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THE COMMERCIAL ANALYSIS OF CANE MOLASSES. I. OPTICAL METHODS.

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IT SEEMS to be assumed by many commercial analysts that the routine methods which they employ in the examination of molasses will yield comparable and trustworthy, even though not wholly accurate, results. There is serious doubt, however, whether such an assumption is warrantable. In the writer's opinion it is not. Reports in his possession, from several laboratories to which similar collections of molasses samples had been sent for examination, are so divergent in their results as to make it impossible to decide, not only as to the actual, but even as to the relative, saccharine strengths of the different samples.[1] It may be reason-

Analysts.	S.	P.	G.	K.
Sample 1.	28.60	30.0	32.0	30.0
	25.00	*22.7*	*24.5*	*20.2*
	53.60	52.70	56.5	50.2
Sample 2.	22.0	22.6	23.4	26.0
	26.88	*26.0*	*27.7*	*24.87*
	48.88	48.6	51.1	50.87
Sample 3.	26.40	27.1	29.4	28.80
	25.64	*24.4*	*25.7*	*24.25*
	52.04	51.5	55.1	53.05
Sample 4.	21.60	22.6	25.8	20.0
	28.09	*27.8*	*28.4*	*26.21*
	49.69	50.4	54.2	46.21
Sample 5.	25.0	26.0	28.2	24.4
	29.76	*29.0*	*29.4*	*26.94*
	54.76	55.0	57.6	51.34

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[1] The three quantities reported for each analysis in the following tabulation represent respectively the percentages of cane-sugar, reducing sugars, and the total sugars of the samples. The reducing sugar percentages are printed in italics.

able to ascribe these divergences in part to careless manipulation; but since the analyses were made by firms specializing in saccharimetry, it seems fair to presume that carelessness could not have been the only source of error, and that variation in, and inadequacy of, the analytical methods employed must also be held responsible for part of the disagreements.

In fact, many sources of inaccuracy have been discovered in the customary methods of sugar analysis; and various means have been proposed, especially in foreign publications, for their removal. But since these methods of greater accuracy have never been combined in the form of a convenient routine procedure, available for daily use in commercial testing laboratories, and since, furthermore, cane-molasses of the poorer grades was for years a practically worthless waste material, little real progress has been made in this country toward the general adoption of more accurate methods for its valuation.

Of late, however, on account of the increasing utilization of molasses as a fodder and as a raw material for the production of alcohol, the value of even the poorest grades has undergone a sharp advance; and for this reason increased precision in analysis is daily becoming more essential. Led by this consideration, the writer began, four years ago, a careful examination of the existing analytical methods, hoping to find a procedure simple and quick enough for routine work, and capable, at the same time, of determining the total sugar of a sample with an error not exceeding about ±0.5 per cent. A method which seemed to satisfy these conditions fairly well was soon found, and was outlined in 1903 in a preliminary note addressed to the Association of Official Agricultural Chemists.[1] It is presented herewith in detail, together with the results of further study to which the writer has subjected it since that time.

THE COMPOSITION OF TYPICAL CANE-MOLASSES.

It is necessary, before discussing the procedure in question, and the writer's work thereon, to consider the character of the material in whose examination it is to be applied, and the influence of variations in that character as a source of error in existing analytical methods.

Obviously, it is impossible to make any sharp classification of the many varieties of cane-molasses, since, from the nearly color-

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[1] Bulletin 81, Bureau of Chemistry, U. S. Dept. of Agr., p. 175.

less table syrups on the one hand to the tarry "black-strap" residuums on the other, they merge into each other by almost imperceptible differences of character. It is legitimate, however, to refer cane-molasses of any kind to some one of three types, *e. g.*, the "first," "second" and "third" molasses of the sugar plantation.[1] It therefore is sufficient for the purposes of this discussion to describe these types, and to consider their characteristic behaviors with relation to analytical processes as illustrative of the behavior of molasses in general.

The relative character of these three types of molasses is well shown by the following tabulations, based on data from a report by Edson.[2]

TABLE I.

		Total solids.	Direct polarization.	Sucrose.	Reducing sugars.	Non-sugars.
Second plant run. P. 35.	First molasses ...	71.56	55.7	58.06	10.39	3.11
	Second " ...	76.7	33.4	36.99	21.34	18.37
	Third " ...	78.8	23.2	29.11	29.36	20.33
Third plant run. P. 39.	First molasses ...	71.88	53.8	54.97	11.57	5.34
	Second " ...	77.5	36.8	39.96	20.10	17.44
	Third " ...	77.6	22.0	26.62	28.52	22.46

It must be borne in mind that the foregoing figures represent types only, and not standards of composition. Naturally, the composition of cane juice varies considerably from season to season and from place to place. Furthermore, manufacturing processes are not everywhere the same; mechanical appliances are liable to differ in design and efficiency, and the skill and care displayed in their management may vary widely. For these reasons there inevitably must be considerable variations in the composition of molasses of any type. But admitting this, it still is clear that

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[1] For readers who are not acquainted with the terminology of sugar manufacture, the following explanation may be useful. Cane juice, after being "defecated" or freed of certain impurities, is evaporated to a thick syrup and is allowed to crystallize. The magma so obtained, called the "first massecuite," is separated by centrifuging into its constituents, the "first sugar" and "first molasses." The molasses, which still contains a large amount of recoverable sugar, is evaporated again, usually after a clarification of some kind, and a "second massecuite" is thus obtained, which in its turn is separated into the "second sugar" and "second molasses." In many localities, the extraction of sugar is abandoned at this point. In Louisiana, however, it is customary to reboil the second molasses and thus to obtain a "third sugar" and a "third molasses." There is also, in this country, at least one refinery which imports West Indian "seconds" for reboiling in this manner.

[2] Record of experiments at the Sugar Experiment Station on Calumet Plantation, Pattersonville, La. Bull. 23, Bureau of Chemistry, U. S. Dept. of Agr., 1889, pp. 35 and 39.

each type has characters which differentiate it unmistakably from its fellows.

