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## THE CHEMICAL ANALYSIS OF THE APPLE AND SOME OF ITS PRODUCTS.

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IN the Fall of 1899, the writer was called upon, by the Pennsylvania Department of Agriculture, to make a chemical study of the apple and its various products. The results of this investigation have been embodied in Bulletin No. 58 of the Department's publications. For the complete tabulation of all the analyses made in connection with this work, together with the discussion of the results, reference is made to the above bulletin. A brief summary of the results is presented,<sup>1</sup> however, in this connection, preliminary to a more complete description of the methods of analysis employed. The latter, in fact, is the main purpose of the present paper, inasmuch as no description of methods was included in the original bulletin. The methods herein described, while designed especially for the examination of apples and apple products, have been used successfully in a few other instances, and the writer believes that, with a few modifications perhaps, they could be employed in the analysis of any of our common fruits.

<sup>1</sup> This is done with the kind permission of Prof. John Hamilton, secretary of the Pennsylvania Department of Agriculture.

## COMPOSITION OF APPLES.

	Water.	Reducing sugars.	Sucrose.	Starch.	Ash.	Acid as malic.	Marc.
Unripe apples (2 analyses)	80.67	6.43	2.84	3.92	0.27	1.14	.. .
Summer apples (6 analyses)	85.00	7.10	3.36	1.04 <sup>1</sup>	0.28	0.68	....
Winter apples (21 analyses)	83.16	8.16	4.16	....	0.26	0.59	1.85 <sup>2</sup>

The above analyses represent simply the composition of the edible or fleshy portion of the apple. These figures, together with other determinations made upon the combined pulp and marc from different varieties of fruit, have furnished the following table :

## APPROXIMATE AVERAGE COMPOSITION OF THE FLESH OF THE RIPE APPLE.

Ingredient.	Per cent.
<i>Inorganic.</i>	
Water .....	84.00
Ash .....	0.30
<i>Organic.</i>	
Sugars :	
Reducing sugars .....	8.00
Sucrose .....	4.00
Starch .....	0.00
Marc :	
Cellulose .....	0.90
Pentosans .....	0.50
Lignin .....	0.40
Organic acids :	
Free acid as malic .....	0.60
Combined acid as malic .....	0.20
Pectin bodies .....	0.40
Crude fat .....	0.30
Protein .....	0.10
Undetermined (tannin, etc.) .....	0.30
	100.00

## THE CHEMICAL COMPOSITION OF APPLE ASH.

Ingredient.	Per cent.
Potash .....	55.94
Soda .....	0.31
Lime .....	4.43
Magnesia .....	3.78
Ferric oxide .....	0.95
Alumina .....	0.80
Chlorine .....	0.39
Silica .....	0.40
Sulphur trioxide .....	2.66
Phosphorus pentoxide .....	8.64
Carbon dioxide .....	21.60
	99.90
Deduct oxygen equivalent to chlorine .....	0.09
Total .....	99.81

<sup>1</sup> One analysis.<sup>2</sup> Eight analyses.

The above analysis was made upon the combined ashes from many different varieties of apples, the flesh of the fruit being the only part taken for incineration.

COMPOSITION OF APPLE JUICES.

	Specific gravity.	Solids.	Reducing sugars.	Sucrose.	Free acid as malic.	Ash.	Pectin.	Albuminoids.	Rotation Ventzke 400 mm. tube.
Juice from summer apples (5 analyses)....	1.0502	12.29	6.76	3.23	0.72	0.29	0.12 <sup>1</sup>	0.03 <sup>1</sup>	— 26.67
Juice from winter apples (4 analyses)....	1.0569	13.96	8.57	3.40	0.43	0.27	0.12 <sup>2</sup>	0.02 <sup>2</sup>	— 45.15

The composition of other fruit juices, from analyses made by the writer, is given for purposes of comparison.

