinegar (which was not genuine vinegar, but made from acetic acid, caramel, etc.) was itself contaminated with sulphuric acid. And he remembered on one occasion working with glacial acetic acid which did not give satisfactory results, and which was found to contain a large proportion of sulphurous acid, from which it was separated by partial freezing, the solidified acid retaining only traces of the impurity.

Dr. SCHIDROWITZ, in reference to alcohol titration, said he had imagined the possibly polyhydric alcohols might have an action similar to that of ethylic alcohol; but, as a matter of fact, glycerol, at any rate, did not act in that way at all.

Mr. ALLEN said that the curious point was that, whereas in this case the addition of ethylic alcohol rendered it possible to titrate a relatively weak acid by a strong indicator, in the case of boric acid no reliable result could be obtained without the use of glycerin, which rendered the acid sensitive to phenolphthalein, but not, of course, to methyl orange.

Mr. BRIANT said that in a recent book on indicators the use of methyl violet was recommended for the purpose of the estimation of mineral acid in vinegar. He had, however, tried this, and had been quite unable to get reliable results with it. He

* ANALYST, i. 105.

would like to hear whether the author had had any experience in the use of methyl violet for this purpose.

Dr. SCHIDROWITZ said that he had not tried methyl violet, though he was aware that this and other little-used indicators had been recommended.

Mr. HEHNER said that many years since methyl violet had been suggested as an indicator. He had found, however, that, although it did act with mineral acids, it was exceedingly insensitive.

Mr. BEVAN said that there were a great many varieties of commercial methyl orange, and if the proper kind were not used very varying indications might be obtained, especially in the presence of alumina salts.

Dr. SCHIDROWITZ said that the methyl orange he had used was obtained from a source which he had always found reliable, and appeared to possess the various properties attributed to methyl orange. In addition, however, he had himself purified it by recrystallization. Moreover, the facts he had mentioned had been observed as such, not merely by himself, but by others previously, as regards both alcohol and methyl-orange paper. They were set out in Glaser's book on indicators, though no practical application of them was there suggested.

Mr. HERBERT E. BURGESS said that he had found specimens of methyl orange from different sources, when examined with regard to their tinctorial power, to vary very widely in that respect.

Mr. ALLEN said that if a specimen of methyl orange gave a good sharp reaction with a mineral acid, and its alkalinity point or neutrality point were well marked, it would, he supposed, be regarded as satisfactory; and no doubt the methyl orange that Dr. Schidrowitz would apply to this determination would fulfil those conditions. Nevertheless, it was a fact that there were several dyes of the methyl-orange order, or closely allied thereto; and in the case of one of these—namely, tropæolin OOO, a salt of naphthol-azobenzene sulphonie acid—the results were exactly the reverse of those ordinarily obtained, a red colour being produced with alkali instead of with acid. This same colouring matter responded to caustic soda, but not to ammonia, and he had attempted to make use of this in the Kjeldahl process, in which it would follow that, if excess of alkali were added, it could be titrated with this particular indicator, while another indicator, such as methyl orange, might be used to titrate the soda and ammonia together, the ammonia being thus obtained without distillation. He had found, however, that the indicator was not sufficiently delicate for the purpose.

With reference to Mr. Bevan's remarks in the above discussion, Dr. Schidrowitz writes that, since the reading of the paper, he has repeated the experiments described therein, and controlled and confirmed them by means of a sample of methyl orange prepared by himself from pure dimethyl-aniline and sulphanilic acid.