Thus, first molasses is characterized by a high direct polarization and a high percentage of sucrose, both usually well above 40°, and close together, and by a small percentage of non-sugars, usually less than 10 per cent. The proportion of reducing sugars, which may vary between 10 and 20 per cent., is not specially characteristic.

Second molasses is characterized by a lower polarization and sucrose percentage, and by a higher proportion of non-sugars. Its direct polarization usually lies between 30° and 36°, while the percentage of sucrose is some degrees higher, commonly between 36 and 44 per cent. The non-sugars may range between 15 and 21 per cent., but are most likely to be in the neighborhood of 18 per cent. Second molasses contains a somewhat larger proportion of reducing sugars than first molasses, commonly between 15 and 22 per cent.; but as in the case of first molasses, their amount is not specially characteristic.

Third molasses usually shows a very low polarization, rarely above 25° and often as low as 15°. It commonly contains, however, from 25 to 30 per cent. of sucrose—more by 7 to 10 per cent. than would be shown by the direct polarization alone. Its proportion of non-sugars is materially higher than that of second molasses. These bodies amount usually to 23 to 25 per cent., and may increase at times to 33 to 35 per cent. As in the case of first and second molasses, the proportion of the reducing sugars has less significance. Ordinarily, however, they are more abundant than in second molasses, and they amount normally to 25 to 30 per cent.

The subjoined data, taken from the writer's laboratory records, show the resemblance of molasses in the Boston market to the foregoing types.

From the standpoint of the sugar-maker the essential difference between the three types of molasses just described is the progressive falling-off in the proportion of sucrose and in the coefficient of purity as we pass from "first" to "third." More significant, however, from the analyst's standpoint, and therefore for the purposes of this discussion, is the simultaneous increase in the proportions of reducing sugars and non-sugars, accompanied by lengthening of the interval between direct polarization and sucrose

TABLE II.

	Total solids.[1]	Direct polarization.	Sucrose.	Reducing sugars.	Non sugars.[2]
			Firsts.		
1.	72.5	42.24	46.45	20.6	5.45
2.	74.7	44.7	45.9	20.8	8.0
3.	72.0	46.3	46.87	16.70	8.43
4.	72.9	43.0	44.1	19.2	9.6
			Seconds.		
5.	77.0	36.7	43.0	20.6	13.4
6.	76.9	35.0	40.3	21.5	15.1
7.	80.0	37.0	41.7	22.4	15.9
8.	77.8	32.7	39.1	22.3	16.4
9.	79.3	33.0	40.4	21.6	17.3
10.	75.0	32.0	38.2	17.8	19.0
11.	82.9	36.3	43.6	19.8	19.5
12.	78.8	34.7	39.1	19.0	20.7
13.	75.7	31.8	35.8	18.3	21.6
14.	82.2	38.3	43.2	17.2	21.8
15.	81.9	41.9	43.7	15.4	22.8
			Thirds.		
16.	76.5	17.0	26.6	29.1	20.8
17.	81.3	17.0	26.9	33.3	21.1
18.	79.2	23.5	32.1	25.8	21.3
19.	80.3	20.1	29.2	27.7	23.4
20.	79.7	19.5	28.0	28.2	23.5
21.	80.2	17.6	28.0	28.7	23.5
22.	80.2	18.2	27.3	27.1	24.0
23.	83.4	20.3	30.8	28.0	24.6
24.	79.9	16.1	28.2	26.8	24.9
25.	80.2	18.2	27.3	27.1	25.0
26.	79.5	20.0	27.2	27.2	25.1
			Abnormal Thirds.[3]		
27.	80.2	28.7	34.3	16.0	29.9
28.	81.0	29.0	34.8	15.7	30.5
29.	80.6	31.1	35.2	11.6	33.8
30.	82.4	32.2	35.5	11.4	35.5

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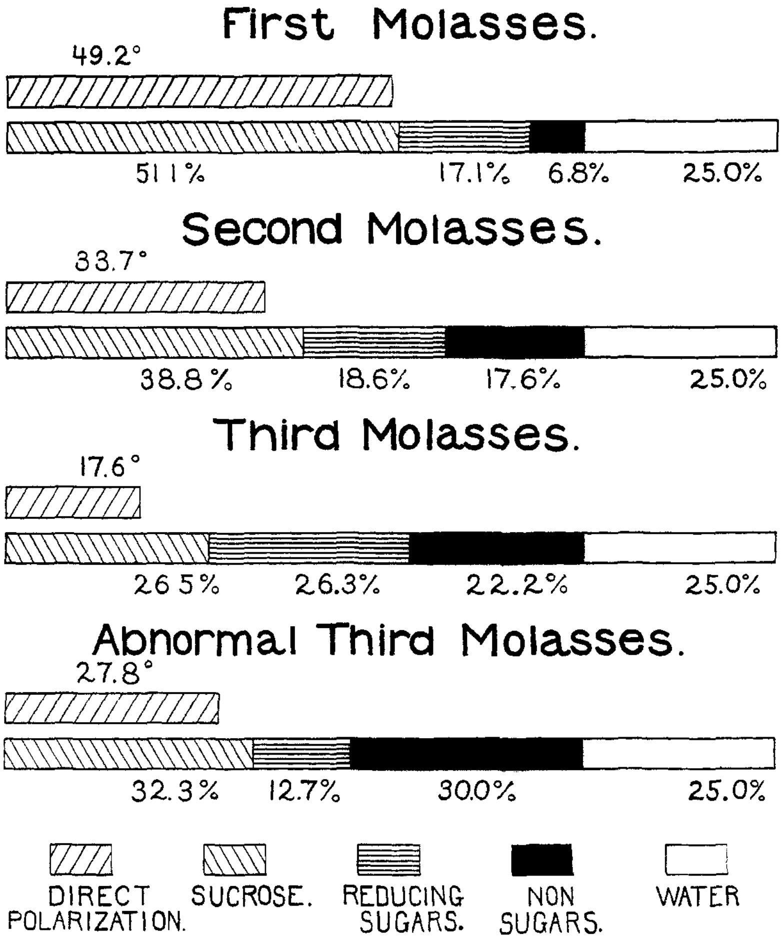
[1] The values in this column do not represent the true percentages of total solids, as determined by the difficult process of desiccation and weighing, but the "Brix degree" of the samples,—an approximation to, and somewhat higher than, the true value.

