

method and its convenience in the assay of commercial almond extracts. It is probable that it could be applied also to the valuation of almond oils.

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THE LEAD VALUE OF MAPLE PRODUCTS.

ALBERT P. SY.

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The addition of lead subacetate or lead acetate to maple products in solution and a determination of the resulting precipitate constitutes one of the most important and most frequently used tests for purity of these products. Lead acetate when added to a pure maple product precipitates the malic and other organic acids, as well as chlorides, sulphates and carbonates, coloring and other organic matters. In cane sugar solutions this precipitation does not take place, and in maple products adulterated with cane sugar the precipitate decreases as the cane sugar increases.

The lead acetate precipitation methods may be divided into four classes: first, those in which the bulk or volume of precipitate is determined—Jones,¹ Hortvet,² Sy;³ second, where the weight of the total precipitate is determined;⁴ third, where the amount of acid radicals combined with the lead in the precipitate is determined, Hill and Mosher;⁵ fourth, in which the amount of lead in the precipitate is determined, Winton,⁶ and the method to be described in the following.

The Lead Value of Maple Products.—Since the preliminary note⁷ on this method, sufficient data have accumulated and satisfactory results obtained on inspection samples of maple products, so that it is thought of interest to analysts to give the method in detail.

By "lead value" is meant the amount of lead precipitated by adding a solution of lead acetate to 100 grams of sugar or 100 cc. of sirup. The preliminary results with this method were obtained by the following procedure: to 50 grams of sugar or 50 cc. of sirup about 200 cc. of water were added, the solution heated to boiling, excess of a saturated solution of lead acetate added, allowed to settle and filtered. The lead was then determined in the precipitate by the usual method, as lead sulphate,

¹ 17th Annual Rpt. Vermont Exp. Sta., p. 454.

² THIS JOURNAL, 26, 1532.

³ *Ibid.*, Sept., 1908, p. 1429.

⁴ Inland Revenue Dept., Ottawa, Can., Bull. 140.

⁵ *Tech. Quarterly*, 1905, 146.

⁶ THIS JOURNAL, 26, 1204.

⁷ *J. Franklin Inst.*, 1906, 71.

and calculated to Pb per 100 grains or 100 cc. No special precautions were observed as to the amount of water used, either for dissolving the sample or washing the precipitate; sometimes the solutions were filtered hot, sometimes cold. However, even under these circumstances, the results obtained gave striking differences between pure and adulterated maple products, as will be seen from the following table:

| Description of sample. | Known to be. | "Lead value." |
|-------------------------------|-----------------------|---------------|
| Carrier sugar..... | Pure maple | 0.331 |
| Ranke sugar..... | Pure maple | 0.455 |
| Franklinville sugar..... | Pure maple | 0.343 |
| Little Valley sugar..... | Pure maple | 0.373 |
| Bryant sugar..... | Pure maple | 0.386 |
| Coöperative No. 1 sugar..... | Adulterated | 0.048 |
| Coöperative No. 2 sugar..... | Adulterated | 0.046 |
| Coöperative No. 3 sugar..... | Pure maple | 0.197 |
| Brown sugar (cane)..... | Cane sugar | 0.052 |
| Granulated sugar (cane)..... | Cane sugar | 0.006 |
| Maple sugar made in lab..... | Pure maple | 0.429 |
| Half maple and half cane..... | Fifty per cent. maple | 0.213 |
| Sirup No. 10202..... | Pure maple | 0.225 |
| " No. 10203..... | Adulterated | 0.044 |
| " No. 10204..... | Adulterated | 0.048 |
| " No. 10201..... | Adulterated | 0.033 |
| " No. 10188..... | Adulterated | 0.083 |
| " No. 10306..... | Pure maple | 0.320 |
| " No. 12130..... | Adulterated | 0.061 |
| " No. 12221..... | Pure maple | 0.208 |
| " No. 12679..... | Adulterated | 0.060 |
| " No. 13305..... | Pure maple | 0.190 |
| " No. 13306..... | Adulterated | 0.005 |

Although these results show that it was possible to differentiate between pure and adulterated samples, it was thought desirable to so modify the method that it would give concordant results on the same sample by the same or by different analysts. Experiments were made on the following points:

(1) *Lead Acetate for Precipitation.*—In all but one of the other methods known to the writer, the basic lead acetate is used. The use of the neutral salt for precipitating the acid radicals present in sugars as impurities was first suggested by Blyth;¹ it is also used in the Hill and Mosher method.² The advantages of the neutral over the basic lead acetate are that the former does not undergo change as quickly as the latter when exposed to the air; its composition does not vary as does that of the basic salt, the formula of the latter varying from $Pb(OH)C_7H_5O_2$ to

¹*Foods, Their Composition and Analysis*, p. 111.

²This method which the authors never published, is mentioned by Professor Woodman in *Tech. Quarterly*, 1905, 146.

