XCIV. THE EVALUATION OF THE PURITY OF VARIOUS ORGANIC PRODUCTS BY THE DICHROMATE METHOD.

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THE writer has previously described [1914] a method for the volumetric estimation of carbon, the essence of which is oxidation by a mixture of phosphoric acid and potassium dichromate and the measurement of the CO_2 produced. It was shown that where methyl groups are present the substance is not oxidised to carbon dioxide alone but to a mixture of carbon dioxide and acetic acid; for example, lactic acid, alanine and ethyl alcohol each yield one molecule of acetic acid per molecule of substance taken; that is to say each methyl group gives rise to one molecule of acetic acid. The method proved of service in estimating the amount of such substances as mannitol and glycerol or, in the case of a mixture, of the residual oxidisable material after a fermentation. It is possible with a few cc. of solution to estimate how much material remains after fermentation, and so on.

At the time of publishing this method the writer was unaware of Martin's method [1904] for the estimation of alcohol. Martin's method is now probably fairly generally employed in industry; certainly in France. It is exceedingly accurate and is applicable to very dilute solutions of alcohol. Martin distils the alcoholic solution into a mixture of equal parts of *N* potassium dichromate and sulphuric acid; the steam keeps the mixture hot and the oxidation is immediate, the alcohol being oxidised to acetic acid (1 cc. *N* dichromate = 0.0115 g. alcohol). The measurement of the reduction of standard dichromate solution is made by a solution of iron of about a fifth the strength of the dichromate, which increases the speed and accuracy with which one can work. The method is clearly much simpler than my own but is without some of its advantages; one cannot for instance apply it to the oxidation of a substance without knowing whether it is oxidised to acetic acid or to carbon dioxide or both. Provided however we know what are the products of oxidation, we could probably employ the dichromate method for estimating many substances; and its application to the estimation of impurities in non-oxidisable substances seems obvious.

In the second place, by a combination of Martin's method with my own one can obtain two constants which permit the estimation of the proportions of many substances, *i.e.* (1) the dichromate method, measuring the dichromate

reduced; (2) the dichromate method measuring the CO_2 produced and when necessary the acetic acid formed.

As special apparatus is required for the measurement of CO_2 it is much more convenient to employ method (1) where one constant suffices, as in estimating the amount of any pure substance.

In calculating the dichromate value of any aliphatic substance the rule is that the substance is completely oxidised to CO_2 except the carbon atom of a methyl group and the next adjacent carbon atom which appear as acetic acid; thus

or for each cc. *N* lactic acid we require 4 cc. *N* dichromate.

Exp. 1. 25 cc. of a lactic acid solution = 27.4 *N*/10 were mixed with 11 cc. *N* potassium dichromate, and 25 cc. concentrated sulphuric acid added rapidly. The excess dichromate was titrated with ferrous sulphate solution. Found:

27.4 cc. *N*/10 lactic acid reduced 10.77 cc. *N* dichromate;

1 cc. *N* lactic acid reduces 3.93 „

Theory 4.00 „

The experiment was repeated using twice the concentration of dichromate. Found:

27.4 cc. *N*/10 lactic acid reduced 11.27 cc. *N* dichromate;

or 1 cc. *N* lactic acid reduces 4.11 „

Theory 4.00 „

Thus even with a wide range of oxidising agent (doubling the dichromate) the reaction follows the above equation. The acetic acid produced is clearly not oxidised further, in agreement with what the writer previously found [1914].

On the other hand, substances devoid of CH_3 groups should, according to the writer's theory, yield no acetic acid but only CO_2 and H_2O . The following were tried: malonic, tartaric and citric acids, ethylene glycol; with the following results:

Exp. 2. The weight of substance mentioned in each case was dissolved in 10 cc. of water and 22 cc. *N* dichromate added. To this mixture 25 cc. concentrated sulphuric acid were added. The excess of dichromate was titrated by ferrous sulphate solution.

Results:

Ethylene glycol 0.1274 g. reduced 19.94 cc. *N* dichromate

Theory 20.55 „

Citric acid 0.0931 g. reduced 7.87 „

Theory 7.98 „

Malonic acid 0.1932 g. reduced 14.86 „

Theory 14.93 „

Tartaric acid 0.1035 g. reduced 3.71 „

Theory 3.76 „

The results are, within experimental error, in support of the theory.