[2] Non-sugars = Brix (Total solids)—(Sucrose and reducing sugars).

[3] Whereas the "thirds" of the foregoing tabulation represent the run of the market, the "abnormal thirds" represent different lots of the final residuum of a single molasses refinery, whose product is always characterized by a percentage of sucrose abnormally high for third molasses, by an exceptionally low percentage of reducing sugars, and by an excessive proportion of gums, ash, and decomposition products.



This diagram represents the average of the molasses analyses shown in the tabulation on p. 696, Edson's two samples of "first molasses" being included with the writer's four samples. To facilitate comparison, all of the averages have been recalculated to a uniform content of 25 per cent. of water.

percentage, and by marked intensification of color. The bearing of the latter facts upon the choice of analytical procedure is most important, and has received heretofore too little consideration on the part of commercial chemists.

THE CUSTOMARY METHODS OF COMMERCIAL MOLASSES ANALYSIS.

It is the usual practice in testing raw sugars to assume that the direct polarization represents the percentage of sucrose, and to avoid in this way the added manipulation involved in Clerget's double polarization method. The character of the errors likely to be introduced by acting on this assumption is shown by the accompanying tabulation of results obtained in the writer's laboratory.

TABLE III.

Sample.	Sucrose by Single polarization.	Sucrose by Double polarization.	Difference.[1]
Cuban centrifugal	96.85	97.00	+0.15
Java "	96.40	95.83	—0.57
San Domingo centrifugal	97.16	97.35	+0.19
Cuban second sugar	91.23	90.80	—0.43
Muscovado 1	90.50	90.90	+0.40
" 2	88.20	89.00	+0.80
" 3	92.10	91.40	—0.50
" 4	86.54	86.00	—0.54
	Mean of —differences		—0.51
	" " + "		+0.39
	" " all "		—0.06

It will be seen from the foregoing figures that, although the direct and double polarization values for sucrose may differ for any individual sugar sample by about ±0.5 per cent., the mean of these differences becomes very small when a number of samples are examined. In the end, therefore, use of the double polarization method would probably add but little to the accuracy of sugar-testing.[2]

Since the "single polarization" procedure works well in the examination of raw sugars, many chemists have assumed that it also may be adopted legitimately in the analysis of cane-molasses;[3]

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[1] While these differences unquestionably are due in part to experimental error, it is most improbable that such error is responsible for more than a small part of any of them, since they are not altered materially by making careful duplicate analyses. Similar differences are shown by results obtained in the laboratory of the Bureau of Chemistry (Bull. **13**, "Foods and Food Adulterants," Part **6**: "Sugar, Molasses and Syrup, Etc.," p. 672) and by Nasini and Villavecchia (Sul peso normale pei saccarimetri. Publio. de lab. chim. centr. delle gabelle, Rome, 1891, pp. 28-29).

[2] Indeed, it is likely that the true percentage of sucrose may be more nearly represented by the direct polarization than by the quotient obtained after double polarization, since the latter value is far more liable to be affected by experimental error.

[3] Aime Girard and Laborde: *Comptes rendus*, 1876, p. 214; 1877, p. 800; Morin: *Ibid.*, 1877, p. 802; Beaufret: *Bull. de l'Ass'n des Chimistes*, **13**, 133; see also, for criticism of the foregoing writers, Pellet: *Bull. de l'Ass'n des Chimistes*, **13**, 757; Pellet and Barbet: *Ibid.*, **13**, 948.

and, indeed, for certain purposes it often may be followed without the introduction of serious error. The following tabulation, which summarizes the six analyses of first molasses already reported, shows that the mean error due to the difference between the direct and double polarization values is usually very small for goods of this grade.

TABLE IV.

First molasses.	Sucrose by Direct polarization.	Sucrose by Double polarization.	Errors.
Edson	55.70	58.06	2.36
"	53.80	54.97	1.17
No. 1	42.24	46.45	4.21
" 2	44.7	45.9	1.2
" 3	46.3	46.87	0.57
" 4	43.0	44.1	1.1
Means	47.62	49.39	1.77

Such first molasses as comes upon the market is ordinarily destined for the grocery trade, and since its value for this purpose is fixed by color and flavor rather than by the percentage of sugar which it may contain, understatement of the sucrose by 2 or 3 per cent. may be of little importance in a trade analysis.[1] Moreover, the minus errors shown by the tabulation are reduced somewhat by other errors of opposite sign, due to the method employed in preparing the solution for analysis, and having the effect of raising the direct polarization.

As is well known, molasses is prepared for polarization by dissolving a definite amount—usually the so-called "normal weight"—in a little water, adding lead subacetate solution until satisfactory decolorization is produced, making the volume of the mixture up to some definite quantity—usually 100 cc.—and filtering. Obviously, the volume of the solution is less than the definite final volume of the mixture, inasmuch as a certain part of this space is occupied by the precipitate of lead and coloring-matters; and on this account the concentration and polarization of the solution are increased somewhat beyond their proper values.[2] Methods have been proposed by Scheibler[3] and by Sachs[4] for correction of

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[1] Of course it is necessary for the food analyst, searching for added glucose, always to use the Clerget method for sucrose.

[2] Wiley's "Principles and Practice of Agricultural Analysis," Vol. III, p. 102: Spencer's "Handbook for Sugar Manufacturers," p. 47.

[3] *Ztschr. Ver. Rubenzucker Industrie*, **25**, 1054 (1875).

[4] *Ibid.*, **30**, 229 (1880).

the error due to the bulk of this precipitate, which may be very considerable in the case of materials containing large proportions of coloring-matter.[1] The writer has employed the Scheibler "double dilution" method in the examination of several samples of molasses, with the following results:

TABLE V.