$Pb_3O_2(C_2H_3O_2)_2$, this probably being one of the causes of the discrepancies noticed in methods where the lead precipitate is weighed or its volume measured. The neutral salt does not precipitate caramel; it is more soluble in water and therefore more readily washed out of the precipitate than the basic salt. Basic lead acetates precipitate sugar much more readily than the neutral salt.

(2) *Filtering the Lead Acetate Precipitate.*—The precipitate consists principally of lead malate and results as to its solubility are reported in the following section. According to Partheil and Hübner¹ the solubility of lead malate increases very much for temperatures higher than 20°. On this account the solution containing the lead precipitate should be allowed to cool, and not filtered warm, as is done in some methods.

(3) *Washing the Precipitate.*—To determine the solubility of lead malate, $Pb_2C_4H_4O_5 \cdot 3H_2O$, this salt was prepared from pure malic acid and neutral lead acetate. The following results on solubility, both in water and in a 65 per cent. cane sugar sirup, were obtained:

| 100 cc. at 20°. | Dissolved lead malate. | Equivalent to $PbSO_4$. | Equivalent to Pb. |
|-------------------------|------------------------|--------------------------|-------------------|
| Water..... | 0.1547 | 0.1193 | 0.0814 |
| Sirup, 65 per cent..... | 0.1701 | 0.1312 | 0.0895 |

It must be remembered that these results show the solubility of $Pb_2C_4H_4O_5 \cdot 3H_2O$ in pure water and in a 65 per cent. sirup; in the precipitation of free malic acid by lead acetate in maple products there is formed a corresponding quantity of free acetic acid in which lead malate is somewhat soluble. It becomes necessary, therefore, to use the same amount of water for each sample, both for making the solution and for washing the precipitate.

The effect of different amounts of water, used for dissolving the sample, on the lead value are shown in the following table; it also shows that the lead precipitate is not all lead malate, being considerably less soluble than shown for pure lead malate in the above table; the following table also shows that the solubility of the precipitate varies for different samples.

| | Cc. water used for dissolving. | Cc. water used for washing ppt. | Lead per 50 gm. sugar. | "Lead value." |
|------------------------------|--------------------------------|---------------------------------|------------------------|---------------|
| Maple sugar A, 50 grams..... | 150 | 100 | 0.270 | 0.540 |
| " " " " " | 200 | 100 | 0.254 | 0.508 |
| " " " " " | 250 | 100 | 0.234 | 0.468 |
| " " " " " | 300 | 100 | 0.200 | 0.400 |
| Maple sugar B, 50 grams..... | 150 | 100 | 0.385 | 0.770 |
| " " " " " | 200 | 100 | 0.348 | 0.696 |

(4) *Fermented Samples.*—Occasionally it is desirable to analyze a sample that has begun to spoil or ferment. In the early part of the work on this method, the samples were diluted and precipitated without

¹ Arch. Pharm., 241, 413.

being boiled, as was the practice in the other methods. In some cases it was found that fermented, adulterated samples gave high results, producing as much lead precipitate as some pure samples. On the supposition that the products of fermentation, especially carbon dioxide, were the cause of this, subsequent samples were heated to boiling before adding the lead acetate; results after this were in better agreement with facts. The fact that no account is taken of the fermentation products, and that the samples are not boiled, no doubt accounts for irregular results by other methods, where precipitation is made directly. The following table shows the effect on the results by several methods on fresh and fermented samples:

| Adulterated sirups. | Canadian method, Wt. of Pb. ppt. from 5 gm. sample. | Winton "Lead number." ¹ | Volume of Lead ppt. from 5 gm. ² | "Lead value." |
|------------------------|---|--|---|------------------|
| No. 41 fresh..... | 1.90 | .. | 1.7 | 0.102 |
| Fermented 5 days..... | .. | .. | 2.2 | 0.111 |
| Fermented 10 days..... | 5.70 | .. | 3.6 | 0.126 |
| No. 37 fresh..... | 1.38 | 0.26 | 1.3 | .. |
| Fermented 14 days..... | 1.60 | 0.44 | 2.0 | .. |
| | (sirup No. 26) | | | |
| No. 48 fresh..... | (6.60) | .. | .. | 0.020 |
| Fermented 7 days..... | (8.9) | .. | .. | 0.035 |

At this rate of increase in values, some of these samples would soon give data corresponding to those of pure products.

