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THE ANALYSIS OF SUGAR MIXTURES.[1]

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THE various methods employed in the analysis of sugars may be roughly classified as follows:

(1) Optical methods.

(2) Reduction methods.

(3) Methods involving special reactions (such as yield of hydrazone, osazone, furfural, mucic acid, etc.).

In the case of a single sugar, any one of the above methods is sufficient for the determination. The percentage, for example, of arabinose in a solution may be determined by the polariscope, from the weight of reduced copper, from the weight of diphenylhydrazone, or from the quantity of furfural obtained on distillation with hydrochloric acid. In the analysis of a mixture of sugars, however, several factors must be determined before the percentage of each admits of calculation. The most important of these factors may be said to be the copper-reducing power, since it is from this that the total sum of reducing sugars is estimated. Very complete tables have been constructed by different analysts, giving the copper equivalent of the various reducing

[1] The greater part of this paper constitutes a report by the associate referee upon "Special Methods of Sugar Analysis," for the Twenty-second Convention of the Association of Official Agricultural Chemists, Washington, November, 1905. Read at the New Orleans Meeting of the American Chemical Society.

sugars, but unfortunately the early investigators in this field have so varied the conditions of their determinations, that there is a complete lack of uniformity among the many methods of procedure. Tables and methods are frequently confused even by experienced workers, and in case a mixture of sugars is present the analyst is still further perplexed, not knowing in terms of what sugar to express his results. In such case it has been the almost universal custom among chemists to express total reducing sugars as invert sugar, although this method of expression is only correct, to quote von Lippmann,[1] "when the mixture of reducing sugars consists of equal parts, dextrose and levulose; in all other cases this value cannot be accurately determined and dependent calculations are therefore rendered more or less unreliable."

During the past few years the writer has had occasion to make many separations of various sugars, as they occur in mixtures, and in all cases has adhered to the principle of first estimating the total reducing sugar as dextrose.[2] This method of procedure, however irrational it may seem in view of the difference in reducing power of the various sugars, offers nevertheless a complete solution of all difficulties, for by the use of a constant ratio established in terms of dextrose, for each sugar, the percentages of the different constituents in a mixture can be easily calculated.

The Action of Reducing Sugars upon Fehling Solution.—It has long been known that the dextrose equivalent of the copper reduced from a Fehling solution is not a constant quantity, but varies with the composition of the reagent, time and manner of boiling, and concentration of the sugar solution employed. Soxhlet[3] showed among the first, that when a reducing sugar acted upon the Fehling solution, the first portion added reduced most strongly and the succeeding portions gradually less strongly. The statement usually made that the reducing power of a sugar diminishes with its concentration is not, however, absolutely true and requires some modification. The reducing power of a sugar will remain constant for any concentration provided the same amount

[1] Chemie der Zuckerarten, 3rd Ed., 1, 898.

[2] The names dextrose and levulose are used in accordance with the usage of technical sugar chemists in America in place of the more correct *d*-glucose and *δ*-*l*-fructose.

[3] J. pr. Chem. [2] 21, 227.

of copper in solution is maintained throughout the experiment. In other words, the reducing power diminishes not on account of the increased concentration of the sugar, but because less copper remains in solution to be acted upon. This can be easily demonstrated by taking sugar solutions of the same concentration and varying the amount of copper in the Fehling solution.

Example.—0.1 gram of dextrose in 25 cc. solution gave 0.1964 gram copper by Allihn's method, the 30 cc. of the copper reagent containing 0.5276 gram of copper. A second experiment was made with the same sugar solution, using, however, a Fehling solution containing 0.3312 gram copper (0.5276 gram—0.1964 gram). In this case only 0.1826 gram of reduced copper was obtained. The sum of the weights of reduced copper for the two experiments is 0.3790 gram; that required for 0.2 gram of dextrose by Allihn's method is 0.3775 gram—a difference of 0.0015 gram, which is within the limits of experimental error.

