

## Determination of Malic Acid in Maple Sirup\*

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The 1958 report [*This Journal*, 42, 349 (1959)] gave results of a collaborative study for the determination of malic acid in maple sirup by a modification of the ion exchange procedure of Goodban and Stark. A referee sample of sirup was sent to 16 chemists, all of whom were willing to collaborate; however, only 8 submitted their data in time to be included in the report. These data gave a low coefficient of variation (V, %) for the interlaboratory values and it was recommended that the ion exchange method for determining malic acid in maple sirup be adopted as first action.

Subsequent to the preparation of that report, data were received from 5 of the other collaborators. Since these data included less than the 10 replicates requested and because 2 of these collaborators submitted only single values, a statistical analysis of these additional malic acid values for the 1958 referee sample of sirup is not included in this report. However, the averages of 4 of these collaborators' data were: 0.56%, 0.55%, 0.55%, and 0.58%, which are concordant with the average, ( $\bar{x}$ ), 0.54%, of the collaborators' mean values given in the 1958 report. The data reported by the fifth collaborator did consist of 10 replications and showed good precision, but the

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values were low by 20% and had a mean of only 0.44%. This low value is no doubt due to some constant error; however, since no explanation accompanied the report, these data are not included.

The collaborators questioned the possible effect that the deleading process would have on the malic acid content of maple sirup and whether or not the process would cause interference with the ion exchange method of malic acid analysis. This was an important consideration since nearly all sirups sold by sirup processors are deleading to remove possible lead dissolved from farm sirup-processing equipment. This process consists of adding a soluble phosphate salt to the sirup to precipitate any lead present, the sirup is then heated (digested) to cause growth of the lead phosphate crystals and to speed filtration, which is done by a pressure filter and filter aid.

A number of commercial maple sirup samples, before and after deleading, were obtained from sirup processors to check the effect of this process on the malic acid values as determined by the modified ion exchange method. The samples were taken from tanks containing several thousand gallons of composites of farm-made sirups.

Table 1 shows the effect of preliminary filtration and of deleading on the malic acid content of 5 samples of pure maple sirup. The table gives the number of replications ( $n$ ), the maximum, minimum, and average ( $\bar{x}$ ) values of per cent malic acid, and the standard deviation ( $s$ ) for the " $n$ " values.

The designations of the treatments are: "none" (the sirup is as received from maple farms); "filtered" (the as-received sample has been filtered through a felt filter); and "deleading" (the sirup has been treated according to the process described above). All malic acid values are on a 65.5° Brix basis.

### Results

The average of the " $n$ " determinations for malic acid in the deleading sirups was noticeably lower than those for the other treatments. The differences between the average malic acid values for the sirups before deleading (treatment "none") and for the same sirups after deleading were 0.063%, 0.046%, and 0.059%. While these differences are small, they are nevertheless significant. The lower values for malic acid in the deleading sirup may be due to any of three causes, one of which is the very efficient filtration that is a part of the deleading

**Table 1. Effect of filtering and deleading on the malic acid content of pure maple sirup determined by the ion exchange method of analysis**

Sample	Treatment	$n$	Malic Acid, %		$\bar{x}$	$s$
			Maximum	Minimum		
A	none	5	0.564	0.522	0.555	0.017
	filtered	8	0.608	0.572	0.596	0.012
	deleading	9	0.504	0.470	0.488	0.011
B	none	10	0.592	0.561	0.570	0.031
	filtered	10	0.605	0.498	0.572	0.036
	deleading	10	0.591	0.502	0.524	0.030
C	none	9	0.583	0.535	0.554	0.012
	filtered	9	0.581	0.472	0.551	0.037
	deleading	9	0.568	0.471	0.495	0.038
D	filtered	8	0.560	0.537	0.548	0.007
	deleading	10	0.484	0.450	0.472	0.010
E	deleading	9	0.519	0.494	0.502	0.010

process. This filtration, because of the use of filter aid, would remove the finely suspended sugar sand which might have passed the farmer's felt filter. This was shown not to be the case since refiltration without heat of the felt-filtered samples, using highly retentive filter papers, caused no change in the malic acid values. The second cause could be an adsorption of malate ions on the lead phosphate crystals and removal from solution along with them. The third and most probable cause is related to the precipitation of additional sugar sand (malic acid salts) during each successive heating of maple sirup at 210–220°F. Since heating (hot digestion) is part of the deleading process, some additional malic acid salts are precipitated which are removed by the process filtration.

Not all farm-made sirups are filtered prior to sale and these may contain varying amounts of suspended sugar sand. Therefore it is advisable to filter all sirup samples prior to malic acid analysis. To do this the sirup is heated to 160–170°F and filtered by suction through a Buchner funnel with a dry wool or Orlon felt filter pad.

It is advisable to know the history of the sirup, since those which have been deleading will contain 10% less malic acid than untreated samples.

#### Recommendations

It is recommended<sup>1</sup>—

- (1) That the ion exchange method for

<sup>1</sup> These recommendations were approved by the General Referee and Subcommittee D and were adopted by the Association. See *This Journal*, 43, 138 (1960).

malic acid in maple sirup (a modification of the Goodban and Stark method), adopted as first action in 1958, be adopted as official since the method is specific for malic acid. Collaborative study showed that it yielded concordant results of high precision and that it is not affected by the presence of phosphate ions.

- (2) That collaborative studies be continued to determine whether or not the malic acid content of maple sirup is sufficiently constant to be used as a measure of its purity.

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