The only exception to the rule seems to be succinic acid. This peculiar behaviour of succinic acid in resisting oxidation has previously been described. Under the conditions detailed above, succinic acid was not appreciably oxidised.

Exp. 3. 20 cc. *N*/20 succinic acid were mixed with 22 cc. normal potassium dichromate and to this 25 cc. concentrated sulphuric acid added. The excess of dichromate required for reduction 124.3 cc. ferrous sulphate solution; control dichromate and sulphuric without succinic acid required 126 cc.

2 cc. ferrous sulphate corresponds to 0.4 cc. dichromate and this represents an oxidation of at most 1.2 cc. of the succinic acid solution, *i.e.* 5 %. Allowing for error, we may say that from 2 to 5 % was oxidised; but the oxidation is often less than this.

By choosing the right concentration of reagents therefore it is possible to avoid the oxidation of any appreciable amount of succinic acid present. The concentration recommended is as follows:

- (a) Water containing the unknown, 10 cc.
- (b) *N* potassium dichromate 10
- (c) Sulphuric acid, conc. 20

Add (c) rapidly to the mixture of (a) and (b).

It has been shown that with the exception of succinic acid, aliphatic substances follow the rule described by the writer. We may therefore calculate directly what the oxygen equivalent of any substance will be, and it is a simple matter to construct tables for mixtures of any two substances. The following table shows the application of this principle.

Table I. *Mixture of two alcohols.*

1 cc. <i>N</i> dichromate oxidises	1/6	mol. (in mg.)	methyl alcohol	or	0.00533 g.
" "	1/4	"	ethyl	"	0.0155
" "	1/10	"	propyl	"	0.0060
" "	1/16	"	butyl	"	0.004623

To draw up the table we calculate how much dichromate corresponds to one decigram of each of the two substances. The difference between these two values we may divide up into a hundred parts; we can then read off at a glance the percentage of both constituents corresponding to the dichromate titration value obtained.

Dichromate values of alcohols.

0.1 g. methyl alcohol	reduces	18.740 cc. <i>N</i> dichromate
0.1 g. ethyl	"	8.695 "
0.1 g. propyl	"	16.670 "
0.1 g. butyl	"	21.620 "

The marked difference between the oxygen values of methyl, ethyl and other alcohols makes the method of useful application in the case of a mixture of two alcohols of which ethyl alcohol is one.

Polyhydric alcohols also follow the same rule:

0.1 g. ethylene glycol	reduces	16.120 cc. <i>N</i> dichromate
0.1 g. glycerol	„	15.220 „
0.1 g. mannitol	„	14.285 „

All these figures have been verified by experiment except butyl alcohol. By a simple calculation from the weight taken and the dichromate value, the proportions in the case of a mixture of two alcohols such as methyl and ethyl alcohol, or ethyl and propyl alcohol can be ascertained.

Table II. *Mixtures of any two acids.*

The acid mixture should be approximately decinormal. The mixed acids are first titrated or the titre estimated by neutralising with lime and estimating the calcium. The oxygen value of 1 cc. of a normal solution must be determined and the oxygen values of the constituents calculated from the rule given. The following values may be given as examples:

1 cc. <i>N</i> formic	acid reduces	2.00 cc. <i>N</i> dichromate
„ oxalic	„	1.00 „
„ acetic	„	0.00 „
„ malonic	„	4.00 „
„ lactic	„	4.00 „
„ succinic	„	0.00 „
„ propionic	„	6.00 „
„ butyric	„	12.00 „
„ valerianic	„	18.00 „

(or an increment of 6 cc. *N* dichromate for each CH_2 group).

Amino acids follow the same rule:

1 cc. <i>N</i> glycine	reduces	6.00 cc. <i>N</i> dichromate
„ alanine	„	4.00 „

By a simple calculation the proportions of two acids in a mixture can be ascertained, provided there is a difference in their oxygen value.

REFERENCES.

- Grey (1914). *J. Chem. Soc.* **105**, 2204.
 Martin (1904). *Rev. intern. Falsif.* **17**, 48. *Chem. Soc. Abstr.* ii. 520.