The reducing action of any sugar upon the Fehling solutions may be expressed in general terms as follows: If for the first minute quantity s of a given sugar a definite amount c of copper is reduced, then for any multiple n of s the weight of copper would be nc, if the same amount of copper in the Fehling solution were always maintained. The latter condition, however, is never realized in practice, and with the continuous removal of copper from solution the value nc becomes $nc—(n—1+n—2+n—3+\ldots\ldots n—n)k$. When working with weighable quantities of sugar, this expression should be modified to $c+(n—1)d—(n—2+n—3\ldots\ldots n—n)k$, in which d is the difference between the weights of copper for the first two members of the series s and $2s$. The values of d and of the constant k are easily determined empirically and knowing these it is possible to construct tables for any of the reducing sugars.

The difference in reducing power of the various sugars upon Fehling's solution can be expressed very simply. If a definite weight d of a sugar D and a definite weight l of a sugar L reduce the same weight of copper, then the ratio d/l will be a fixed quantity. In other words, the various reducing sugars bear a constant ratio to one another for the same weight of reduced copper. This can be made more evident by an inspection of the following table, where a comparison of the reducing power of

dextrose, levulose and galactose is given. The method of Allihn[1] was followed as in all the experimental work of this article.

TABLE I.

A. Weight of levulose taken. Gram.	B. Weight of copper found. Gram.	C. Weight of dextrose corresponding to B. Gram.	D. Ratio C/A	E. Weight of galactose taken. Gram.	F. Weight of copper found. Gram.	G. Weight of dextrose corresponding to F. Gram.	H. Ratio G/E
0.0500	0.0887	0.0453	0.906	0.0500	0.0867	0.0443	0.886
0.1000	0.1789	0.0916	0.916	0.1000	0.1772	0.0906	0.906
0.1200	0.2139	0.1100	0.917	0.1200	0.2101	0.1080	0.900
0.1500	0.2653	0.1375	0.917	0.1500	0.2595	0.1344	0.896
0.1800	0.3153	0.1650	0.917	0.1800	0.3096	0.1618	0.899
0.2000	0.3479	0.1831	0.916	0.2000	0.3408	0.1792	0.896
0.2200	0.3799	0.2013	0.915	0.2200	0.3723	0.1970	0.896
0.2500	0.4267	0.2284	0.914	0.2500	0.4223	0.2259	0.904
		Average,	0.915			Average,	0.898

The figures under A and B are taken from the table of Hönig and Jesser (Z. Ver. deutschen Zuckerindustrie, 38, 1027) whose results the writer has fully confirmed.

The figures under C and G are taken from Allihn's table.

The figures under E and F are taken from laboratory results by the writer.

In a similar manner the ratio of xylose to dextrose was found to be 0.983 and of arabinose to dextrose 1.032.

By means of these dextrose ratios, determinations can be made of any reducing sugar by Allihn's method, the weight of dextrose in the table divided by the proper dextrose ratio giving the weight of sugar sought. The advantages of such a method of analysis are apparent; only one table is required for all the reducing sugars; the necessity of having many different stock solu-

[1] The method of Allihn was chosen as it is the one adopted by the Association of Official Agricultural Chemists, and is perhaps most extensively used by sugar chemists. Allihn's method has been criticized on the ground that the two minute boiling does not effect a complete reduction of the Fehling solution. This objection has really but little force; the method is purely a conventional one and if the details are carefully followed, accurate results can be secured. For very minute quantities of reducing sugars, however, the method of Allihn is not so well adapted as the methods of Kjeldahl or Pflüger which heat twenty and thirty minutes respectively. For a full discussion of these points see Lippmann: Chemie der Zuckerarten, Vol. I, pp. 583-612.

tions of Fehling solution is avoided; and all determinations are made under perfectly similar methods of procedure.

The dextrose equivalent of a mixture of reducing sugars is equal to the sum of the dextrose equivalent of the individual sugars. The statement has been made that in a mixture of sugars the reducing power of the individual sugars is somewhat modified by the other members present. The writer has subjected this statement to a thorough test and can discover no such influence.

A number of known mixtures of sugars were analyzed by Allihn's method and the total reducing sugars as dextrose compared with the calculated sum of the dextrose equivalents. The results of the experiments are given in Table II.

TABLE II.