These investigations finally led to adopting the following:

Method for Obtaining "Lead Value."—To 50 cc. of sirup or 50 grams of sugar add 200 cc. water; heat to boiling, add 20 cc. of a 10 per cent. solution of neutral lead acetate; cover, and heat again to boiling. Let stand until cold, filter and wash with water (20°). Transfer filter and precipitate to a 400 cc. beaker, add 15 cc. concentrated nitric and 10 cc. concentrated hydrochloric acids, cover and heat on an asbestos plate, or ordinary hot plate; when the filter is disintegrated, remove the beaker from the plate, cool and add 10 cc. of concentrated sulphuric acid; heat to fumes to expel all nitric acid. If blackening does not clear in a few minutes, carefully add 5 cc. more of nitric acid after cooling a little and again heat to sulphuric acid fumes. Now cool, add 50 cc. of water, cool and add 100 cc. of alcohol; let stand six hours or over night. Filter and determine the lead sulphate, preferably by using a tared asbestos-packed Gooch, wash with alcohol, dry and ignite at a low red heat. The weight of $PbSO_4$ multiplied by 1.366 (2×0.683) gives the weight of lead precipitated by 100 cc. or 100 grams of sample. The *lead value* of a pure product should not be less than 0.250, and is usually over 0.300. The

¹ THIS JOURNAL, 28, 1204.

² Sy, *Ibid.*, Sept., 1908.

following *lead values* were obtained on samples of maple sugar known to be pure.

| Sample No. | Lead value. |
|------------|--------------|
| 1..... | 0.580 |
| 2..... | 0.384 |
| 3..... | 0.762 |
| 4..... | 0.468 |
| 5..... | 0.470 |
| 6..... | 0.376 (min.) |
| 7..... | 0.648 |
| 8..... | 1.024 (max.) |
| 9..... | 0.708 |
| 10..... | 0.498 |

These sugars were quite dry, the average moisture content being only 3.58 per cent. The following products were made by the writer from sap; they gave "lead values" as shown:

| | "Lead value." |
|-----------------------------------|---------------|
| Sugar from sap of hard maple..... | 0.429 |
| Sirup from sap of hard maple..... | 0.482 |
| Sirup from sap of soft maple..... | 0.438 |

A complete chemical analysis of 31 samples of maple sirup bought in the open market showed that 13 samples gave data for pure maple products, while 18 showed adulteration.

13 Commercial Sirups, Pure.

| | |
|---------------------------|-------|
| Minimum "Lead Value"..... | 0.260 |
| Maximum " "..... | 1.100 |
| Average " "..... | 0.577 |

18 Commercial Sirups, Adulterated.

| | |
|---------------------------|-------|
| Minimum "Lead Value"..... | 0.024 |
| Maximum " "..... | 0.165 |
| Average " "..... | 0.076 |

While there is considerable variation in the *lead values* of pure products, due to locality, method of manufacture, and handling, yet there is such a large difference between pure and adulterated products that there is no chance for a "doubtful" interpretation. Experience with this method has given satisfactory results, in no case "doubtful," and in all cases concordant with the results of a complete chemical analysis. The advantages of this method are:

1. The use of neutral lead acetate instead of the basic salt.
2. A reduction of the analytical error to a minimum, the gravimetric result being multiplied by only 2, 50 cc. or grams of sample being taken.
3. The method is gravimetric instead of volumetric.
4. Account is taken of the solubility of the lead precipitate and the amount of water to be used for diluting and washing is specified.

5. Error due to products of fermentation in old or spoiled samples is avoided by boiling before precipitating.

6. With the average moisture content of 10-12 per cent. for sugars, and 33-35 per cent. for sirups, the lead values are in each case on about the same amount of dry substance. It might be a good plan to make a moisture determination on each sample and calculate the *lead values* to "dry substance."

BUFFALO LABORATORY.

TYPEWRITER CARBON PAPERS.

By A. M. DOYLE.

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Typewriter carbon papers are much used in the departments of the government and for this reason an investigation into their qualities was made by the Contracts Laboratory of the Bureau of Chemistry. The paper foundation was tested for tensile strength, length and width; stretch under strain, both length and width; weight, inked and clean; thickness of inked paper; kind of pulp used and degree of beat. The ink, as distinct from the paper, was separated into its constituents of oil or wax, dye and pigments, and moisture and ash were determined. The written matter was rated on a scale of ten and was also subjected to sunlight and solubility tests.

Of the twenty-eight samples examined, five were copy papers and the others record. Copy papers included black, blue, purple and green, all of standard weight; record papers consisted of black, blue and purple; full-inked and semi-inked; standard weight, light weight and feather weight. Tables I, II and III represent the three classes of results. In Table I the physical tests have been arranged according to the weight of the paper, as described by the manufacturer, while in Tables II and III they are divided first into record and copy; then according to color—black, blue and purple, in the order named; and finally, within each group according to weight, from standard to feather weight.

Discussion of Results.

A comparison of the figures for the weight of the paper per square centimeter indicates that No. 2292 should be classed with light weight papers, Nos. 2290, 2293, 2294, 2301 and 2302 with standard weight, and Nos. 2300, 2381 and 2382 with the light weight; but otherwise these papers, grouped as indicated by the manufacturers on the label of the package, follow closely certain weight limits. Inked papers average less than 2 mg. per square centimeter for feather weight, from 2.2-2.4 mg. for light weight and a little less than 3 mg. for standard weight. The cleaned papers, free of ink, weigh less than 1 mg. for feather weight,