Kind of juice.	Specific gravity.	Solids.	Reducing sugars.	Sucrose.	Free acid as malic.	Ash.	Pectin.	Albuminoids.	Rotation Ventzke 400 mm. tube.
Strawberry ....	1.0420	9.64	5.90	0.89	1.28	0.61	0.63	0.38	— 5.28
Red raspberry.	1.0463	11.01	5.13	2.31	1.44	0.60	0.88	0.75	+ 7.32
Black raspberry	1.0567	13.65	9.52	...	1.85	0.60	0.72	0.38	- 25.20
Black cherry. very sweet...	1.1034	24.30	16.35	...	1.47	0.79	0.30	0.63	— 29.80
Red cherry, sour	1.0461	11.22	7.33	...	1.32	0.57	0.25	0.56	— 12.96

Closely related to apple juice is what is known as "second pressings", used so extensively at present for jelly-making and vinegar stock. It is made simply by wetting apple pomace with water and repressing.

COMPOSITION OF SECOND PRESSINGS.

Specific gravity.....	1.0376
Rotation Ventzke 400 mm. tube .....	— 31.94
Per cent.	
Solids .....	9.14
Reducing sugars.....	6.87
Sucrose .....	1.49
Ash .....	0.20
Undetermined (pectin, malic acid, etc.).....	0.58

The composition of completely fermented cider and vinegar is

<sup>1</sup> Four analyses.

<sup>2</sup> One analysis.

shown by the following figures, compiled from analyses made upon samples of known purity.

## COMPOSITION OF CIDER AND CIDER VINEGAR.

	Specific gravity.	Solids.	Ash.	Reducing sugars.	Acetic acid.	Malic acid.	Alcohol.	Pectin.	Albuminoids.	Rotation 400 mm. tube.
Cider (6 analyses) . . . . .	1.0006	2.34	0.29	0.32	0.61	0.25	5.51	0.04	0.02	— 2.34
Vinegar (4 analyses) . . . . .	1.0184	2.00	0.44	0.52 <sup>1</sup>	6.19	0.14	none	0.17	0.01	— 2.01 <sup>1</sup>

## COMPOSITION OF MISCELLANEOUS APPLE PRODUCTS.

	Moisture.	Reducing sugars.	Sucrose.	Ash.	Free acid as malic.	Albuminoids.	Pectin.	Marc.
Evaporated apples (2 anal.)	27.61	32.80	19.02	1.10	4.08	0.87	...	5.53
Apple butter (1 anal.) . . . . .	52.58	37.20	1.14	0.97	2.52	0.25	2.15	1.14
Cider jelly (1 anal.) . . . . .	44.53	49.50	2.18	1.39	3.61	...	1.60	none
Apple pomace (1 anal.) . . . . .	70.76	8.09	2.40	0.49	...	1.25	...	...

## METHODS OF ANALYSIS.

The methods employed in making the determinations contained in the preceding tables are in many cases simply the ordinary processes described in most books on commercial or agricultural analysis. The methods<sup>2</sup> of the official agricultural chemists were employed as far as possible. Only such departures, from the usual methods as it was found advisable to make, will be described.

<sup>1</sup> The writer desires at this point to call attention to a statement made by Doolittle and Hess in a recent number of this Journal (22, 219). It is said that "the solids of pure cider vinegar give no rotation with the polariscope, and little or no reducing action on Fehling's solution after the customary clarification with lead acetate." This is certainly a mistake. Of the many samples of pure cider vinegars examined by the writer at the Pennsylvania Experiment Station during the past four years, not one has failed to give a decided rotation to the left, when examined in the 400 mm. tube of the polariscope; likewise all have appreciably reduced Fehling's solution, whether previously clarified with animal charcoal or lead subacetate.

An unpublished experiment conducted by the writer at this Experiment Station shows that levulose is the only sugar present in properly fermented cider vinegar, the sucrose and dextrose having both disappeared in the course of the alcoholic fermentation. The acetic fermentation, which sets in before the last traces of levulose have been destroyed, seems to prevent the complete removal of the sugar by alcoholic fermentation, and the percentage of levulose continues, thereafter, nearly constant.

<sup>2</sup> Bulletin No. 46, revised edition, U. S. Department of Agriculture, Division of Chemistry.

