THE DETERMINATION OF THE DENSITY OF MOLASSES.

By F. W. HAYES and E. P. HEDLEY.

Last year, the Committee of Chemical Control (Proc. S.A. Sugar Tech. Assn., 1931, 10) recorded that they had discussed the methods in use for determining the density of molasses, and promised the publication of the results of a series of comparative tests using hydrometer (1 : 1 dilution), refractometer and pyknometer methods.

These tests have now been carried out and are recorded in what follows. Although this subject has been investigated by many workers it has always been done in countries where mixed canes are crushed, and it was thought that perhaps some uniformity in results might be found in South African Molasses. South Africa at present mills only Uba cane, and is therefore unique in having an apparently uniform raw material to deal with.

In the accompanying table (No. 1.) is given a summary of the figures obtained. All the experimental work was done in duplicate or triplicate, and whilst these results, where experimental conditions were identical, agreed well amongst themselves, beyond this there is no apparent uniformity.

Description of Methods (Table 1).

Column 1.—Abbé Instrument used, with strong daylight globe. Molasses heated to 80° C. for ½ hour, cooled overnight and skimmed.

Column 2.—Same solution used as for hydrometer, 1,000 gms. untreated molasses and 1,000 gms. water.

Column 3.—Pyknometer Method :— The sample is placed in a 250 ml. beaker and heated at 80° C. in an oven for ½ hour. Allowed to cool and stood at room temperature overnight. The froth is skimmed from the surface and the sample poured into a funnel with a glass rod ground into the stem to serve as a stopper. After filling the funnel the rod is withdrawn, and the molasses allowed to run into the pyknometer. This consists merely of a narrow-necked 100 ml. flask, cut off and ground to the 100 ml. mark.

Column 4.—A 25 gm. Specific Gravity bottle fitted with a thermometer was used. 25 gms. molasses (treated as in 1 and 3) accurately diluted with 25 gms. of water. All determinations made at 26.5° C.

Column 5.—Official Method of spindling with standardised hydrometer, 1,000 gms. untreated molasses and 1,000 gms. H_2O.

Discussion of Methods Used.

Refractive Solids (Undiluted).—The Refractometer with undiluted molasses gave more satisfactory results than any other method. The advantage of rapidity is obvious, and even with dark products the experimental error need not exceed $\pm$ .05%. Many investigators incline to the view that the refractometer gives figures which are more reliable and nearer the truth than other methods. Sandera ([1]), Browne ([2]) and Markovits ([3]) might be mentioned amongst these. The last named, however, points out that although the refraction of carbohydrate and other constituents of molasses does not appear to vary much, yet the comparisons are based on total solids by drying at 102° C., at which temperature some of the constituents in such an impure material as molasses may react to form decomposition products.

Refractive Solids (50% Solution).—This figure shows a rise of about 1.5 on dilution with a series of tests carried out with the refractometer on unheated samples. This confirms the results found by Schoorl ([4]), who shows a similar rise on a 24% molasses solution, and attributes the difference to the influence of salts on the refraction in diluted solutions ; maintaining that while tables constructed for pure sucrose are used to calculate the result, then with impure solutions like molasses the error will increase in proportion to the dilution and the salt content.

Again, it is shown by Browne (Handbook of Sugar Analysis, p. 66) and Spencer and Meade (Handbook for Cane Sug. Manuf. and Chems. 1929, p. 322) that the refractometric method suffers from the same contraction error as spindling, as the volume of a water and molasses solution is less than the sum of the individual volumes.

Pyknometer (undiluted).—These results compare well with neither the refractometer nor the hydrometer, and no fixed factor or relationship can be found. Extraordinary difficulty was experienced in freeing many samples from entrained air and herein lies the main source of error in this method. Note particularly samples Nos. 3 and 4. This molasses was extremely viscous and it was impossible to get rid of all occluded gases.

Duplicate tests of all samples under the same conditions agreed well.

Whilst the error introduced by gas in suspension is the principal objection to the pyknometer, there are other sources of inaccuracy which may be summarised as follows :—

(A.)—In converting from specific gravity to degrees Brix tables worked on pure sucrose are used.

(B.)—Heating to 80° C. even for ½ hour is not to be recommended. A duplicate series was run, heating only to 60° C., and in all cases these showed a higher specific gravity. Undoubtedly decomposition of some sort at these temperatures does take place and the literature on the subject, though not very extensive, is fairly conclusive. Gustavson and Pierce ([5]) found that 1.96% of the substance (exclusive of water and an unidentified oil) is driven off at temperatures up to 70° C. and this distillate was found to contain SO_2, NH_3, and iodoform producing substances. Markovits ([2]) further states that the decomposition products are larger in cane than in beet molasses and can be given off at temperatures much below 70° C. Spencer and Meade ([6]) and Prinsen Geerligs ([7]) point to the breaking up of laevulose and possible formation of water. Further references are given ([8]).