Sugars.	Grams sugar in 25 cc. 1.	2.	3.	Total weight of sugars. Gram.	Dextrose equivalent. Calculated. Gram.	Found. Gram.	Error.
Dextrose, levulose...	0.0967	0.0904	.....	0.1871	0.1794	0.1780	+0.0014
" " ...	0.0484	0.0452	.....	0.0936	0.0898	0.0906	—0.0008
" " ...	0.0461	0.1408	.....	0.1869	0.1749	0.1755	—0.0006
" " ...	0.0231	0.0704	.....	0.0935	0.0875	0.0877	—0.0002
" " ...	0.0740	0.0198	.....	0.0938	0.0921	0.0927	—0.0006
" galactose..	0.1786	0.0585	.....	0.2371	0.2311	0.2294	+0.0017
" " ..	0.0893	0.0293	.....	0.1186	0.1156	0.1161	—0.0005
" " ..	0.0265	0.0960	.....	0.1225	0.1127	0.1132	—0.0005
Levulose, galactose..	0.0681	0.0175	.....	0.0856	0.0780	0.0764	+0.0016
" " ..	0.0155	0.1070	.....	0.1225	0.1102	0.1097	+0.0005
" arabinose	0.1853	0.0569	.....	0.2422	0.2282	0.2267	+0.0015
" "	0.0927	0.0285	.....	0.1212	0.1141	0.1131	+0.0010
Galactose, xylose ...	0.2162	0.0429	.....	0.2591	0.2361	0.2369	—0.0008
" " ...	0.1081	0.0215	.....	0.1296	0.1181	0.1183	—0.0002
Xylose, arabinose...	0.1513	0.0433	.....	0.1946	0.1934	0.1933	+0.0001
" " ...	0.0757	0.0217	.....	0.0974	0.0967	0.0981	—0.0014
" " ...	0.0495	0.1535	.....	0.2030	0.2070	0.2083	—0.0013
" " ...	0.0248	0.0768	.....	0.1016	0.1035	0.1044	—0.0009
Dextrose, arabinose, xylose.....	0.1371	0.0226	0.0609	0.2206	0.2203	0.2210	—0.0007
Dextrose, galactose, levulose.....	0.0646	0.0822	0.0967	0.2435	0.2270	0.2280	—0.0010

The weights in columns 1, 2 and 3 are given in the order of the respective sugars as named.

The calculated dextrose equivalents of the mixtures were found by multiplying the weights of each sugar by its dextrose ratio and adding together the products.

The greatest difference between the calculated values of the dextrose equivalent and those determined by experiment is 0.0017 gram, which is within the limits of experimental error. It is therefore safe to conclude from the results of Table II that the dextrose ratio of a sugar remains the same, whether it occurs alone or in the presence of other reducing sugars.

Application of Method to Analysis of Sugar Mixtures.—In the case of mixtures containing two reducing sugars the calculations are made from determinations of the reducing power and polarization.

Let x = per cent. of a given sugar A;
y = " " " " " " B;
a = dextrose ratio of sugar A;
b = " " " " B;
R = per cent. of total reducing sugars as dextrose;
then I, $ax+by=R$.

The polarization of a mixture of sugars is equal to the sum of the polarizations of the individual sugars present. As the S. & H. type of saccharimeter is the form of polariscope most commonly used, all polarizations were made with this instrument, 26.048 grams of material being taken for analysis, and the readings made in a 200 mm. tube. The polarization (Ventzke) of any sugar is equal to its percentage multiplied by a polarization factor, found by dividing the specific rotation of the sugar by the specific rotation of sucrose (+66.5).

Let α = polarization factor of sugar A;
β = " " " " B;
P = polarization (Ventzke) of mixture;
then II, $\alpha x+\beta y=P$.

From formulas I and II we obtain

$$x=\frac{bP-\beta R}{\alpha b-a\beta},$$

and

$$y=\frac{R-ax}{b}.$$

The above formulas were applied to the analysis of known mixtures of the common reducing sugars, dextrose, levulose, galactose, xylose and arabinose. The sugars employed in the work were obtained as pure as possible from reliable firms and

determinations of their specific rotations showed them to be of normal purity.

