THE DETECTION OF METHYL ALCOHOL.

BY HEYWOOD SCUDDER AND ROBERT B. RIGGS.

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LEACH and Lythgoe[1] recommend as a confirmatory test for the detection of methyl alcohol, oxidation of the solution by a hot copper spiral and testing for formaldehyde by heating with milk and hydrochloric acid containing ferric chloride.

We have tried this test on 10 per cent. aqueous solutions of ethyl alcohol, acetic acid and acetone, and in each case there developed a violet color indistinguishable from that given by pure methyl alcohol. After oxidation the solutions were filtered before adding the milk and acid. The color obtained depends somewhat on the conditions of the test. Leach directs the use of a few drops of the oxidized solution.

In the case of acetone, if the whole of the oxidized solution was used, a distinct violet color appeared momentarily during the heating, changing to a brownish yellow. If only a few drops of the oxidized solution were used the violet color was deep and persistent. But on adding to this the rest of the oxidized solution (which contained a good deal of unaltered acetone) and heating, the violet color disappeared, changing to brownish yellow. In this case the excess of the acetone gave a color that obliterated the color due to formaldehyde.

In the case of ethyl alcohol there is a difference in the depth of the violet color between tests made with a few drops and with the whole of the oxidized solution, but the violet always persists.

Acetic acid showed no difference in color whether a few drops or the whole solution was used.

Oxalic acid gave a brown with a faint violet tinge, when a few drops of the oxidized solution were tested, but excess of the oxidized solution destroyed this violet, leaving only the brown. The violet tinge was sufficiently marked to be noticeable to one unaccustomed to the test.

A blank test of the milk used, showed no trace of a violet tinge under any variations of heating.

The cause of the failure of this test is its delicacy in detecting formaldehyde. The formation of small amounts of formaldehyde in the oxidation of many organic compounds, especially

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[1] This Journal, 27, 965 (1905).

when the oxidant is heated copper or platinum, is well-known,[1] and warnings have been given of the caution necessary in applying any test for methyl alcohol that depends on a very delicate test for formaldehyde.

In the case of the compounds tested, the violet color came from formaldehyde. If a sufficient amount of some other compound reacting with milk and acid was present (as in the case of acetone and oxalic acid) the violet color became changed or obliterated, otherwise it persisted.

In its present condition this test can not be depended on as a general one for the detection of methyl alcohol in mixtures.

The Sanglé-Ferrière Cumiasse Test[2] we have modified so that it can be performed more simply. This modification shows 2 to 3 per cent. of methyl alcohol in ethyl. To 10 cc. of the aqueous solution to be tested are added 0.5 cc. of concentrated sulphuric acid and 5.0 cc. of a saturated solution of potassium permanganate. The temperature should be kept at 20°–25°. At the end of two minutes enough sulphurous acid is added to give a colorless solution (an excess is not harmful). The solution is boiled till it does not smell of sulphur dioxide nor of acetaldehyde, then the resorcinol test for formaldehyde is applied. If no flocks appear but a pink ring is present, they can often be developed by standing for one to two hours, then heating the upper layer just to boiling. The ring first formed is usually sufficiently characteristic to show methyl alcohol and in case of doubt a blank test with ethyl alcohol can be made, but the flocks give positive evidence and no blank is required.

The use of sulphurous acid to reduce any excess of the permanganate and to dissolve the hydroxide avoids the troublesome precipitation by tannic acid and sodium carbonate with subsequent filtration.

Variations in the temperature below 18° are harmful from the reduced speed of the reaction, above 30°, from loss of formaldehyde. Great excess of acid is harmful. Less acetaldehyde seems to be formed from ethyl alcohol in this oxidation than in the oxidation with a hot copper spiral.

Formation of Flocks in the Resorcinol Test for Formaldehyde.—

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[1] Mulliken, Brown, French: Am. Ch. J. 25, 115 (1901); Scudder: This Journal, 27, 894 (1905).

[2] Ann. chim. anal. appl. 8, 82 (1903).

If to the solution to be tested are added an equal volume of concentrated hydrochloric acid and two drops of a 0.5 per cent. solution of resorcinol and the whole is boiled one or two minutes, characteristic flocks will appear, if sufficient formaldehyde is present.

The advantage of using hydrochloric acid instead of sulphuric acid is that no darkening of color from overheating or charring is possible. The disadvantage is that the delicacy of the test is lessened. It is not possible to get flocks in mixtures of methyl and ethyl alcohols when less than 5 per cent. methyl alcohol is present. The boiling, of course, prevents any formation of a contact ring. But when sulphuric acid is used, the color of the flocks is often destroyed by too rapid shaking, with consequent overheating, especially when only a small amount of formaldehyde is present.

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A METHOD FOR THE DETERMINATION OF LEAD NUMBER IN MAPLE SYRUP AND MAPLE SUGAR.

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THE copious precipitate formed in maple products by basic lead acetate furnishes a means not only of clearing the solution for polarization but also of detecting the admixture of refined cane-sugar. Jones[1] and also Hortvet,[2] working independently of each other, have devised methods for measuring the bulk of this precipitate after separation with the aid of a centrifuge. The method devised by Jones was especially designed to test the products delivered by farmers to wholesalers, while Hortvet's method was devised with reference to the official inspection of the commercial products. Both serve well the purpose for which they were intended; they are easily carried out and give comparative results of great value. These results, however, can hardly be accepted as fixed constants, since the precipitate varies not only in composition but its volume is also dependent on the speed of the centrifuge and other details of manipulation.

Although volumetric methods of a similar nature are successfully employed for the determination of the gravimetric per-

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[1] Vt. Agr. Expt. Sta. Rep. 17, 454 (1904).

[2] This Journal, 26, 1532 (1904).