	Bulk of lead precipitate. cc.	Plus error.	Direct polarization.	
			Observed.	Corrected.
First Molasses:[2]				
No. 1	0.33	0.14°	42.24°	42.10°
No. 3	0.53	0.24°	46.30°	46.06°
Second Molasses:				
Cuban No. 2	2.64	0.84°	31.92°	31.08°
Cuban No. 4	2.64	0.96°	36.20°	35.24°
Third Molasses:				
No. 119	4.58	0.79°	17.68°	16.87°
A—C	5.20	0.94°	18.06°	17.12°
McCahan	4.00	1.13°	28.16°	27.03°

It is evident that sucrose percentages calculated on the basis of uncorrected polarizations will bear the same ratios to the true sugar percentages as the observed polarizations bear to the corrected ones. The following tabulation shows, in addition to the foregoing polarizations, the uncorrected and corrected percentages of sucrose in the same samples of molasses, together with the error which would be caused in each case by assuming that the uncorrected polarization represented the actual sucrose content of the sample.

TABLE VI.

	Direct polarization.		Sucrose percentage.		
	Observed.	Corrected.	Uncorrected.	Corrected.	Error.
First Molasses:					
No. 1	42.24°	42.10°	46.45°	46.31	—4.07
No. 3	46.30°	46.06°	46.87	46.63	—0.33
Second Molasses:					
Cuban No. 2	31.92°	31.08°	36.16	35.21	—3.29
Cuban No. 4	36.20°	35.24°	41.40	40.50	—4.30
Third Molasses:					
No. 119	17.68°	16.87°	29.50	28.21	—10.53
A–C	18.06°	17.12°	27.40	25.97	—7.91
McCahan	28.16°	27.03°	32.22	30.93	—2.77

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[1] Wiechmann, *Bull. de l'Ass'n des Chimistes*, **21**, 631 (1903), and Horne, This Journal, **26**, 186 (1904), have shown that the plus error introduced in the polarization of a raw sugar, through failure to correct for the bulk of the lead precipitate, may amount to 0.05°–0.98° Ventzke.

[2] Sachs' method, applied to these two samples of first molasses, gave practically identical results, the bulks of the lead precipitates being respectively 0.40 cc. and 0.60 cc., instead of 0.33 cc. and 0.53 cc.

Comparison with the values given in Table IV (p. 698) shows that the errors given therein for samples 1 and 3 have been slightly reduced through operation of the "precipitate error."

As has been said, it may be legitimate in some cases to determine the cane-sugar of first molasses by single polarization; but, on the contrary, it is bad practice to follow the same procedure in testing second and third molasses. Goods of the latter grades are valued according to their saccharine strength, and errors which may amount to a tenth or more of the total sucrose, as in the case of second molasses, or to a third of the total sucrose, as in the case of Sample 119, are not to be tolerated. It will not do to say that a constant correction may be applied to the direct polarization of low-grade molasses in order to approximate the true percentage of sugar; for as is shown by the three "third" samples of the foregoing tables, the errors are far from being constant. The only safe procedure, therefore, is to determine the sucrose by double polarization, and to take account of the error due to the bulk of the lead precipitate.

In testing molasses of fine quality, containing but little coloring-matter, no special difficulty is encountered in carrying out these operations. On the contrary, the assay of dark low-grade materials is made very difficult by the large proportion of colored decomposition products which they contain. For example, Samples 1 and 3 of the foregoing tabulation were decolorized sufficiently for polarization in solutions of normal strength, by 1.5 cc. and 2 cc. of the writer's lead subacetate solution, corresponding to 2 cc. and 2.7 cc. of the solutions commonly employed.[1] The sugar filtrates were clear enough to be polarized with ease and great accuracy, and contained so little lead that inversion was accomplished without the slightest difficulty. On the other hand, Samples 119 and A-C were less perfectly clarified by 23-cc. portions of the writer's lead solution, corresponding to 31 cc. of the usual solutions. Only with difficulty could the filtrates from these samples be polarized accurately; and they contained so much lead that the inversion process was materially retarded by the precipitation of lead chloride, and replacement of the strongly ionized hydrochloric acid by weakly dissociated acetic acid.[2]

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[1] 300 grams of lead acetate, 100 grams litharge, 1 liter of water.

[2] Samples 119 and A-C were average New Orleans third molasses,—not exceptionally black. The writer has seen specimens of the abnormal thirds mentioned in Table II which still gave dark filtrates after the addition of at least a half more basic acetate solution. Unfortunately, it was impossible to get one of these black samples for study, at the time of preparing this paper.

It has been a universal practice in the past in dealing with these very dark samples of molasses, to add a strongly basic lead solution so long as any precipitate continued to form, and if the filtrate was still too dark for convenient polarization, to continue the decolorization by using bone-black. The latter reagent has been found, however, to absorb considerable amounts of sugar, on which account its use has been discountenanced by the International Commission for Uniform Methods of Sugar Analysis.[1] Furthermore, the employment of excessive quantities and of strongly basic solutions of lead acetate has been strongly condemned during the past decade, so far as the clarification of materials containing invert sugar is concerned, on account of the danger of precipitating or isomerizing a portion of the sugar of the sample.[2]

Under these circumstances the molasses analyst may well have wondered what course he should pursue, and have determined that even an approach to accuracy is unattainable.

THE PROPOSED METHOD OF MOLASSES ANALYSIS.

Polarization in a Dilute Solution.—Many analysts who have had to work with deeply colored specimens of molasses have resorted at times to the expedient of making up the solution for polarization to something less than normal strength, instead of using bone-black and excessive amounts of lead solution; but it seems commonly to have been supposed by them that in so doing they were sacrificing accuracy to convenience. The writer is convinced, on the contrary, that the highest accuracy attainable in the polarization of dark materials is to be reached by working with comparatively weak solutions, and his own practice in most cases is to make up the normal weight of molasses—26.048 grams—to a final volume of 500 cc. Many, doubtless, to whose attention this paper may come, will be inclined to maintain that this procedure offers too great a chance for the multiplication of error. To such the answer may be returned that the process has been subjected to four years rigorous test, and that it has proved its worth, as will presently be shown.

Sources of Error in Molasses Analysis.—Before coming to a final decision regarding the merits of the procedure in question,

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[1] Abstract of Proceedings, Third Session International Commission, this Journal, **23**, 59 (1901).