In making up the various mixtures the sugars were weighed in a small stoppered flask. After adding the requisite amount of water the flask was reweighed and the percentages of each sugar in the solution calculated. After the sugars were dissolved, the solutions were allowed to stand twenty-four hours before beginning the analysis, in order to remove all possibility of error through multirotation.

Separation of Levulose and Dextrose.—

Dextrose ratio of levulose = 0.915.

Polarization factor of levulose (20° C., 10 per cent. sol.) = $\frac{-90.18}{+66.5} = -1.356.$

" " " dextrose = $\frac{+52.74}{+66.5} = 0.793.$

Owing to the great susceptibility of levulose to variations in specific rotation through changes of temperature and concentration, the use of a fixed polarization factor is only possible when the analyses are made under perfectly similar conditions. The value of the polarization factor of levulose for different temperatures and concentrations is given in the following table:

TABLE III.

Temp. Degrees.	Concentration. 1 per cent.	2 per cent.	3 per cent.	4 per cent.	5 per cent.	10 per cent.	25 per cent.
15	—1.384	—1.385	—1.387	—1.389	—1.390	—1.398	—1.422
20	—1.341	—1.343	—1.345	—1.346	—1.348	—1.356	—1.380
25	—1.299	—1.301	—1.303	—1.304	—1.306	—1.314	—1.338
30	—1.257	—1.259	—1.261	—1.262	—1.264	—1.272	—1.296

The above figures were calculated from the general formula of Jungfleisch and Grimbert, $[\alpha]^t_D = -(101.38 - 0.56t + 0.108(c - 10))$.

The variations of the polarization constant due to concentration are so small that they do not affect the accuracy of the calculations appreciably and a 10 per cent. concentration was taken as the basis. The influence of temperature, however, is so pronounced that it cannot be disregarded.

The following formulas were employed in the analysis of levulose and dextrose mixtures:

I. Per cent. levulose $(L)_{20°} = \frac{0.793R - P}{2.08}$,

II. Per cent. dextrose = R—0.915 L.

For other temperatures than 20° the value of the denominator in equation I is 2.12 (15°), 2.04 (25°), 2.00 (30°).

In the following table are given the analyses of seven mixtures containing known amounts of levulose and dextrose.

TABLE IV.

Taken.				Found.		Error.	
Levulose. Per cent.	Dextrose. Per cent.	R.	$P^{t°}$.	Levulose. Per cent.	Dextrose. Per cent.	Levulose. Per cent.	Dextrose. Per cent.
0.99	2.06	3.01	+0.35 22°	0.98	2.11	—0.01	+0.05
1.59	5.92	7.41	+2.65 23°	1.56	5.98	—0.03	+0.06
3.17	11.83	14.54	+5.30 23°	3.02	11.78	—0.15	—0.05
4.52	4.84	9.06	—2.15 22°	4.51	4.83	—0.01	—0.01
5.63	1.85	7.02	—6.00 23°	5.61	1.89	—0.02	+0.04
9.04	9.67	17.80	—4.30 22°	8.90	9.66	—0.14	—0.01
11.26	3.69	14.04	—12.00 23°	11.23	3.76	—0.03	+0.07
				Average error,		—0.06	±0.04

The percentage of invert sugar in mixtures of dextrose and levulose is easily found by combining the smaller percentage with an equal amount of the other component. The dextrose ratio of invert sugar is $\frac{1.915}{2}$ = 0.958, and since 100 parts of invert sugar correspond to 95 of sucrose, the dextrose equivalent of an inverted sucrose solution gives almost exactly the amount of sucrose. One part of dextrose $= \frac{0.95}{0.958}$ = 0.993 part sucrose.

Separation of Dextrose and Galactose.—

Dextrose ratio of galactose = 0.898.

Polarization factor of galactose (20°, 10 per cent. sol.) $= \frac{+80.49}{+66.5} =$ 1.21.

The specific rotation of galactose varies somewhat with temperature and concentration, the differences, however, being much less than those of levulose. The following values for the polarization factor of galactose at different temperatures and concentrations were calculated from the general formula of Meissl.[1]

TABLE V.

