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**Collaborative Study of the Determination of Formaldehyde in
Maple Sirup**

Collaborative Study of the Determination of Formaldehyde in Maple Sirup

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A modified Nash method for the determination of formaldehyde in maple sirup has been studied collaboratively by 13 chemists in 9 states and 2 provinces of Canada. As a result of the satisfactory precision obtained by these analyses, the method has been recommended for adoption as official, first action.

The use of a paraformaldehyde germicidal pellet to control microbial growth in the maple tree taphole has brought about the need for an analytical method to measure the residual traces of formaldehyde in maple sirup made from sap of treated tapholes. The method must be specific for formaldehyde and not measure other carbonyl compounds such as those formed by the degradation of sugars. The method must also be sensitive to very low levels of formaldehyde since the Federal Food and Drug Administration regulation states that maple sirups shall not contain more than 2 ppm of formaldehyde as a result of taphole treatment.

Last year the General Referee on Maple Products proposed a specific method (1) based on that described by Nash for measuring these very small amounts of residual formaldehyde in maple sirup. Since the method gave satisfactory results in the Referee's laboratory, it was decided to study it collaboratively.

Two test samples of sirup containing about 1 and 2 ppm added formaldehyde were prepared from the same stock of maple sirup. Aliquots of these were sent to the collaborators with a supply of the original stock for preparing their standards. The collaborators were also supplied a copy of the analytical procedure (1), directions for making standards, a questionnaire, and a data sheet.

Each collaborator was requested to make at least three determinations on each of the two test samples and at least two measurements on the sirups of known concentrations they would prepare for constructing standard absorption curves. All values obtained were requested for use in statistical analysis.

Results and Discussion

Fifteen chemists agreed to participate in this 1963 collaborative study. All the collaborators submitted results. However, two sets of data were not included because of mold spoilage of one sample and atypical values of another, which were discarded according to the method of Sachs (2). The results obtained on the two 1963 collaborative samples are given in Table 1. Values were recorded for n = number of determinations, \bar{x} = collaborator's mean, $\bar{\bar{x}}$ = mean of all determinations, s = standard deviation of a single observation, and $s_{\bar{x}}$ = standard deviation of laboratory means. 95% CL = the confidence limits of $\bar{\bar{x}}$.

Sample A, containing about 1 ppm or added formaldehyde, was reported by the collaborators to have an average ($\bar{\bar{x}}$) formaldehyde content of 0.91 ppm from 39 determinations ranging from 0.22 to 1.56 ppm with a standard deviation of ± 0.28 and confidence limits at the 95% level of 0.092 ppm.

Sample B, with approximately 2 ppm of added formaldehyde, was found by the collaborators to contain an average ($\bar{\bar{x}}$) of 2.05 ppm formaldehyde ranging from 1.58 to 2.90 with a standard deviation for each determination of 0.34 and confidence limits at the 95% level of 0.112 ppm.

The interlaboratory agreement between means was satisfactory for both samples, and

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Table 1. Summary of formaldehyde values for 1963 collaborative study on maple sirup ($n = 3$)

Coll.	Formaldehyde, ppm		
	Maximum	Minimum	\bar{x}
Sample A ^a			
1	1.10	0.90	0.97
2	0.75	0.58	0.62
3	0.90	0.85	0.88
4	0.75	0.74	0.75
5	0.85	0.77	0.80
6	1.25	1.07	1.17
7	1.56	1.40	1.48
8	0.88	0.70	0.79
10	0.83	0.66	0.74
11	0.67	0.22	0.43
13	1.05	0.93	0.97
14	1.20	0.70	0.96
15	1.25	1.20	1.22
Sample B ^b			
1	2.90	2.15	2.63
2	1.59	1.58	1.59
3	1.92	1.85	1.92
4	2.12	2.12	2.12
5	2.28	1.91	2.08
6	2.05	2.02	2.03
7	1.93	1.81	1.88
8	1.80	1.60	1.76
10	1.80	1.63	1.73
11	2.65	2.10	2.48
13	1.90	1.83	1.86
14	2.60	2.40	2.50
15 ^c	2.20	2.10	2.15

^a $\bar{x} = 0.906$; $s = 0.283$; $s_{\bar{x}} = 0.237$; 95%CL = ± 0.0925 .
^b $\bar{x} = 2.05$; $s = 0.340$; $s_{\bar{x}} = 0.318$; 95%CL = ± 0.112 .
^c $n = 2$.

the intralaboratory precision was high in all but two cases. One collaborator showing relatively poor precision also reported low values for Sample A, indicating trouble with the distillation part of the procedure.