[2] See Pellet's numerous papers on molasses analysis, published during the last twelve years in the *Bull. de l'Ass'n des Chimistes.*

we must consider its relation to the errors which may arise from the following sources:

(1) Inaccuracy in weighing and measuring.
(2) Use of too much or too basic lead solution.
(3) Change in rotatory power of the material in solution.
(4) Faulty construction of the polariscopic apparatus.
(5) Inaccuracy in reading the saccharimeter.

Certain of these errors have been touched upon in the preceding discussion; all of them will now be considered with such added detail as may be necessary.

Errors of Weighing and Measuring.—Since it is proposed that the normal weight of molasses shall be made up to a final volume of 500 cc., and *not* that one-fifth of the normal weight shall be made up to 100 cc., it is obvious that the usual procedure and the modification now proposed stand on the same footing with reference to errors of weighing.

So far as errors of measurement are concerned, it is clear that the "fifth-normal" method—as the proposed modification will be designated throughout the remainder of this paper—possesses incontestable advantages.

In the first place, a 500-cc. flask is more likely to be calibrated accurately than is a 100-cc. flask. The internal diameter of the neck of the larger container will ordinarily be from a quarter to a half greater than that of the smaller, and the cross-section of the larger neck will be from a half larger to twice as large as that of the smaller. It follows that, equal pains being taken in calibration, the mean error per 100 cc. should be about one-third as great in a 500-cc. flask as in one containing 100 cc.[1] This fact counts, furthermore, for greater accuracy every time that a solution is made up in the larger size of flask, since the mean error of an individual filling will be only one-third as great as in the flask of the smaller size.

In the second place, every sugar analyst will recall the tenacious foam which forms in making up molasses solutions, often defying ether spray and obscuring the meniscus, and the persistence with which the thick slimy mixture retains air bubbles of considerable size, not merely in the region of the meniscus, but frequently well down in the body of the flask. These sources of annoyance, which

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[1] See, in this connection, the specifications of the Committee for Coöperation with the National Bureau of Standards, this Journal, **26**, Proceedings, p. 22.

almost always appear in preparing a molasses solution of normal strength, are practically removed by working with the fifth-normal solution.

In the third place, use of the fifth-normal solution adds to the facility of analysis by giving the analyst more room to work in. Thick black molasses often requires a good deal of water for transference from the weighing-dish to the sugar flask, and it happens not infrequently that the analyst finds that he has not room enough left in a 100-cc. flask for the amount of lead solution which he needs to add. Furthermore, it is easier to remove stray drops of water from inside the neck of a large flask, and if a drop or two chance to be left the effect upon the concentration of the solution is only one-fifth as great as it would be in the small flask.

Errors Due to Lead Acetate Solution.—In discussing the customary method of analysis, reference was made to two errors arising from the use of lead acetate in clarification; and other errors were hinted at, such as the precipitation or isomerization of sugars. These errors, being of serious character, deserve further consideration in connection with the proposed fifth-normal procedure.

First, as to the error due to the bulk of the precipitate, it is obvious that it must vary as the ratio of the space occupied by the precipitate to the total volume of the mixture, or in the case of precipitates of constant bulk, inversely as the total volume of the mixture. This fact is very prettily demonstrated by certain of the writer's results.

Five of the molasses samples which were studied by the Scheibler dilution method,[1] respectively, Cuban No. 2, Cuban No. 4, 119, A-C, and McCahan, were made up in solutions of three concentrations. Of each sample, three 26-gram portions were taken; the same volume of lead subacetate solution was added to each of the three for clarification, enough being taken to decolorize the strongest solution sufficiently for accurate polarization, and the three were finally made up to the volumes of 100, 200 and 500 cc. All precautions were taken to insure the accuracy necessary in the work. The filtrates were protected from evaporation, their first portions being rejected; and before polarization they were acidified, if necessary, with acetic acid, allowance being made for any alteration of volume. Standardized flasks and polariscope tubes were used, the cover-glasses employed were free of blemishes, and previous

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[1] See pp. 698 and 699.

to each series of polarization zero-point determinations were made upon each polariscope tube, fitted with its covers.[1] Constant temperature was maintained during each set of observations, at least five settings and readings were made for every zero-point or polarization, and the mean observed polarization of each solution was corrected for the minute variation in zero-point, previously determined for the tube used with that solution. The corrected observed polarizations of the half- and fifth-normal solutions were multiplied respectively by two and by five, and the values so obtained were compared with the corrected observed polarization of the normal solution for the purpose of ascertaining the true polarization of the molasses under examination. In computing the true polarizations three sets of combinations of the observed values were made, *i. e.*, $a+b$, $a+c$ and $b+c$, and the mean of the three values derived from these combinations was taken in each case as the true polarization for that sample of molasses. The results which were thus obtained are shown in the following tabulation:[2]

TABLE VII.

		Normal solution.		Half-normal solution.		Fifth-normal solution.	
Sample.	True polarization.	Observed polarization.	Error.	Observed polarization.	Error.	Observed polarization.	Error.
Cuban No. 2.	31.08	31.92	+0.84	31.50	+0.42	31.26	+0.18
Cuban No. 4.	35.24	36.20	+0.96	35.80	+0.56	35.40	+0.16
No. 119	16.87	17.68	+0.81	17.26	+0.39	17.03	+0.16
A–C	17.12	18.06	+0.94	17.60	+0.48	17.30	+0.18
McCahan	27.03	28.16	+1.13	27.75	+0.72	27.18	+0.15
Means	.....	.....	+0.94	.....	+0.51	.....	+0.17

It is clear at a glance that the use of the fifth-normal solution offers a decided advantage with regard to the magnitude of the error due to the bulk of the lead precipitate; and still another point of vantage must be mentioned which does not show in the tabulation. It has been found in the course of this study that the

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[1] The writer finds it most satisfactory to use for his work the so-called "conversion tube," provided with a central aperture for the thermometer. Such tubes are readily filled and emptied through the side opening and if care is taken in rinsing, they may be used repeatedly without other cleaning.

