

THE DETECTION OF METHANOL IN THE PRESENCE OF ETHYL ALCOHOL.

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ABSTRACT.

By interaction with hydriodic acid, the alcohols are converted into iodides which are distilled into a solution of trimethyl amine in absolute alcohol and there converted into the corresponding quaternary ammonium derivatives. The precipitation of the very sparingly soluble tetramethyl ammonium iodide indicates the presence of methanol in the original sample provided other methoxy compounds are absent. This method allows the detection of 0.1% methanol in a 1 c.c. sample or of 0.2% methanol in a 0.1 c.c. sample. A wide range of alcoholic beverages gave negative tests for methanol as also did formaldehyde and higher alcohols.

PROCEDURE.

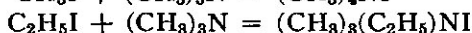
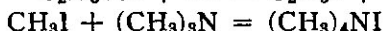
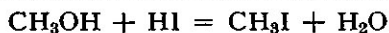
One c.c. of the sample and 5 c.c. of constant boiling hydriodic acid are pipetted into an 18x150 mm. pyrex test tube and a small piece of tin foil added. The test tube is closed with a rubber stopper through which extends a glass tube bent at a right angle. The contents are heated to gentle boiling over a small flame, and the vapors absorbed in 10 c.c. of a 10% solution of trimethyl amine in absolute alcohol. Care is taken that hydriodic acid is not driven over and that the trimethyl amine solution is not sucked back. A white, granular precipitate indicates the presence of methanol in the sample.

NOTES.

1. This is a modification of Willstätter and Utzinger's method¹ for the determination of methoxy and ethoxy groups. The hydriodic acid reacts with the alcohols to form the corresponding alkyl iodides which are distilled into the solution of trimethyl amine in absolute alcohol. Here tetramethyl ammonium iodide and trimethyl ethyl ammonium iodide are

1. Willstätter and Utzinger, *Ann. d. Chem.*, **382**, 148-50 (1911).

produced. The former is very insoluble in absolute alcohol and comes down as a white, granular precipitate. The latter is much more soluble and crystallizes in needles.



2. The hydriodic acid is prepared by dropping water onto phosphorus pentiodide (red phosphorus and a slight excess of iodine) and absorbing the hydrogen iodide in water. No phosphine is formed when iodine is in excess. The dilute solution is fractionated, and the constant boiling fraction (125-126°) is collected and stored in small amber, glass-stoppered bottles.

3. In each test one piece of tin foil 0.5 sq. cm. in area and weighing approximately 20 mg. is amply sufficient. Its role is to prevent bumping.

4. The trimethyl amine solution is prepared from para-formaldehyde and ammonium chloride by the method of Adams and Brown². Less odour escapes if the coil condenser and absorbent alcohol are cooled with a solid carbon dioxide and alcohol mixture, and if, after completion of the preparation, the last traces of the amine are removed by attaching the exit to the condenser to a water pump.

5. Starting with a 1 c. c. sample of mixed methyl and ethyl alcohols, the presence of 1% or more of methanol is indicated by a fine, granular precipitate in less than 1 minute; 0.1% of methanol yields a precipitate in less than half an hour; and 0.05% of methanol, no precipitate. When very slight, this precipitate can be seen best in the sunlight as shining particles. The precipitate is always granular. On long standing needles of trimethyl ethyl ammonium iodide may form, especially if the temperature is below 20°C. They redissolve when gently warmed.

2. Adams and Brown, "*Organic Syntheses*," John Wiley and Sons, New York. 1921, vol. 1, pp. 76-78.

6. The method as outlined can be modified to detect methanol in samples smaller than 1 c.c. One-tenth c.c. of the sample, 0.5 c.c. of constant boiling hydriodic acid and a minute piece of tin foil are heated in a 15x100 mm. pyrex test tube and the iodides absorbed in 1.0 c.c. of a 10% solution of trimethyl amine in absolute alcohol. Then 0.2% of methanol in ethyl alcohol yields a precipitate within 2 minutes, while 0.1% methanol gives no positive result. 0.2% methanol in a 0.1 c.c. sample corresponds to 0.15 mg. of methanol.

7. The presence of ethyl alcohol increases the sensitivity of the test. One c.c. of a 0.1% solution of methanol in water gives a negative result whereas 1 c.c. of a 1% solution of methanol in water gives a heavy precipitate in less than a minute. It is probable that in the distillation the ethyl iodide helps to drive over traces of methyl iodide.

8. Gin, whiskey, brandy, rum, Italian vermouth, sherry and port have been tested for methanol with negative results. It is a surprising and useful fact that formaldehyde (and para-formaldehyde) gives a negative test. Likewise do the higher alcohols. Oil of wintergreen (methyl salicylate), as well as other compounds containing methoxy groups, gives a positive test. Hydriodic acid in relatively large amounts gives a precipitate of trimethyl ammonium iodide, therefore care must be taken that the heating be not too strong or prolonged.

9. The effect of replacing the reagents with closely related substances has been investigated. When hydrobromic acid is substituted for hydriodic, the test is less sensitive for 1 c.c. of 2% methanol in ethyl alcohol gives a precipitate after 15 minutes while 1% methanol gives no precipitate. The replacement of trimethyl amine by dimethyl aniline is not satisfactory and the use of commercial 90%, instead of absolute, alcohol in the amine solution is not recommended.

10. The estimation of methanol in the presence of ethyl alcohol will be dealt with in a further paper.