

## MINERAL ACIDS IN VINEGAR.

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IN a paper recently read by Messrs. F. W. Richardson and J. L. Bowen (*Journ. Soc. Chem. Ind.*, 1906, **25**, 836-838), an improvement was suggested of the Hehner method of estimating free mineral acids in vinegar, based on the assumption that the ash of malt vinegar chiefly consists of normal phosphate of potash, with a small quantity of phosphate of lime; and that if sulphuric acid were added to such vinegar, it is, up to a point, masked by the normal salts present, and further, that if acetates are present, they also combine with an equivalent quantity of sulphuric acid, with the liberation of acetic acid.

There is nothing new in this, for attention has been called to these reactions in the past; but Richardson and Bowen suggest what appears to be, theoretically, a more efficient method for detecting fraudulent addition of mineral acid to vinegar.

The proposal they bring forward is, as they say, an extension of the Hehner method, and it consists in using indicators that enable first the di-hydrogen phosphate in the acid solution of the ash to be titrated, then the di-basic phosphate, the amount of the tri-basic salt, or perhaps, more correctly, the normal salts, being obtained by adding together the amount of alkali required to neutralize to the first stage, and twice that required in the second. Should the figure obtained be in excess of the acid added to the vinegar, for the purposes of the determination, it must be, according to Richardson and Bowen, in consequence of the addition of mineral acid to the vinegar equivalent to the excess of alkali used.

If this process is worth anything as an indication of the addition of free mineral acids in very small quantities, it is necessary to assume that the mineral matter present in a pure malt vinegar consists of saturated or normal salts, or that in course of evaporating or charring the bases and acid radicles will unite to form saturated compounds, without loss.

Messrs. Richardson and Bowen quote figures supporting their contention; but they do not give a detailed analysis of the vinegar they experimented with.

It is well known what varying and unsatisfactory figures are obtained in determining the alkalinity of the soluble ash in vinegar analyses; and I have long been aware that there is a connection between this and the variations in mineral matter present in some brands, quite apart from any question of adulteration. The wide range through which the mineral constituents of fermented vinegars may vary is well illustrated in the Table III. (see succeeding paper); and with a view to testing this method three pure vinegars were selected, which varied considerably as to the salts present. The full analyses of these samples will be found in Table III. (*loc. cit.*), the distinguishing letter in this table indicating the same vinegar as the corresponding letter in Tables I. and II. They were selected as types—A, of vinegars made with normal well, or town, water; B, made with water heavily charged with chlorides and sulphates; and C, made with a very hard water, but in which some cereal had been used which was low in phosphates.

Before deciding the relative advantages of lacmoid and methyl orange, a number of experiments were made with each indicator on the vinegars themselves, and also on a solution containing about 1.25 per cent. of sulphuric acid and 1 per cent. of di-hydrogen potassium phosphate. With methyl orange the point of neutrality was, of course, well marked, and there was practically no difference in the reading whether or not the solution had been previously boiled and rapidly cooled before making the titration. This shows that the carbon dioxide, if present, does not here influence the result; in all cases, however, it was found necessary to boil the solution to expel carbon dioxide before titrating to phenolphthalein. There was some difficulty with lacmoid in determining the exact point of neutralization when using either the paper or the solution; and this was less distinct in the case of the solution of the ash than in the made-up solution. There was a further difficulty of deciding the end reaction with phenolphthalein when the solution was blue with lacmoid, more especially as the first pink tint given in titrating these phosphatic solutions is very faint. It was also found with sample B that before the solution of the ash was neutral to phenolphthalein an excess of soda had been added. These considerations induced me to discontinue the use of lacmoid.

As the solution of the ash had to be boiled to remove carbon dioxide, it was necessary to determine, in view of the quantities of chlorides present, whether there was not a loss of hydrochloric acid during ebullition, but repeated determinations failed to show that there was any appreciable loss under the conditions of the experiment. As a matter of convenience,  $N/3$  soda and sulphuric acid was used in these experiments, and the burette was made especially narrow to give greater accuracy in reading; the burette had been checked against the pipettes, and these proved by the balance. The steps taken are the same as recommended by Richardson and Bowen, but only 5 c.c.  $N/3$  soda was added to the 25 c.c. vinegar, and 10 c.c.  $N/3$  sulphuric acid to the ash; after filtering, the acid solution was boiled for five minutes, cooled rapidly, titrated to methyl orange, again boiled for five minutes, and the titration finished to phenolphthalein whilst hot.

In Table I. are given the figures obtained, and they show, by Richardson and Bowen's method of calculation, the addition of mineral acid in each case. In contrast with this, Hehner's method shows an alkalinity recorded in terms of  $K_2O$ .

TABLE I.

Sample Mark.	C.c. $N/3$ Soda added.				Richardson and Bowen Method.	Hehner Method.
	To the 25 c.c. of Vinegar.	To Neutralize to Methyl Orange.	To Neutralize to Phenolphthalein.	Total to Saturation of Phosphates.	$H_2SO_4$ Per Cent.	Alkalinity as $K_2O$ Per Cent.
	(X.)	(Y.)	(Z.)	(X + Y + 2Z.)		
A ...	5	3.35	1.15	10.65	0.042	0.103
B ...	5	4.15	1.5	12.15	0.140	0.053
C ...	5	4.2	1.1	11.4	0.091	0.050

## THE ANALYST.

Examples of calculation :

*Richardson and Bowen's Method.*—An excess of  $N/3$  soda, 0.65 c.c.  
 $0.65 \times 0.0163 \times 4 = 0.042$  per cent. sulphuric acid.

*Hehner's Method.*—A shortage of  $N/3$  soda, 1.65 c.c.  
 $1.65 \times 0.0156 \times 4 = 0.103$  per cent. alkalinity as potash.

The alkalinity of the soluble ash given in Table 3 (*loc. cit.*) bears a distinct relation to the above figures. A shows 0.02 per cent. as  $K_2O$ ; B, 0.007; and C., 0.006. It would thus appear that while *Hehner's* method would not detect a small addition of mineral acid, *Richardson and Bowen's* method errs as far on the other side, and finds what is not there.

Attempts were made to ascertain how far the sulphates, obtained by direct precipitation from the vinegar, agree with those found in the ash after evaporating and igniting; and here there are discrepancies which cannot be satisfactorily explained on the assumption that the carbonaceous matter reduces them to sulphides. Doubtless this occurs to an extent, but it can hardly account for a loss in the case of B of as much as 0.062 per cent. of sulphuric acid, and only of 0.007 in F. These figures would appear to confirm my view that the phosphates are wholly or partially present in the acid state, and that ignition brings about the expulsion of an equivalent quantity of sulphates, whilst normal and perhaps pyrophosphates are formed. The undermentioned figures are given, for what they may be worth, in tabular form :

TABLE II.

Sample Mark.	A.	B.	C.	D.	E.	F.	G.
Sulphates in vinegar (as $H_2SO_4$ )	0.041	0.146	0.134	0.046	0.033	0.243	0.176
Ditto in ash ...	0.043	0.084	0.124	0.054	0.012	0.236	0.147
Difference ...	+0.002	-0.062	-0.010	+0.008	-0.021	-0.007	-0.029

It is to be hoped that little more will be heard of the presence of mineral acids in vinegar. I am in a position to assert that the practice of adulterating vinegar in this way has long ceased, hence to work out new processes for their determination is clearly waste of time.