Temperature. Degrees.	10 per cent.	15 per cent.	20 per cent.
10	1.242	1.248	1.254
20	1.210	1.216	1.222
30	1.179	1.185	1.191

[1] J. pr. Chem. [2] 22, 97. $[\alpha]_D^t = 83.037 + 0.0785\,p - 0.209\,t$.

The concentration influence of galactose upon the polarization factor is too slight to influence the calculations appreciably; the temperature influence, however, should be regarded in case the readings are made very much above or below 20°.

The following formulas were employed in making the separations of dextrose and galactose:

I. Per cent. dextrose $(D)_{20°} = \frac{1.21\,R - 0.898\,P}{0.498}$,

II. " " galactose $= \frac{R - D}{0.898}$.

At 25° formula I would be $D = \frac{1.195\,R - 0.898\,P}{0.482}$.

In the following table are given the analyses of 4 mixtures containing known amounts of dextrose and galactose.

TABLE VI.

Taken.				Found.		Error.	
Dextrose. Per cent.	Galactose. Per cent.	R.	$P^{t°}$.	Dextrose. Per cent.	Galactose. Per cent.	Dextrose. Per cent.	Galactose. Per cent.
2.12	7.68	9.06	+11.0 25°	1.97	7.89	−0.15	+0.21
4.24	15.35	18.16	+21.9 25°	4.23	15.51	−0.01	+0.16
7.15	2.34	9.29	+ 8.5 25°	7.20	2.33	+0.05	−0.01
14.29	4.68	18.35	+17.0 25°	13.82	5.04	−0.47	+0.34
				Average error,		±0.17	±0.18

The average error in the above series of experiments is nearly four times that found in the separation of levulose and dextrose. This was to be expected since, owing to the small difference in the specific rotations of dextrose and galactose, the errors of observation are doubled; in the analysis of the dextrose-levulose mixtures on the other hand the wide range in the specific rotation diminishes the experimental errors one-half (compare Formula 1 for both separations).

Separation of Levulose and Galactose.—

In making this separation the following formulas were employed:

I. Per cent. levulose $(L)_{20°} = \frac{1.21\,R - 0.898\,P}{2.324}$,

II. " " galactose $= \frac{R - 0.915\,L}{0.898}$.

The susceptibility of the specific rotations of both levulose and galactose to temperature variations necessitates a considera-

ble temperature correction if the readings are not made at 20°. This can be done by using the polarization factors given in Tables III and V. At 30°, *e. g.*, formula I would be $L = \frac{1.179\,R - 0.898\,P}{2.221}$

In the following table are given the analyses of 4 mixtures containing known amounts of levulose and galactose.

TABLE VII.

Taken.				Found.		Error.	
Levulose. Per cent.	Galactose. Per cent.	R.	$P^{t°}$.	Levulose. Per cent.	Galactose. Per cent.	Levulose. Per cent.	Galactose. Per cent.
1.24	8.56	8.78	+ 8.75 $^{28°}$	1.14	8.62	+0.10	+0.06
2.47	17.12	17.78	+17.40 $^{25°}$	2.46	17.29	−0.01	+0.17
5.44	1.40	6.11	− 5.35 $^{28°}$	5.38	1.33	−0.06	−0.07
10.89	2.80	12.31	−10.50 $^{29°}$	10.76	2.74	−0.13	−0.06
				Average error,		±0.07	±0.09

Separation of Levulose and Arabinose.—

Dextrose ratio of arabinose = 1.032.

Polarization factor of arabinose (20°) $= \frac{104.5}{66.5} = 1.571.$

The formulas employed for the separation of levulose and arabinose are the following:

I. Per cent. levulose $(L.)_{20°} = \frac{1.571\,R - 1.032\,P}{2.836}$,

II. " " arabinose $= \frac{R - 0.915\,L}{1.032}$.

The specific rotation of arabinose varies somewhat with changes in temperature and concentration, but these variations are not great enough to seriously affect the calculations. The temperature corrections for levulose, however, must be made as usual. The denominator in equation 1 becomes 2.88 at 15°, 2.793 at 25°, and 2.75 at 30°.

