

### Determination of Formic, Acetic and Propionic Acids in Fermenting Mixtures.

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The procedure involves the use of the partition method<sup>1, 2</sup> for the determination of organic acids, in conjunction with the separate determination of the formic acid by oxidation with mercuric oxide. The determination of the formic acid in this manner is necessary because the partition method will not serve to determine formic in the presence of acetic acid. By means of a nomogram the formic acid determination is read off and connected by means of a straight edge to the partition reading; the percentages of acetic and propionic acids are read off on the appropriate lines on the nomogram.

The acidity of the acid distillate should be adjusted to approximately 0.03 normal.

Two hundred cc. of the mixture are boiled for half an hour with about 3 gm. of mercuric oxide in a flask. The carbon dioxide liberated during the process is determined, and the formic acid calculated and expressed in terms of normality as percent of total acid present.

Fifty-five cc. of the acid mixture are shaken for 1½ minutes in a separatory funnel with 25 cc. of ethyl ether. Fifty cubic centimeters of the aqueous phase are then removed and titrated. The cc. of alkali required to titrate these 50 cc. of the acid divided by the cc. of alkali required to neutralize 50 cc. of the acid before partition gives the partition constant, K.

Constants established for each acid are: for formic K = 84.5, for acetic K = 82.1, and for propionic K = 58.8.

Expressing the percent of formic, acetic, and propionic acid present by F, A, and P respectively the following equations are set up:

$$\begin{array}{r} 0.845 F + 0.821 A + 0.588 P = K \\ F + \quad A + \quad P = 100 \end{array}$$

or since F is determined separately,

$$\begin{array}{r} 0.821 A + 0.588 P = K - 0.845 F \\ A + \quad P = 100 - F \end{array}$$

<sup>1</sup> Werkman, C. H., *Ind. Eng. Chem.*, 1930, **2**, 302.

<sup>2</sup> Osburn, O. L., and Werkman, C. H., *Ind. Eng. Chem.*, 1931, **3**, 264.

Solving these equations for A and P in terms of K and F we have:

$$\begin{aligned}A &= 4.291 K - 1.103 F - 252.36, \text{ and} \\P &= 352.36 + 0.103 F - 4.291 K\end{aligned}$$

The percent of each acid is expressed as a true normality percent, *i. e.*, the number of cubic centimeters of the normal acid per 100 cc. of total normal acid.

The presence of acids other than the 3 mentioned may be detected by partitioning 60 cc. of the acids with 100 cc. of ether and establishing constants as above. If the results of such a partition indicate a different ratio of propionic to acetic acid, then some foreign acid is indicated. The individual constants for 60 cc. of the acid mixture and 100 cc. of ethyl ether are: for formic  $K = 63.5$ , for acetic  $K = 58.5$ , and for propionic  $K = 27.16$ .