*Determination of Moisture and Solids.*—This, apparently the most simple of all analytical processes, was found at the outset of the work to offer the greatest difficulties. The methods ordinarily prescribed recommend that the material be dried at 100° C., or even higher, until a constancy in weight is attained. In making determinations by any of these methods the writer has found it impossible to obtain any such constancy in weight; the residue would continue to lose, until its percentage became finally much less than the sum of the percentages of the different solid constituents. A decomposition of some kind was indicated and the unreliability of drying at a high temperature clearly shown.

The difficulty experienced is undoubtedly due to a breaking-up of the sugars of the fruit, principally levulose. This has been found true in the case of other bodies containing levulose, as has been shown by Carr<sup>1</sup> and Sanborn in their experiments upon "the dehydration of viscous organic liquids." These writers, after making "upward of 5,000 separate determinations, ranging over all the better-known methods and covering such materials as pure sugar and levulose solutions, honey, molasses, molasses "flowers," sorghum, beet and maize juices, etc., etc," "conclude that it is impossible to dehydrate, quantitatively, solutions containing levulose without the occurrence of decomposition, if the temperature be 100°, the environment air, and the pressure equal to that of the atmosphere." The method finally adopted by Carr and Sanborn, to prevent this decomposition of levulose during dehydration, consists in drying the material on pumice stone in flat-bottomed dishes, at 70° C. and a vacuum of 25 inches.

The writer has been unable to find any work relating to the dehydration of fruits, or the products therefrom, *in vacuo*, but the same necessity would exist for such dehydration as with other levulose-containing materials, the presence of levulose in most fruits being sufficiently indicated by the marked levorotation, which the clarified juices give to the plane of polarized light.

In the various analyses, previously recorded, the writer effected dehydration in most cases by drying the material at 70° C. in a vacuum as recommended by Carr and Sanborn, using, however, perforated brass or copper tubes filled with asbestos for absorbing the liquid, instead of pumice stone in dishes as in the method of the above authorities.

<sup>1</sup> Bulletin 47, U. S. Department of Agriculture, Division of Chemistry, p. 134. See also this Journal, p. 17, (23) of proceedings.

The perforated tubes employed measured 9 cm. long by 2 cm. in diameter. In the case of liquids, fruit juices, cider, vinegar, etc., the tubes are nearly filled with freshly ignited asbestos,—the latter being tightly packed with a rod against the sides in the upper half of the tube, thus leaving a central cavity extending part way into the asbestos. Each tube thus prepared is placed into a glass-stoppered weighing-bottle of sufficient size, and the whole weighed. About 5 cc. of the liquid to be analyzed are then delivered from a pipette into the cavity in the asbestos, the object of the cavity being to secure a rapid absorption, and even distribution of the liquid through the asbestos. The weighing-bottle is then immediately stoppered and reweighed, the increase in weight being the amount of substance taken. After removing the stopper, the bottle, together with the inner tube, is conveyed to a vacuum drying apparatus, where it is dried in an upright position, at a constant temperature of 70° C. During the first few hours of the drying, a slight current of air is drawn through the vacuum compartment, in order to remove the large excess of moisture at first given off. In the last stages of the drying the air current is decreased, and the vacuum kept at about 25 inches. Eight to ten hours are generally sufficient to secure complete dehydration; at the end of this time the weighing-bottle is removed from the oven, placed in a desiccator and, when cold, re-stoppered and weighed.

The bottles are then replaced in the oven and dried for a second period of a few hours to ascertain if constant weight has been secured. The first drying, however, has generally been found sufficient. A longer drying of several days has been found to produce no change in weight, when once dehydration was secured, showing that no decomposition of levulose is produced.

In determining moisture or solids in apples and other fruits the same method is employed, with the exception that the perforated tubes are filled only about one-fourth with asbestos. The grated pulp of the fruit to be analyzed is well sampled and mixed, and a small portion of 5 to 10 grams transferred through a short-necked funnel into the tube, when the bottle is restoppered and weighed. The drying is conducted as previously described; the slight amount of liquid, which sometimes oozes out into the weighing-bottle, does no harm.

In drying fruit products of much consistency, such as jelly, it

is best to dissolve a weighed amount of the material in water, before adding to the asbestos, in order to secure a better absorption. The same necessity of drying *in vacuo* at low temperature exists with evaporated fruit products, such as dried apples. In such cases the use of the inner perforated tube is dispensed with altogether. The finely cut material is weighed out directly in the weighing-bottle and the process conducted as already described.