None of the collaborators raised questions of major consideration, although several worthwhile suggestions were made about minor details of procedure. These have been incorporated into the present method. Several collaborators felt that it was difficult to maintain uniform distillation rate when using the micro gas burner. Consequently,

many of them substituted an oilbath or electric heater for the micro gas burner. These different types of heaters did not significantly affect the accuracy or precision of results obtained by the 13 collaborators. Several comments were made about the confusing description of the Nash reagent by its inclusion of molarity values of the constituents. Therefore, a simpler formula for this reagent has been included in the present procedure.

Based on the results of this study, minor changes were made in the procedure published in the 1962 report, and the revised procedure is presented in this paper.

METHOD

Apparatus

(a) *Distillation apparatus*.—30 ml micro Kjeldahl flask fitted with 19/38 F outer joint and 4" water-cooled West condenser with 19/38 F inner joint bent at 90° angle. See Fig. 1.

(b) *Spectrophotometer*.—Suitable for measuring absorption at 415 $m\mu$; with matched 1 cm cells or matched test tubes.

Reagents

(a) *Nash's Reagent "B"*.—Dissolve 150 g NH_4OAc , 3 ml HOAc , and 2 ml acetylacetone in 200–300 ml H_2O in 1 L flask and dil. to mark.

(b) *Formaldehyde*.—37%. Assay by 4.111–4.112.

Preparation of Standard Solutions

(a) *Solution A*.—1000 ppm. Weigh 5.26 g CH_2O (for 37.4% soln; use equiv. amount with other concn) into 2 L vol. flask contg some H_2O and dil. to vol.

(b) *Solution B*.—50 ppm. Pipet 10 ml *Soln A* into 200 ml vol. flask and dil. to vol. with H_2O .

(c) *Solution C*.—100 ppm. Pipet 10 ml *Soln A* into 100 ml vol. flask and dil. to vol. with H_2O .

(d) *Solution D*.—200 ppm. Pipet 10 ml *Soln A* into 50 ml vol. flask and dil. to vol. with H_2O .

(e) *Formaldehyde standard solns*.—Prep. 1, 2, and 4 ppm std solns by pipetting 10 ml *Solns B, C, and D*, resp., into 500 g sirup and stirring mechanically 15 min.

Determination

Weigh 20 ± 0.20 g sample into tared 30 ml micro Kjeldahl flask. Add 2 drops antifoaming agent, and connect the West condenser.

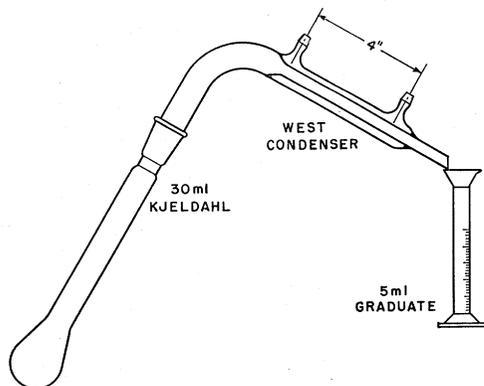


Fig. 1—Distillation apparatus.

Mount app. at oblique angle and heat flask with micro heater (preferably elec.) previously adjusted to distill 3 ml H₂O from sirup in 12–14 min. Collect 3 ml distillate in 5 ml graduate with funnel top. Using transfer pipets, place 1 ml distillate in 13 mm i.d. test tube, and add 1 ml H₂O and 2 ml Nash's reagent. Heat 30 min. in H₂O bath at $37 \pm 1^\circ$ to develop color. Transfer colored soln to 1 cm spectrophotometric cell and measure absorbance at 415 m μ against H₂O.

Blanks

To det. absorbance due to reagents, substitute 1 ml H₂O (from same source as used in detn) for 1 ml sample distillate. Subtract absorbance of blank from that for sample to obtain absorbance due to CH₂O. Or, as simpler procedure, measure absorbance of sample with instrument adjusted to zero absorbance for blank.

Obtain concn of CH₂O in sirup from absorbance, using std curve.

Preparation of Standard Curve

Construct std curve by plotting absorbances obtained for sirups contg 1, 2, and 4 ppm CH₂O against concn of added CH₂O in ppm.

Straight line relationship is obtained for std curve. Project this line to Y axis (absorbance); Y intercept indicates blank for sirup. Since sirup used to construct curve from absorbance values may be atypical, draw and use parallel curve with zero intercept. Correct

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ppm values obtained from this curve for av. sirup blank (ca 0.9 ppm).

Recommendation

It is recommended that the adaptation of the modified Nash method for the determination of formaldehyde in maple sirup, described in this report, be adopted as official, first action.

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- (1) Willits, C. O., Costilow, R. N., and Underwood, J. C., *This Journal*, **46**, 331 (1963).
- (2) Sachs, Rose, *ibid.*, **42**, 741 (1959).

The recommendation of the Associate Referee was approved by the General Referee and by Subcommittee D and was adopted by the Association. See *This Journal*, **47**, 131 (1964).