In the following table are given the analyses of two mixtures containing known amounts of levulose and arabinose.

TABLE VIII.

Taken.				Found.		Error.	
Levulose. Per cent.	Arabinose. Per cent.	R.	$P^{t°}$.	Levulose. Per cent.	Arabinose. Per cent.	Levulose. Per cent.	Arabinose. Per cent.
7.41	2.28	9.05	− 6.1 $^{27°}$	7.39	2.22	−0.02	−0.06
14.82	4.55	18.14	−12.3 $^{26°}$	14.80	4.46	−0.02	−0.09
				Average error,		−0.02	−0.07

In the estimation of levulose and arabinose we have a wider range of specific rotations than with any other mixture of two sugars and a corresponding reduction in the experimental sources of error.

Separation of Xylose and Arabinose.—

Dextrose ratio of xylose = 0.983.

Polarization factor of xylose $= \frac{+18.79}{+66.5} = 0.283.$

The formulas employed for the separation of xylose and arabinose were the following:

I. Per cent. xylose $(X) = \frac{1.571\,R - 1.032\,P}{1.252}$,

II. " " arabinose $= \frac{R - 0.983\,X}{1.032}$.

In the following table are given the analyses of four mixtures containing known amounts of xylose and arabinose.

TABLE IX.

Taken.				Found.		Error.	
Xylose. Per cent.	Arabinose. Per cent.	R.	P°.	Xylose. Per cent.	Arabinose. Per cent.	Xylose. Per cent.	Arabinose. Per cent.
1.98	6.14	8.35	$+10.2^{25^{\circ}}$	2.05	6.13	+0.07	—0.01
3.96	12.28	16.66	$+20.3^{25^{\circ}}$	4.17	12.17	+0.21	—0.11
6.05	1.73	7.85	$+4.5^{25^{\circ}}$	6.14	1.75	+0.09	+0.02
12.10	3.46	15.46	$+8.8^{25^{\circ}}$	12.14	3.42	+0.04	—0.04
				Average error,		+0.10	±0.05

The Determination of Dextrose, Levulose and Sucrose in Mixtures.—The analysis of a mixture of dextrose, levulose and sucrose is a problem which frequently confronts the sugar chemist. The polarization of a mixture of the three sugars is expressed by the formula

$$S + 0.793D - 1.356L = P_{20^{\circ}}.$$

Substituting the above equation in the formulas employed for the separation of dextrose and levulose alone, we obtain, letting S equal the per cent. sucrose by Clerget:

I. Per cent. levulose $(L)_{20^{\circ}} = \frac{0.793\,R + S - P}{2.08}$,

II. Per cent. dextrose[1] $= R - 0.915\,L$.

[1] For other schemes for determining dextrose, levulose and sucrose in mixtures, see Zamaron: Bull. de l'Assoc. des Chimistes, 1902, p. 182; Buisson: Ibid. 1903, p. 499; 1904, p. 1233; Remy: Ibid. 1904, p. 1002; Stein: The Sugar Cane, 30, 206 (1898). None of these authorities, however, takes into

There are two sources of error involved in the separation by the above formulae which require some consideration. The first of these is

The Slight Reducing Action of Sucrose upon the Fehling Solution.—The reducing action of sucrose upon Fehling's solution is proportional, first, to the concentration of the sucrose and, second, to the amount of copper left unreduced. If enough reducing sugars are present to precipitate nearly all the copper from the Fehling solution the inversion of the sucrose will be very slight. This can be seen from the following series of experiments with sucrose and dextrose mixtures, in which by changing the percentages of dextrose varying amounts of copper were reduced:

TABLE X.

Expt. No.	Sucrose taken. Per cent.	Dextrose taken. Per cent.	Dextrose found. Per cent.	Error. Per cent.	Remarks.
1.....	80.00	4.00	4.82	0.82	Fehling about one-fifth reduced.
2.....	80.00	8.00	8.65	0.65	Fehling about two-fifths reduced.
3.....	80.00	16.00	16.42	0.42	Fehling about four-fifths reduced.
4.....	80.00	20.00	20.16	0.16	Fehling nearly all reduced.