It might be supposed that, with fermented ciders and vinegars, owing to the disappearance of levulose during fermentation, a determination of the solids by the vacuum method at 70° C. and by drying at 100° C. in the usual way would show no decided difference. Such, however, is not the case with completely fermented ciders and vinegars; a constancy in weight is attained by drying at 100° C., but the percentage of solids is invariably less than that obtained by the vacuum method. The following is an example of this; the experiment was performed upon a pure cider vinegar.

	Per cent.	
	I.	II.
Solids by drying at 100° C., two days.....	1.48	1.50
Solids by drying at 100° C., three days .....	1.47	1.49
Solids by drying <i>in vacuo</i> at 70° C., two days ....	3.29	3.39
Solids by drying <i>in vacuo</i> at 70° C., three days....	3.28	3.39

The percentage of reducing sugar was only 0.16 per cent. so that decomposition of levulose does not explain the discrepancy. It may be due partly to the volatilization of glycerol, which is formed during the alcoholic fermentation. Indications, however, point to the presence of other substances, besides levulose, in fruit products, which are decomposable at 100° C.

*The Calculation of Solids in Fruit Juices from the Specific Gravity.*—The application of this principle, by means of the Brix spindle, in the analysis of juices from the beet and sugar-cane is too well known to require mentioning; it has also been applied by Kulisch<sup>1</sup> in the analysis of apple juices, the degrees Brix or Balling, corresponding to the specific gravity of the juice at 17.5° C., being the percentage of solids. The writer has compared this method of estimating solids with the actual determination, and the agreement has usually been very satisfactory. Instead of using degrees Brix the solids of juices may be calculated from the formula  $245(S-1)$ ,  $S$  being the specific gravity of the

<sup>1</sup> "Landwirthschaftliche Jahrbücher. 19. 110 (1890).

juice at 17.5° C. Such methods of estimating solids are, of course, only applicable in the case of fresh juices, before the beginning of the alcoholic fermentation. The following table gives the percentage of solids, as estimated and actually determined in a number of different juices.

No.	Kind of juice.	Specific gravity 17.5° C.	Degrees Brix.	Solids by formula	Actual solids at
				245 (S-I). Per cent.	70° C. <i>in vacuo</i> . Per cent.
1	Apple juice (second pressing)	1.0376	9.39	9.21	9.14
2	" "	1.0474	11.73	11.61	11.36
3	" "	1.0481	11.90	11.78	11.51
4	" "	1.0484	11.97	11.86	11.87
5	" "	1.0488	12.07	11.96	11.71
6	" "	1.0517	12.75	12.67	12.78
7	" "	1.0525	12.94	12.86	12.77
8	" "	1.0539	13.26	13.21	13.29
9	" "	1.0559	13.73	13.70	13.94
10	" "	1.0560	13.76	13.72	12.83
11	" "	1.0568	13.94	13.92	13.84
12	" "	1.0613	14.99	15.01	14.90
13	" "	1.0722	17.50	17.69	16.82
14	Strawberry juice.....	1.0420	10.44	10.29	9.64
15	Red raspberry juice.....	1.0463	11.47	11.34	11.01
16	Black raspberry juice.....	1.0567	13.92	13.89	13.65
17	Red cherry juice.....	1.0461	11.42	11.29	11.22
18	Black cherry juice.....	1.1034	24.42	25.33	24.30
	Average.....		13.42	13.41	13.16

The formula, as a rule, gives results slightly closer to the actual percentage of solids, except in case of juices of very high gravity, as No. 18 of the preceding table. The difference between actual and calculated results rarely exceeds 0.2 or 0.3 of a per cent.; there is occasionally, however, a notable discrepancy as in the case of apple juices Nos. 10 and 13. Calculating the solids from the gravity of a juice is sufficiently accurate for many purposes; such an estimation is preferable, in any case, to the old method of determining solids by drying at 100° C.

*Ash.*—This was determined according to the official method, about 20 grams of material being taken for analysis. In incinerating large quantities of material, to obtain ash for the ash analysis, it is necessary to exhaust the charred mass first with water. The insoluble residue is collected on a filter, burned, and this ash added to the residue left on evaporating the aqueous extract. The whole is then heated to a low redness till the ash is white.