[2] The papers of Wiechmann, and of Horne, upon the error due to the bulk of the lead precipitate, have called forth assertions from Gonnermann, Molenda, and Vermehren, to the effect that no such error is perceptible. It may be that the foregoing writers have failed to perceive it, but its existence is not to be denied on that account. When adequate precautions are taken, it is readily demonstrable.

bulks of these precipitates bear a fairly constant ratio to the amounts of lead solution used in clarification. Now, as has been said, enough of the reagent was added in all the solutions represented in the foregoing table to clarify the normal solutions thoroughly. If, as would have been the case in routine analytical work, the aim had been merely to decolorize the fifth-normal solutions sufficiently for accurate polarization, much smaller quantities of the acetate reagent would have sufficed. Thus, it has been found that Sample 119 is clarified better in fifth-normal solution by 8 cc. of the writer's lead acetate than by 22 cc. in a normal solution. Therefore, since the bulk of the lead precipitate and the error due thereto are proportional to the amount of lead solution employed, this error would be reduced to about one-third of the value given in the table, *e. g.*, to 0.05°-0.06° V. in routine analyses of such molasses.

Another argument for employing the fifth-normal procedure in molasses polarization is that we are able thereby to diminish the excess of lead which appears in the clarified solutions. The first portions of subacetate solution which are used for clarification give up most of their lead to the precipitate of coloring-matters, and comparatively little of the metal remains dissolved. As more of the reagent is added precipitation continues, but at the same time a constantly increasing proportion of the lead appears in the filtrate rather than in the precipitate. As has been said already, this accumulation of lead acetate in the normal sugar solution may at times become sufficient to interfere with inversion. The following experiment is instructive in this connection.

Two 26-gram portions of molasses Sample 119 were taken, one of which was treated with 22 cc. of basic acetate solution and made up to 100 cc., while the other received 11 cc. of the lead reagent and was made up to 500 cc.[1] The lead in the two filtrates was determined as sulphate with the following results.:

(1) *Normal Solution.*—Fifty cc. of filtrate gave 1.2370 grams lead sulphate, corresponding to 0.8530 gram lead oxide, sufficient for the neutralization of 0.2977 gram hydrochloric acid.

(2) *Fifth-normal Solution.*—Fifty cc. of filtrate gave 0.0775 gram lead sulphate, corresponding to 0.0534 gram lead oxide enough to neutralize 0.0186 gram hydrochloric acid.

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[1] The filtrate from the mixture of normal concentration was about two and one-half times as strongly colored as the other, despite the fact that it had received twice the quantity of lead acetate.

Five cc. of hydrochloric acid (sp. gr. 1.19), the amount ordinarily used in inverting 50 cc. of a sugar solution, contain about 2.261 grams of HCl, and of this amount 13.2 per cent. would be neutralized by the lead salts contained in 50 cc. of the foregoing normal filtrate, whereas only 0.82 per cent. would be neutralized by an equal volume of the fifth-normal solution.

Retardation of inversion is, however, only one of the ways in which the presence of an excess of lead subacetate in a sugar solution may interfere with accurate analysis of the latter. For example, it was found some years ago by C. H. Gill[1] that the polarization of a molasses solution may be raised considerably by the addition of an excess of basic lead acetate, not merely through the formation of a bulky precipitate, but in consequence of some action of the reagent upon the sugars themselves. The increase in polarization, which is produced only in the presence of invert sugar and in an alkaline solution, is roughly proportional to the excess of lead added and is destroyed by acidification of the solution. It is believed to result from the formation, in alkaline solution, of a soluble compound of lead and levulose whose behavior toward polarized light is very different from that of levulose itself. Gill recommended the addition of sulphurous acid to the clarified solution for the purpose of destroying this compound and of restoring the polarization to its proper value; and Spencer, somewhat later, proposed the use of acetic acid for the same purpose. Still later, it was suggested by Edson[2] that a certain amount of reducing sugar is actually precipitated when basic acetate is used for clarifying cane-molasses, and it was recommended that neutral acetate be employed in its place for this purpose.[3] Still more recently, this doctrine has been advocated vigorously in France, especially by Pellet.[4]

It is not easy to decide as to the soundness of the various allegations regarding the precipitability of levulose. Edson's publication on the subject was very scanty, and his conclusions were opposed strongly by Weld[5]; and though Pellet has published many papers dealing with the question, and has cited much experimental evidence, his work is not always well planned and his arguments

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[1] *J. Chem. Soc.*, April, 1871, p. 91.

[2] *J. Anal. Appl. Chem.*, 4, 381 (1890).

[3] See also Bull. **46**, revised edition, Bureau of Chemistry, U. S. Dept. of Agr., p. 39.

[4] *Bull. de l'Ass'n des Chemistes*, **13**, 757, 836; **14**, 28, 131; **15**, 605.

[5] *J. Anal. Appl. Chem.*, **5**, 310 (1891).

are not always justified by his facts. This much may be said, however; if it *be* true that neutral or acidified lead acetate should be used in clarifying molasses for analysis, polarization in fifth-normal solutions is decidedly advantageous, for, as Pellet himself admits, the neutral acetate of lead is so poor a clarifying agent that it may fail to decolorize dark molasses far enough to permit polarization, even in a 100 mm. tube.[1] It may be said, furthermore, that there seems to be very little danger of precipitating levulose, even when a strongly basic lead solution is employed, in working at fifth-normal concentration. The writer has saved many of the precipitates obtained in the routine clarification of dark molasses, and after washing them free of soluble sugars and decomposing them with carbon dioxide and hydrogen sulphide, has tested the residues for glucoses with Fehling's solution and with phenylhydrazine. No sign of the precipitation of levulose has been observed as yet.[2]

Errors Due to Changes in Rotatory Power of Materials in Solution.—It is well understood that the specific rotatory powers of all sugars are liable to variation on a number of accounts. Changes in concentration and temperature, and the influence of other solutes which may be present in the sugar solution, are recognized to be the most important causes of variation, and the question may be raised legitimately whether any of these influences tend to favor either the usual or the "fifth-normal" procedure rather than the other.