(C.)—Evaporation whilst heating and standing overnight.

Pyknometer (50% Solution).—This figure roughly approximates that given by the hydrometer. But there is no definite relationship and any concordance is probably due to a compensation of errors. Subject to the same dilution errors as the hydrometer and refractometer, there is the additional irregularity in converting specific gravity to degrees Brix using sucrose tables. The heated sample was used and a small inaccuracy in weighing would occur with any air left in suspension.

Brix Hydrometer (50% Solution).—Little need be said regarding this method. Duplicate tests agreed well but there is no fixed relationship to the Refractive Solids, though results are always higher.

The errors due to dilution and the different specific gravities of the salts in solution have been gone into very fully by various writers. Browne (2) (p.32) shows maximum contractions of from .8937 c.cs. for 55.42 gms. sucrose and 44.58 gms. water to 0.9958 c.cs. for 56 gms. sucrose and 44 gms. water. Again, Spencer and Meade (6) (p. 321) state that the difference in figures given by spindling at varying dilutions is partly due to the contraction of a sugar solution in water and partly to a similar contraction of the solution of the salts in the molasses. Further references are given (9).

Further Methods Used.

Newkirk's Vacuum Pyknometer (10).—He states "Investigations at this Bureau established the fact that the removal of gases was best effected by use of vacuum." A modified form of the pyknometer was used and determinations made on several of the samples which had presented difficulty with the ordinary pyknometer method. However, whilst a few samples lost air more readily than by heating, and showed an increase in specific gravity over the first method, others proved most refractory in this respect, and No. 3 stood for 8 months in the pyknometer under vacuum and still showed considerable gas in suspension.

Sidersky's Method was used and gave similar results to the pyknometer with undiluted molasses.

The direct determination of water in molasses by distillation with an immiscible liquid of low Boiling Point has been used by various investigators. We are now carrying out experiments on azeotropic mixtures, and intend at a future date to communicate to this body the results we are obtaining.

In conclusion, we would point out that though the work done on densimetric methods has brought nothing new to light, yet it bears out the contention of other workers that there is no satisfactory correlation of results with the different methods. If some arbitrary standard is not to be adopted it would appear that a vast amount of work has still to be done on the subject.

Markovits (3) concludes "It is impossible to obtain the correct water content of sugar-house by-products by the existing analytical methods. It is also impossible to determine accurately the total solids. The best we can accomplish is to determine the non-volatile solids with a fair degree of accuracy." And Prinsen Geerligs (11) "No fixed factor can be found for converting degrees Brix to dry substance."

References.

(1) Z. Zuckerind. Czechoslovak. Rep. (1928) **53,** 1.

(2) Handbook of Sugar Analysis (1912 ed.).

(3) The Planter and Sugar Manufacturer (1926), **76,** No. 5, 90–91.

(4) Archief (1921), **29,** No. 31, 1055–1059.

(5) Ind. and Eng. Chem. (1924), **16,** No. 2, 167–168.

(6) Handbook for Cane Sugar Manuf. and Chemists (1929), p. 324.

(7) Cane Sugar and its Manufacture (1924), p .41.

(8) Geerligs, Int. Sug. Jour. (1893), **25,** 407.
Lafar, Oe. Zeit. Zuck (1913), **42,** 737.
Schneller, Journ. of A.O.A.C. (1926), **9,** No. 2, 156–165.

(9) Browne, Handbook of Sugar Analysis (1912), pp. 32 and 35.
Prinsen Geerligs, Cane Sugar and its Manufacture (2nd ed.), pp. 307 and 309.
Noel Deerr, Cane Sugar (1921), p. 490.

(10) Technologic Paper No. 161., Bur. of Stands. Wash., D.C., U.S.A. (1920).

(11) Cane Sugar and its Manufacture (1924), p. 309.

TABLE 1.