Owing to the action of the greater excess of unreduced copper, five times as much sucrose was inverted in Experiment 1 as in Experiment 4, though the quantity of sucrose taken was the same in each experiment; in other words, the error due to the reducing action of sucrose is inversely proportional to the amount of dextrose present.

The following correction for this error has been found by the writer to give very concordant results: The grams of sucrose in the 25 cc of solution to be analyzed by Allihn's method are divided by the milligrams of dextrose found + 40; the quotient will give the required correction in grams to be subtracted.

The probable error involved in such a mode of correction can be seen from the following series of experiments which were made under a wide range of conditions:

account the large difference in reducing power of dextrose and levulose, so that a considerable error may result in the calculations, especially if there be a wide difference in the percentages of dextrose and levulose.

TABLE XI.

A Sucrose taken. 25 cc. Gram.	B Dextrose taken. 25 cc. Gram.	C Dextrose found. 25 cc. Gram.	D Calc. correction. Gms. sucrose+ mgs. dextrose+40. Gram.	E Corrected dextrose. C—D. Gram.	F Error. B—E. Gram.
0.25	0.0500	0.0523	0.0027	0.0496	+0.0004
0.25	0.1000	0.1028	0.0018	0.1010	—0.0010
0.25	0.1500	0.1518	0.0013	0.1505	—0.0005
0.25	0.2000	0.1990	0.0010	0.1980	+0.0020
0.50	0.1000	0.1045	0.0032	0.1013	—0 0013
0.50	0.1500	0.1532	0.0026	0.1506	—0.0006
0.50	0.2000	0.2032	0.0020	0.2012	—0.0012
0.50	0.2500	0.2513	0.0016	0.2497	+0.0003
1.00	0.0500	0.0603	0.0100	0.0503	—0.0003
1.00	0.1000	0.1082	0.0068	0.1014	—0.0014
1.00	0.2000	0.2053	0.0041	0.2012	—0.0012
1.00	0.2500	0.2520	0.0034	0.2486	+0.0014
2 00	0.0500	0.0666	0.0186	0.0480	+0.0020
2.00	0.1000	0.1137	0.0130	0.1007	—0.0007
2.00	0.2000	0.2075	0.0080	0.1995	+0.0005
2.00	0.2500	0.2555	0.0067	0.2488	+0.0012

The second of the errors previously referred to is the error encountered in the determination of sucrose by the Clerget method which results from

The Change in Rotation of Levulose in Neutral and Acid Solution. —The influence of this error has long been recognized; the work of Spohr, Wohl, Ost, Soxhlet, Herzfeld, Lippmann, Jungfleisch and Grimbert, Hammerschmidt, Weber, Tolman and many others, has conclusively demonstrated that the addition of hydrochloric acid increases the specific rotation of levulose. This increase naturally affects the calculation of sucrose by Clerget's formula, the effect being a plus error, which is proportional to the percentage of levulose present in the mixture and to the amount of acid employed in the inversion.

The extent of this error in practical work is shown in the following series of experiments:

TABLE XII.

Experiment No.	Levulose taken. Per cent.	Dextrose taken. Per cent.	Sucrose taken. Per cent.	Sucrose found by Clerget. Per cent.	Error. Per cent.
1	0.87	0.88	26.81	26.87	+0.06
2	1.87	1.89	14.94	15.03	+0.09
3	3.30	3.35	41.34	41.44	+0.10
4	4.10	4.14	33.59	33.77	+0.18
5	4.60	4.65	4.71	4.89	+0.18
6	7.25	7.35	21.76	21.96	+0.20
7	8.16	8.25	25.08	25.35	+0.27

The error in the determination of sucrose is thus seen to increase with the amount of levulose present. It is very evident from the above table that this error is too great to be disregarded in our commercial work; common centrifugal molasses, according to analysis made at Audubon Park, contains approximately 15 per cent. levulose and this would affect the sucrose determination by about 0.50 per cent. The correction to be deducted depends necessarily upon the concentration of the acid used for making the inversion and the dilution of the sugar solution. For 10 cc. of fuming hydrochloric acid (sp. gr. 1.18) and 100 cc. of sugar solution, the correction according to the previous table would be 0.036 per cent. for each percentage of levulose. It is interesting to note that the same value 0.036 is deduced from the results given by Lippmann,[1] showing the effect of hydrochloric acid upon the rotation of invert sugar.