*Reducing Sugar.*—This was calculated, in the various analyses given, simply as invert sugar. Strictly speaking this is not correct, for the dextrose and levulose of fruit juices are present in, by no means, equal proportions, as in apple juices where the percentage of levulose is nearly double that of dextrose. Nevertheless, when these sugars are not separately determined, it has seemed to the writer more accurate to consider the reducing sugar as invert rather than dextrose or levulose alone. The invert sugar is calculated from the weight of reduced copper according to the tables of Meissl and Wein; such small amounts of sucrose, as are present in fruit juices, do not affect the accuracy of the determination.

In the determination of reducing sugar in fruit juices, 20 cc. of the filtered juice are measured out into a 500 cc. flask, about 300 cc. of water are added, and, after neutralizing carefully with sodium hydroxide using phenolphthalein, the volume is completed to the mark. Twenty-five cc. of this solution (1 cc. of original liquid) are taken for the copper reduction. The reduced cuprous oxide is filtered in asbestos tubes and, after drying, reduced in a current of hydrogen, and the weight of copper determined. In case of partly fermented juices larger amounts of liquid can be used for dilution. With completely fermented ciders and vinegars, which contain but very little sugar, the liquid after neutralizing needs little if any dilution. In calculating the percentage of reducing sugar, it is, of course, necessary to take into account the specific gravity of the liquid analyzed.

In determining reducing sugar in apples and other whole fruits the following method was adopted: 100 grams of the grated pulp are washed on a muslin filter in a large funnel, with repeated quantities of cold water, the filter being squeezed after each addition of water to hasten the removal of the sugar. The filtrate is caught in a 2-liter flask, and the washing continued until the liquid is nearly up to the mark. After completing the volume, the flask is shaken, and 200 cc. (10 grams of fruit) of the filtered solution are transferred to a 250 cc. flask; this solution is neutralized with soda as before and the volume made up to 250 cc. from which 25 cc. (1 gram of fruit) are taken for the copper reduction.

The same method is used with evaporated fruit products, as with whole fruit, except that a smaller amount of material is taken for analysis. Twenty-five grams of the finely cut material

are treated with 200 cc. of water for several hours in a large beaker until the substance has swollen to a soft pulp. The material is then brought upon the muslin filter, and washed to 2 liters as before.

With fruit jellies, 10 grams of the material are dissolved in water, neutralized, and made to 1 liter.

*Sucrose*.—This was determined in the majority of cases from the increase in the copper-reducing power, after inversion with hydrochloric acid. In making the analysis the method of procedure is as follows :

The same amount of solution (juice, aqueous extract of fruit, etc.) is taken as in the determination of the reducing sugars ; one-tenth its volume of concentrated hydrochloric acid is added, and the flask placed in a water-bath at 70° C. The contents of the flask, after reaching a temperature of 67°–70° C., are kept within this limit for exactly five minutes when the solution is cooled, neutralized, and made up to the same volume as in determining reducing sugars. Twenty-five cc. of this solution are taken for the copper reduction, the calculation being made to invert sugar as before. The difference between the percentage of invert sugar before and after inversion, multiplied by 0.95, will give the percentage of sucrose.

Sucrose has also been determined in fruit juices by means of the polariscope. 52.096 grams of juice are made to 100 cc. Fifty cc. of this solution are clarified with 5 cc. of lead subacetate, and the reading taken in the 200 mm. tube at about 20° C. The remaining 50 cc. are inverted with 5 cc. of concentrated hydrochloric acid, as described above, cooled rapidly and diluted to 100 cc. The reading is taken in the 200 mm. tube, at the same temperature as the first solution, clarifying, if necessary, with animal charcoal. The first, or direct reading increased by

0.1 and divided by 2 =  $a$ , the invert reading =  $b$ ,  $100 \frac{(a - b - t)}{142.4 - \frac{t}{2}} =$

percentage of sucrose,  $t$  being the temperature of the solutions at time of reading.