The effect of changes of concentration upon the specific rotatory power of sucrose has been studied by many investigators, with a variety of results. Certain writers—the more important being Hesse,[3] Schmitz,[4] Tollens,[5] and Seyffart[6]—have published data which indicate that the specific rotatory power increases slightly within the limits of concentration represented by the Ventzke scale, as the proportion of sugar in the solution decreases. Tollens,[7] however, has expressed the opinion in his later papers that the specific rotation increases for a time only, as the concentration decreases,

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[1] *Bull. de l'Ass'n des Chemistes*, **15**, 607 (1897).

[2] This question is being investigated in the writer's laboratory, and will be discussed fully in a later communication.

[3] *Ann. Chem.* (Liebig), **176**, 97.

[4] *Ber. chem. Ges.*, 10, 1414 (1877).

[5] *Ibid.*, 10, 1043.

[6] Pogg. *Ann.*, 2nd ser., **41**, 113 (1890).

[7] *Ber. chem. Ges.*, **17**, 1751.

that it reaches a maximum in the region of $C = 20$, and that it decreases from that point until it reaches the hypothetical value 66.386° at $C = 0$. Certain results obtained by Nasini and Villavecchia[1] tend to support the latter view.

Formulae have been published, giving the specific rotation in terms of the concentration, and supporting the views held respectively by Schmitz,[2] and by Tollens, and Nasini and Villavecchia.[3] With the aid of these the writer has calculated the specific rotatory powers for sucrose solutions of six concentrations, together with the Ventzke polarizations as modified by the variations in specific rotation.

TABLE VIII.

		Schmitz.		Tollens-Nasini-Villavecchia.	
$C =$ grams in 100 cc.	Nominal polarization.	$[\alpha]_D^{20}$	Polarization.	$[\alpha]_D^{20}$	Polarization.
26.0	100.00	66.332	100.00	66.502	100.00
19.5	75.00	66.364	75.03	66.515	75.01
13.0	50.00	66.426	50.08	66.508	50.01
6.5	25.00	66.471	25.05	66.481	24.99
2.6	10.00	66.587	10.04	66.456	9.99
1.3	5.00	66.612	5.02	66.446	5.00

Although the relations of the two sets of values for $[\alpha]_D$ differ very noticeably, it will be seen that the effect of their differences upon the polarizations is very slight; too slight, indeed, to be of any consequence in the region where molasses polarizations would fall. Further evidence of this fact is afforded by the following experimental results.

Four sucrose solutions were prepared, two of which contained about 6.5 grams in 100 cc., while the others were diluted to exactly one-fifth the concentration of the first two. These solutions were polarized in a 200-mm. tube with the following results:

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[1] "Sul peso normale pei saccarimetri," Rome, 1891.

[2] $[\alpha]_D^{20} = 66.639 - 0.02082\,C + 0.000034603\,C^2$ (Schmitz). "Optical Rotation of Organic Substances," Landolt-Long, p. 597.

[3] $[\alpha]_D^{20} = 66.435 + 0.00870\,C - 0.000235\,C^2$. Calculated by Landolt on the basis of observations by Tollens, and Nasini and Villavecchia, *Ibid.*, p. 465.

TABLE IX.

		Solution 1.		Solution 2.	
	Zero error.	Full strength.	Fifth strength.	Full strength.	Fifth strength
	+0.02°	25.00°	5.00°	24.32°	4.85°
	—0.02°	24.95°	4.95	24.32°	4.88°
	—0.02°	25.05°	5.00°	24.35°	4.88°
	—0.02°	25.00°	4.95°	24.35°	4.90°
	0.00°	25.05°	5.05°	24.30°	4.90°
	0.00°	.....	5.00°	24.32°	4.88°
	+0.02°	.....	4.95°	24.32°	4.85°
	0.00°	.....	5.00°	24.35°	4.82°
	0.00°	.....	5.05°	24.35°	4.88°
	+0.02°	.....	5.00°	24.30°	4.85°
Means:	0.00°	25.01°	4.995°	24.328°	4.869°
			5		5
			24.975°		24.345°
Mean errors.	±0.005°	±0.02°	±0.065°	±0.007°	±0.040°

It is clear that the results obtained by polarizing a sucrose solution of one-fifth the usual concentration and multiplying the observed polarization by 5, agree very closely with those obtained in polarizing the solution of full strength.

The changes undergone by the specific rotatory power of invert sugar, in consequence of variation in the concentration of its solutions, have been studied by Gubbe[1] and by Ost,[2] and have been found somewhat greater than those observed for sucrose. Taking Gubbe's "concentration" formula as the basis of reckoning,[3] the writer has computed the specific rotations and the corresponding Ventzke polarizations for solutions of four concentrations within the range of the amounts contained in molasses.

TABLE X.

Concentration.	$[\alpha]_D^{20}$	Polarization.
8.421	—19.961	—9.70
4.210	—19.809	—4.81
1.684	—19.718	—1.92
0.842	—19.687	—0.96

With the aid of these figures it is possible to calculate the effect of alterations in concentration on the polarization of molasses

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[1] *Ber. chem Ges.*, **18**, 2207.

[2] *Ibid.*, **24**, 1636.

[3] $[\alpha]_D^{20} = -19.657 - 0.0361\,C$. "Optical Rotation of Organic Substances," Landolt-Long, p. 592.

solutions. For the purpose of this computation we may assume the following data:

TABLE XI.

	High-grade molasses.		Low-grade molasses.	
	Sucrose.	Invert sugar.	Sucrose.	Invert sugar.
Sugar percentages	50.00	16.20	25.00	32.40
Concentration in normal solution	13.00	4.21	6.50	8.42
Concentration in fifth-normal "	2.60	0.84	1.30	1.68

Taking the sucrose polarizations given in Table VIII and calculated on the basis of the Schmitz formula, we have the following results:

TABLE XII.

	High-grade molasses.		Low-grade molasses.	
	Normal.	Fifth normal.	Normal.	Fifth-normal.
Sucrose polarization	50.08°	10.04	25.05°	5.02°
Invert sugar polarization	—4.81°	—0.96°	—9.70°	—1.92°
Direct polarization	45.27°	9.08°	15.35°	3.10°
		5		5
		45.40°		15.50°
Fifth-normal result high, by		0.13°		0.15°

With regard to the changes of specific rotatory power which would arise from making up and polarizing molasses solutions at some other temperature than the standard one of 20° C., it is impossible to see that there would be any choice between the use of solutions of normal or fifth-normal strength.