In the following table the results obtained upon analyzing ten mixtures containing known amounts of sucrose, dextrose and levulose, according to the methods just described, are given.

TABLE XIII.

Taken.			Direct polarization.	t° Invert polarization.	Sucrose by Clerget.	R	R corrected for sucrose.	Found.		
Dextrose. Per ct.	Levulose. Per ct.	Sucrose. Per ct.	P		Per ct.			Dextrose. Per ct.	Levulose. Per ct.	Sucrose (cor. for levulose.) Per ct.
1.13	0.52	6.19	+ 6.55	— 1.70 (23°)	6.23	1.69	1.65	1.20	0.49	6.22
0.52	1.11	6.24	+ 5.20	— 3.25 (18°)	6.26	1.63	1.58	0.56	1.12	6.23
2.26	1.01	12.38	+13.05	— 3.41 (23°)	12.42	3.25	3.20	2.37	0.91	12.40
1.04	2.22	12.47	+10.35	— 6.49 (1°)	12.48	3.25	3.17	1.15	2.21	12.43
5.21	9.99	15.59	+ 6.57	—14.00 (26°)	15.70	14.66	14.52	5.22	10.16	15.55
10.02	5.43	16.16	+17.06	— 4.26 (26°)	16.27	15.24	15.10	10.06	5.51	16.14
10.42	19.98	31.12	+13.14	—28.01 (26°)	31.41	28.88	28.72	10.23	20.21	30.91
20.03	10.86	32.31	+34.12	— 8.52 (24°)	32.55	29.89	29.72	19.80	10.84	32.28
5.00	5.00	90.00	+86.90	—32.01 (27°)	90.08	10.48	9.86	5.08	5.22	89.95
1.00	1.00	98.00	+97.05	—30.80	97.97	2.43	1.82	0.75	1.17	97.94
								Average error,	±0.11	±0.10 ±0.05

A number of other analyses of various sugar mixtures have

[1] Chemie der Zuckerarten, 3rd Ed., p. 922.

been made according to the principles above outlined, but the examples given are sufficient to illustrate the practicability and accuracy of the methods of separation. The work is being continued upon other mixtures, particularly those of the simpler reducing sugars with the higher saccharides maltose, lactose, and raffinose. It is needless to remark that in working with unknown mixtures the character of the different constituents must be determined by careful qualitative tests before beginning the work of analysis.

The application of some of the methods described to various problems of the sugar-cane industry, will form the subject of another paper.

[CONTRIBUTION FROM THE SUGAR EXPERIMENT STATION OF THE LOUISIANA STATE UNIVERSITY.]

THE FERMENTATION OF SUGAR-CANE PRODUCTS.[1]

BY C. A. BROWNE, JR.

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THAT the juice of the sugar-cane and the various products prepared therefrom are exceedingly susceptible to fermentative changes, has been known since the first beginnings of the sugar industry, for we find that the oldest writers upon the subject all make mention of the various phenomena of fermentation. The views upon the subject of fermentation, prior to the epoch-making discoveries of Pasteur, were necessarily very inexact; they are, however, exceedingly interesting in an historical way and one or two extracts from various authorities will bear quoting. The following passage from Porter's classical work upon the sugar-cane is especially characteristic: "If the fresh juice of canes is left to itself, the feculent parts are soonest decomposed. Of the first kind of feculencies one portion sinks to the bottom and the other rises to the surface, while the acid thus produced acts upon the second sort of impurities by diffusing them through the whole fluid mass. The acid which is generated at the very commencement of spontaneous decomposition holds the feculencies in most intimate combination with the fluid part. When the fermentation is well established it is continued for several weeks,

[1] Read before the New Orleans meeting of the American Chemical Society, January 1, 1906.