*Levulose and Dextrose*.—In many cases a separate determination of these sugars has been made. Several courses of procedure have been followed according to conditions.

In the presence of both dextrose and sucrose, the levulose was determined by the difference in polarization of the solutions at widely separated temperatures.<sup>1</sup> With juices, etc., the pure liquid is first clarified by means of animal charcoal, and the polariscope reading taken in a 200 mm. tube, first at about 15° C. ( $v$ ) and then at about 85° C. ( $v'$ ). The tube used should be provided with a metal jacket, through which water of the desired temperature is allowed to circulate. The percentage of levulose  $l$  is calculated from the formula

$$l = \frac{v - v'}{G(t \times -0.0323)};$$

$v - v'$  = the algebraic difference between the two readings and, if levulose is present, will always be a minus quantity, owing to the fact that the rotation of levulose solutions when heated is deflected towards the right.

$G$  = the specific gravity of the liquid.

$t$  = the difference in temperature between the readings.

The value  $-0.0323$ <sup>2</sup> represents the deviation (Ventzke), for each degree centigrade difference in temperature, produced by 1 gram of levulose in 100 cc.

With fruit jellies, etc., a definite weight of the material (20 to 50 grams) is dissolved in 100 cc. of water and the solution, after clarifying, polarized at different temperatures as before. In this case the percentage of levulose, or  $l$ , =  $\frac{100(v - v')}{W(t \times -0.0323)}$ ,

$W$  being the grams of substance in 100 cc.

Knowing the percentage of levulose, and the copper-reducing power of the solution, the percentage of dextrose admits of calculation. Volumetric determinations by Soxhlet upon solutions of invert sugar have shown that for the same volume of Fehling's solution reduced, 1 part of levulose corresponds to 0.924 part of dextrose. Gravimetric determinations made by the writer upon pure solutions of invert sugar show a ratio somewhat lower than this, as the following table shows. The gravimetric method of Allihn was followed :

<sup>1</sup> See Wiley's "Agricultural Analysis," Vol. III, pp. 267-273.

<sup>2</sup> This figure was deduced from the general formula of Jungfleisch and Grimbert which gives the specific rotatory power of levulose for any temperature or concentration. The equation is  $[\alpha]_D = -[101.38 - 0.56t + 0.108(c - 10)]$ , in which  $t$  is the temperature of the solution and  $c$  the grams of levulose in 100 cc. See Landolt: "Das optische Drehungsvermögen, 2 Auflage, p. 524.

<sup>1</sup> Weight of sucrose taken. Gram.	<sup>2</sup> Weight of invert sugar therefrom. Gram.	<sup>3</sup> Weight of copper. Gram.	<sup>4</sup> Corresponding weight of dextrose (Allihn's table). Gram.	<sup>5</sup> Ratio of dextrose to invert sugar.
0.2300	0.2421	0.4315	0.2313	1.047
0.1533	0.1614	0.2950	0.1538	1.049
0.1150	0.1211	0.2230	0.1148	1.055
0.0575	0.0605	0.1120	0.0570	1.061

It is seen that the ratio of dextrose to invert sugar increases slightly as the concentration of the solution diminishes; the variation, however, is not sufficient to make any appreciable difference in the calculations. Taking the average of the above determinations, 1 part of dextrose could correspond to 1.053 parts of invert sugar for the same weight of copper reduced. Since invert sugar is made up of equal parts of dextrose and levulose, 1 part of dextrose would correspond to 1.106 parts of levulose for the same amount of reduced copper, or 1 part of levulose would equal 0.90 part of dextrose.

Knowing the percentage of levulose the percentage of dextrose ( $d$ ) may be found from the formula

$$d = D - 0.9l,$$

where  $D$  = percentage of reducing sugar as dextrose (Allihn's method), and  $l$  = percentage of levulose as found by polarization.

In the absence of sucrose the writer has calculated the percentages of dextrose and levulose from the rotation and copper-reducing power. The factors necessary to know are  $P$ , the specific rotatory power, and  $D$ , the percentage of reducing sugars as dextrose.

