

Determination of Formaldehyde in Maple Sirup: Interfering Substances

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Three carbonyl compounds isolated from maple sirup by distillation as in the AOAC official method for formaldehyde have been identified by mass spectrometry as formaldehyde, acetone, and acetaldehyde. Acetone and acetaldehyde do not interfere with the formaldehyde determination if the procedure of the AOAC official method is followed; acetol and glyoxal also do not cause errors in the formaldehyde value. Tests run have shown the modified Nash method (31.184-31.189) adopted as official final action to be extremely specific for formaldehyde in maple sirup.

Work has been continued on the official method for the determination of formaldehyde in maple sirup (1). In this procedure the formaldehyde is separated from the sirup by distillation. A preliminary study reported last year indicated that other carbonyl compounds in addition to formaldehyde were present in the distillate (2). Therefore, work was initiated by the Associate Referee

Maple Flavor and Imitations to determine if these carbonyl compounds or other possible constituents of the sirup distillate might interfere, causing error in the formaldehyde value.

A maple sirup, U.S. Grade No. 1, that was found to be higher than normal in formaldehyde content was selected for use in this study. The sirup had been made from maple sap obtained from trees treated with a formaldehyde germicidal pellet. Five aliquots of the sirup were distilled according to the official method and the distillates were combined, giving a total volume of 15 ml. This isolate was treated with 2,4-dinitrophenylhydrazine and the hydrazones obtained were analyzed by the gas-liquid chromatographic (GLC) method of Soukup *et al.* (3). The GLC curve is shown in Fig. 1. The compounds represented by the 3 peaks on the chromatogram were identified by mass spectrometry as formaldehyde, acetaldehyde, and acetone. Thus, acetaldehyde and acetone, if they react with the reagent for formaldehyde in the official method, could be listed as interfering substances, altering the true value for the formaldehyde content. Figure 1 also indicates that interference from acetone would be much greater than from acetaldehyde.

To gain further information on the possible error in formaldehyde values due to these 2 compounds, their ultraviolet absorption was studied between 700 and 350 nm in Nash's Reagent B, the color reagent of the method (Fig. 2); acetol and glyoxal absorption curves were obtained in the same way. Acetol (hydroxyacetone) has been isolated from maple sirup by steam distillation. Glyoxal is a well known sugar breakdown product that gives a color reaction with Reagent B (2). The reagent curve shows no absorption above 350 nm and therefore does not interfere with the absorption peak area for the product of the formaldehyde-reagent reaction, diacetyldihydrocollidine (DDL). The wavelength at which absorption is measured in the official method was designated as 415 nm to facilitate the accurate setting of the various spectrophotometers with which the measurements might be made. The curve in Fig. 2 for formaldehyde shows the well defined peak with the maximum unaffected by reagent absorption.

Nash (4), in his development of this method, reported that with Reagent B acetaldehyde produces an absorption peak of similar intensity to the DDL peak but with maximum extinction at 388 nm instead of 412 nm. This absorption is due to the formation of diacetyldihydrocollidine from the acetaldehyde and the acetylacetone in the color reagent. As shown in Fig. 2, when absorption is measured at 415 nm, significant error can be contributed to the formaldehyde value by acetaldehyde. However, Nash reported that the rate of formation of the diacetyldihydrocollidine is so slow that very little interference occurs if color measurements are made within 3 hr after heating the reagent and sample mixture according to the procedure in the method. Nash estimated that 1% interference would be expected from the equimolar proportions of acetaldehyde as formaldehyde. This slow reaction rate was verified in this study for the low concentration level of formaldehyde in maple sirup.