The influence of the non-saccharine materials present in molasses solutions upon the optical activity of the sugars has not been studied in connection with the proposed procedure. All that can be said at present is that the polarizations of normal molasses filtrates which have been diluted exactly five times compare with the original polarizations as follows:

TABLE XIII.

		Second molasses.		Third molasses.	
	Zero error.	Full strength.	Fifth strength.	Full strength.	Fifth strength.
	+0.02°	25.25°	5.10°	18.45°	3.82°
	0.08°	25.20°	5.15°	17.90	3.75°
	0.05°	25.32	5.15°	18.55°	3.75°
	0.02°	25.25°	5.10°	18.10°	3.72°
	0.08°	25.22°	5.12°	18.60°	3.78°
	0.05°	25.25°	5.15°	17.85°	3.72°
	0.05°	25.32°	5.10°	18.30°	3.75°
	0.05°	25.28°	5.15°	18.20°	3.75°
	0.05°	25.30°	5.15°	18.35°	3.72°
	0.05°	25.20°	5.12°	18.15°	3.72°
Means...	+0.05°	25.254°	5.129°	18.25°	3.748°
		—0.05°	—0.05°	—0.05°	—0.05°
Corrected means		25.20°	5.079°	18.20°	3.698°
			5		5
Fifth-strength polarizations × 5			25.39°		18.49°
Fifth-strength results, high by			0.19°		0.29°

It is interesting to notice that these experimental results confirm the prediction of Table XII to the effect that polarizations obtained by use of the fifth-normal solution will be slightly higher, for mixtures of sucrose and invert sugar, than the direct polarizations of normal solutions, when there is no "lead precipitate" error to be reckoned with.

In connection with the subject of specific rotation, it should be said that the factor to be used as a divisor in the Clerget equation deserves further study with relation to the problem of molasses analysis. It has been shown by Herzfeld[1] to vary according to the concentration of sucrose in the solution to be inverted, and it is known also to vary according to the concentration of the hydrochloric acid in such a solution.[2] Furthermore, as Tolman[3] pointed out a few years ago, it varies according to the amount of invert sugar which is present together with sucrose in the material under examination. The writer is using at present the value 142, having found that the results thus obtained agree well with those obtained by determining sucrose in the chemical way, but he pro-

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[1] Stammer's Jahresber, 1890, p. 142.

[2] Lippmann : *Chemie der Zuckerarten* (2nd Edition), p. 800.

[3] This JOURNAL, **24**, 515 (1902); *Bull.* **73**, Bureau of Chem., U. S. Dept. of Agr., p. 75.

poses to investigate the question of this factor at the first opportunity.

Errors Due to Faulty Apparatus and Observation.—The sources of error which already have been discussed have been shown either to favor employment of the "fifth-normal" procedure or to be so slight that the danger of multiplication need not be feared. The errors which now remain to be considered are on the contrary of a more threatening character, since they never can be wholly eliminated and are certain, almost without exception, to be multiplied by 5 in working with fifth-normal sugar solutions. They demand, therefore, serious and detailed consideration, for which there is too little space in the present communication. They will be discussed fully in a paper now in course of preparation upon the graduation of Ventzke saccharimeters and the degree of precision attainable in their employment, and for the moment they can be referred to only in the briefest fashion.

The writer and several of his acquaintances, whose saccharimeters are provided with good scales and verniers, have found it easy to read the scale to about one-quarter of a tenth degree, *i. e.*, to about 0.02°–0.03° V. Furthermore, when the optical parts of the saccharimeter are in good order and the illumination is properly controlled, movement of the wedge through 0.05° will produce a change in the field in the vicinity of the zero-point, which is detected readily by the eye of a practiced observer. When a number of observations are made with proper care, the eye being rested between them, they will be found to differ very slightly and the mean error of their average value will be very small indeed. Evidence of this is given in the errors shown in Table IX.

It is to be understood, of course, that the mean error of a polarization includes in addition to the error of the polarization itself, the error of a zero-point determination taken at the same time. The sum of these mean observation errors should not be more than about ±0.03° V.[1] when quartz plates or fairly colorless solutions are being polarized. If, however, it is attempted to work with dark solutions the magnitude of the error increases rapidly. Thus, the mean error of the value 25.20°, given in Table XIII as the polarization of a full-strength solution of second molasses, is ±0.025° V., whereas the error of the corresponding value of 18.20°

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[1] Compare Schönrock's statement, in "Optical Rotation of Optical Solutions," Landolt-Long, p. 388.

given for the third molasses is about ±0.09°, the latter solution having been about twice as dark as the former.

With such clear solutions as are readily obtainable through use of the fifth-normal procedure the observation error should be kept down to ±0.03°, and in multiplying the observed polarization by 5, to compensate for the dilution of the solution, the error will also be multiplied and will become ±0.15°, which is less than would be obtained ordinarily in polarizing dark solutions of normal strength.

That the degree of precision just described is attainable in routine every-day work has been shown to the writer's satisfaction by the experience of himself and certain of his acquaintances during the past two years; but it is not attainable unless suitable precautions are taken. Faulty illumination, flaws in the prisms or wedges, optically active cover glasses, observation tubes whose ends are not cut in planes perpendicular to their axes, illy divided or corroded scales—all may be responsible for errors far greater than those which have been discussed. It is a part of the analyst's business, however, to know his tools and to guard against errors of this sort.

CONCLUSION.

We now have seen that the errors which may arise in weighing and measuring are likely to favor adoption of the fifth-normal procedure; that those due in one way or another to the use of lead acetate in clarification are decidedly in its favor; that there is little choice between the usual and the proposed procedures so far as the influence of specific rotation is concerned; and finally, that with care the use of fifth-normal solutions for polarization may diminish the observation error in the assay of dark molasses, although without care the opportunity for such error is unquestionably increased.

Of course, no claim is made that precision is attainable by adoption of this procedure; but after four years of routine test in factory analysis and two of careful critical study the writer is convinced that its use has opened the way to an advance in accuracy.

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