To determine the specific rotatory power it is necessary to know the rotation of a known amount of the sample in a tube of definite length. For this purpose in the case of fruit juices, etc., it is best to read the clarified liquid directly in a 400 mm. tube; with more concentrated products 20 grams of substance are dissolved in water and made to 100 cc. For clarification the writer has used animal charcoal in the majority of cases, though lead subacetate answers equally well and in some cases is found necessary. But very little difference has been noticed in the rotation by these two methods of clarification, provided excess of lead solution is avoided. In clarifying with lead the polariscopic reading must, of course, be corrected for the dilution. In case of a sugar polariscope with a Ventzke scale, the reading must be corrected to angular degrees by multiplying by the factor 0.3468.

The formula for calculating the specific rotatory power in the case of liquids is

$$P(20^{\circ} \text{ C.}) = \frac{0.3468 v}{4G}$$

$v$  = polariscopic reading, Ventzke scale, in 400 mm. tube at  $20^{\circ} \text{ C.}$

$G$  = the specific gravity of the solution.

$4$  = the length of the tube in decimeters.

If the material is weighed out and made up to 100 cc. by dilution with water, the formula becomes

$$P(20^{\circ} \text{ C.}) = \frac{0.3468 v}{4W} \times 100,$$

$W$  being the grams of substance taken.

The specific rotatory power of a solution being dependent upon the percentages and specific rotatory powers of its ingredients, we would have for solutions containing dextrose and levulose alone, the formula

$$53d - 90l = 100P.$$

$d$  and  $l$  are the percentages of dextrose and levulose, and 53 and  $-90$  are their respective specific rotatory powers, at  $20^{\circ} \text{ C.}$ , the concentration for each sugar not exceeding 10 per cent.

Substituting the formula  $d = D - 0.9l$  in the previous equation we obtain :

$$l = \frac{53D - 100P}{138}$$

As far as the writer has been able to compare them, these two methods of determining levulose have shown a very close agreement, as the following example, in the case of a partly fermented cider, will illustrate.

Specific gravity of cider = 1.0067 =  $G$ .

Rotation of cider at  $15^{\circ} \text{ C.}$ , 200 mm. tube, Ventzke scale =  $-10.1^{\circ} = v$ .

Rotation of cider at  $85^{\circ} \text{ C.}$ , 200 mm. tube, Ventzke scale =  $-5.5^{\circ} = v'$ .

The difference in temperature of the two readings =  $70 = t$ .

Substituting these values in the formula

$$l = \frac{v - v'}{G(t \times -0.0323)},$$

we find  $l = 2.04$  per cent.

The percentage of reducing sugars as dextrose was  $2.26 = D$ .  
 The rotation of the cider at  $20^{\circ} \text{C}$ ., 400 mm. tube, Ventzke scale,  
 $\alpha = 18.8^{\circ} = \tau$ .

The specific rotatory power of the cider from the formula

$$P(20^{\circ} \text{C.}) = \frac{0.3468 \tau}{4G}$$

is therefore  $-1.62 = P$ .

Substituting the above values for  $D$  and  $P$  in the equation

$$l = \frac{53D - 100P}{138}$$

we find  $l = 2.04$  per cent., the same as before.

The percentage of dextrose in the cider, calculated from the formula  $d = D - 0.9l$ , is 0.42 per cent.

*Starch.*—This substance has been found in all green pomaceous fruits; it no doubt occurs in other classes of fruits in the early periods of their growth, though this is a point which has not been as yet fully investigated. In the ripening of fruits the starch is gradually converted into sugar, and this process continues even after picking until no vestige of starch remains. A determination of starch is, of course, only necessary when its presence is indicated by the iodine reaction.

The estimation of starch in fruits, depending as it does upon its conversion into dextrose, offers special difficulties, owing to the large amount of reducing sugars present, and the first step in any process of analysis must consist in the removal of all the sugars before the conversion of the starch is attempted. The process usually recommended consists in washing a weighed amount of the pulp either directly upon a filter, or by decantation upon the same, until all the sugars are removed. This method of procedure has been found by the writer to be extremely tedious, owing to the large amount of washing required and to the tendency which the pectinous and gummy matters of the fruit have of clogging the filter.

The following process adopted by the writer avoids in great measure this difficulty and, as it is carried out directly in connection with the sugar determination, effects a considerable saving of time.