In Table 1 the rate of color development of formaldehyde, acetaldehyde, and glyoxal with Reagent B is recorded and the slow reaction rate of acetaldehyde is clearly demonstrated. There-

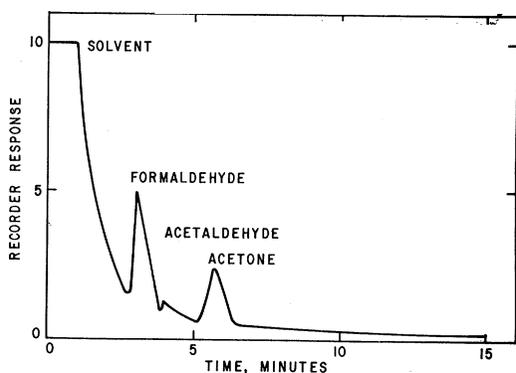


FIG. 1—Gas chromatographic separation of the carbonyl compounds in the distillate of maple sirup.

fore, taking into account this slow rate of reaction and the small amount of acetaldehyde relative to formaldehyde indicated in maple sirup by the curve in Fig. 1, very little error in the formaldehyde value should be caused by acetaldehyde.

The third peak in Fig. 1 was identified as acetone. When mixed with Reagent B, this compound produced no color, even after 24 hr at 37°C. Also, from Fig. 2 it is evident that no absorption occurred at 415 nm from its mixture and heating with Reagent B. Consequently, no interference could occur from this compound.

In addition to the 3 compounds just discussed, acetol has been identified in steam distillates of maple sirup. Last year it was reported that this compound reacted slowly with Reagent B to form the yellow color typical of the formaldehyde reaction. This year, the compound was tested again, using a freshly prepared sample. At the 10 ppm level no color developed in 12 hr with Reagent B and no absorption was obtained at 415 nm. The test was repeated with a 100 ppm solution of the compound. After 24 hr, slight color had developed and an absorption curve was obtained. The absorption curve, recorded in Fig. 2, resembles that for acetaldehyde. This indicated that the reaction with acetol may be due to an impurity. Certainly the lack of evidence of reaction at the 10 ppm level eliminates acetol as a serious interfering substance in this method.

Two different samples of glyoxal were examined in the same manner as acetol with the same results. No interference should occur from this compound. In addition to the 5 compounds discussed in this report, Nash found that chloral, fural, and glucose do not interfere, while amines interfered only slightly.

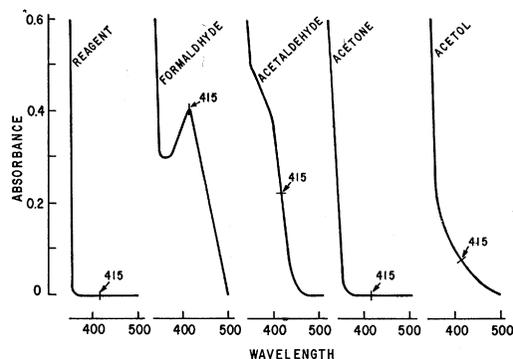


FIG. 2—Absorption curves of some carbonyl compounds in Nash's Reagent B.

Table 1. Absorbance readings at 415 nm of several carbonyl compounds with Nash's Reagent B at 37°C

Compound	ppm	Time, min					
		2	7	15	30	60	120
Formaldehyde	10	0.37	1.0	1.6	—	—	—
Acetaldehyde	10	0.025	0.015	0.026	0.020	0.020	0.023
Formaldehyde	1	0.03	0.12	0.18	0.23	0.25	0.26
Acetaldehyde	1	0.005	0.010	0.010	0.010	0.015	0.015
Glyoxal	1	0.005	0.010	0.015	0.025	0.025	0.025

Conclusions and Recommendation

The official method for formaldehyde in maple sirup has been found to be extremely specific. However, the isolation step (distillation) of the procedure lacks the precision for the high degree of accuracy needed for the determination of formaldehyde in maple sirup. Therefore, it is recommended that work be continued to improve the present official method.

Acknowledgments

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The recommendation of the Associate Referee was approved by the General Referee and by Subcommittee D and was accepted by the Association; their reports will appear in *JAOAC* 55 (March 1972).

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