100 grams of the finely-grated pulp are washed upon a muslin filter with repeated quantities of cold water, until the filtrate

amounts to 2 liters; the muslin is squeezed after each addition of water, as already described under the determination of sugar. In this way practically all of the starch is washed out of the pulp. The filtrate, after being well mixed, is transferred to a tall beaker or cylinder, where it is covered and allowed to stand in a cool place over night. The finely suspended particles of starch will have completely settled by this time to the bottom of the vessel, forming a compact mass. The liquid above the starch is then removed by means of a siphon or decantation down to within a short distance of the precipitate; this solution may be used for the determination of sugars and malic acid.

The precipitate of starch is transferred with small quantities of cold water to a hardened filter-paper and washed to remove the last traces of sugar: 100 cc. of water are usually sufficient for this. The starch thus prepared consists of a white crumbly mass, but is not perfectly pure, owing to the presence of some cellular and albuminoid matter. The starch might be determined at this stage with sufficient accuracy by direct inversion with hydrochloric acid as in the Sachsse method, but the writer has preferred to use the more exact process of first hydrolyzing with diastase.

A starch determination by means of the diastase method should also be made upon the residue left on the muslin filter after the washing, in case the latter should show any reaction with iodine. The writer has never found the residues to yield more than 0.1 or 0.2 per cent. of starch upon the original pulp, so that the determination is rarely necessary if the washing has been properly performed.

The official diastase method<sup>1</sup> was followed throughout, except as regards the neutralization after the inversion with hydrochloric acid. The writer has always preferred a 10 per cent. solution of sodium hydroxide, using phenolphthalein, instead of sodium carbonate as prescribed in the official method; the troublesome frothing incident to the use of the latter substance is thus avoided.

*Marc.*—This represents that part of the fruit, which is insoluble in water. It is best found in connection with the sugar determination; the residue left upon the muslin filter after the

<sup>1</sup> Bulletin No. 46, revised edition, U. S. Department of Agriculture, Division of Chemistry.

washing, is transferred to a dish and dried to a constant weight at 100° C. With the exception of a trace of ash and albuminoid matter, the marc of apples was found to consist almost wholly of cellulose, lignin, and pentosans.

In case the percentages of the different marc constituents are desired, the pentosans are best determined by distilling a weighed amount of the dry marc with successive quantities of 12 per cent. hydrochloric acid, and precipitating the furfural in the distillate by means of phloroglucin.<sup>1</sup> The cellulose is separated from the other marc constituents by the chlorination process of Cross and Bevan.<sup>2</sup> The lignin<sup>3</sup> bodies are estimated by the difference between the cellulose and pentosans and total marc, after correcting for the slight quantities of ash and albuminoid matter.

*Malic and Acetic Acids.*—No attempt was made by the writer to separate the various fruit acids in the analyses previously tabulated. The free acid was determined in every case by titration with decinormal soda, and calculated to malic acid. Besides the free organic acid, a considerable amount of the fruit acids exists in a combined form; the amount of this can be estimated from the alkalinity of the ash. In case of ciders and vinegars, where acetic acid is present, the latter is first removed by steam distillation, and determined by titration with decinormal soda solution; the distillation should be continued until 50 cc. of the distillate shows a neutral reaction. The solution left in the flask after the steam distillation is then titrated and calculated to malic acid as before.

*Pectin.*—This was determined by evaporating a definite amount of the fruit extract, juice, etc., to a small volume and precipitating with a large excess of 95 per cent. alcohol. After standing over night the precipitate was collected in a Gooch crucible, and washed with alcohol to remove all sugar. The precipitate was then dried at 100° C. to constant weight, and after incineration the weight of ash deducted and the loss estimated as pectin.

Other ingredients given in the preceding tables, such as fat, protein, etc., were determined according to the official methods of the agricultural chemists, and require no special description.

<sup>1</sup> For full description of the phloroglucin method for pentosans, see Bulletin No. 46, revised edition, U. S. Department of Agriculture, Division of Chemistry, p. 25.

<sup>2</sup> Cross and Bevan: "Cellulose," p. 95.

<sup>3</sup> See article by Sherman: This Journal, 19, 305.