Sample No.	Refractive Solids Undiluted Molasses	Refractive Solids 50% Dilution	Pyknometer Undiluted	Pyknometer 50% dilution	Brix Hydrometer 50% dilution
	1	2	3	4	5
1	78.74	79.2	78.3	83.7	82.7
2	77.20	77.1	78.1	80.3	78.8
3	81.94	83.2	66.0	85.9	85.6
4	83.32	84.72	77.3	87.8	87.64
5	80.19	81.6	74.8	83.0	83.2
6	80.78	81.04	80.9	84.0	83.62
7	80.34	82.0	77.95	—	83.8
8	81.12	82.60	82.2	84.8	84.56
9	72.74	73.5	74.5	—	75.4
10	78.99	83.1	83.8	—	85.6
11	77.79	—	78.35	—	79.3
12	78.69	78.42	82.4	82.9	82.46
13	79.64	81.3	80.9	—	82.8
14	82.98	84.54	84.8	86.1	86.34
15	78.39	79.4	79.45	80.8	81.0
16	81.87	82.68	83.65	85.3	84.94
17	78.89	79.26	81.85	82.8	82.80
18	80.80	82.26	81.8	82.8	83.18
19	80.50	82.26	85.2	85.7	86.56

The bracketed figures refer to different samples from the same factory.

Experiment Station,
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CHAIRMAN: This paper is another example of the Experiment Station work on our behalf. I hope you will have a good discussion on it. It is an important matter and one to which attention has been given for some time.

Mr. BECHARD: The authors of this paper refer to the irregularity of converting specific gravity to Brix. Surely it is only an apparent error because the Brix spindles are graduated with pure sucrose. Whatever type you use, whether you convert it or otherwise, there is not much in it.

Mr. HAYES: The error will still exist in converting the observed degree Brix, or rather in reconverting specific gravity to degrees Brix, whether the Brix hydrometer is graduated using pure sucrose or not. You are first determining specific gravity, then bringing that to degrees Brix using tables worked on pure sucrose. The error will depend entirely on the impurity of the molasses solutions.

Mr. BLACKLOCK: I think Mr. Hayes has brought out many objections to the 50% method laid down by the Committee of Standardisation of Chemical Control which is based on the reading given by a standard hydrometer in a 50% solution (by weight) of the molasses. This reading corrected for temperature and multiplied by two is taken as the "Brix" of the molasses. There are, of course, many objections to this method, but for mill routine work it will give an apparent purity comparable with the purities obtained in earlier stages of the chemical control sequence. In my opinion it would be more correct and much more convenient to use the Refractometer all through. This instrument can be obtained with a scale giving direct readings of sugar solids, and this scale can be verified from time to time by reference to standard solutions of pure sugar made up in the Laboratory. Generally speaking we have found it possible to read treacles and molasses direct. When dilution methods are used the Refractometer gives invariably a lower and therefore a more correct reading than the Hydrometer. Also the doubled Refractometer reading of the 50% solution agrees very closely with the reading of the undiluted molasses on the same instrument. I believe that the reading given on the Refractometer by the original molasses is a figure more nearly approximating the true total solids than that obtained by any other means, excepting actual drying.

With regard to molasses shipped abroad, this is usually controlled by a density specification, and the Beaumé scale is sometimes quoted in this connection. Obviously the only possible procedure is to adopt the density method used by the chemist representing the buyers. Generally this is a specific gravity method which involves the direct weighing of the de-aerated molasses in some form of pyknometer and converting the specific gravity figure found into degrees Beaumé or Brix by means of the usual tables. This always gives results somewhat higher than the Association's official method, the difference being round about 1.5 but may be much more in the presence of appreciable quantities of insoluble matter suspended in the molasses. As there seems to be no correlation between the two, no factor can be applied to or adjustment made to the factory recorded density to make it comparable with the results from overseas. In respect of molasses shipments then the official method may be departed from and the density calculated from the specific gravity arrived at by weighing in a pyknometer. I have a few figures here which may be of interest.

Sample	Refract. direct	Refract. 50%	Sidersky's method sp. gr.	Sidersky's method Brix	Hydrom. 50%	Solids on drying on quartz sand
A	78.1	79.2	1.4161	80.3	81.4	77.720
B	74.9	75.0	1.4081	79.1	80.6	
C	77.7	76.8	1.3988	78.3	80.0	

Mr. HAYES: What Mr. Blacklock says regarding the 50% solution and the present method as having been in force for a number of years, is perfectly correct; but there you are getting back to the same question as with the bagasse analysis. One standard method has been giving results over a number of years, and it is questionable whether it is advisable to change that method. But I am not in agreement regarding the use of the method right through the factory. You are taking the Brix direct of juices, but with an impure material like molasses, which you have to dilute; and thus introduce the error of the contraction of the solutions, you are not really getting a comparative density figure. Certainly on past years working you will get a fairer purity comparison with molasses than if you change to the use of the refractometer. I agree in that it would be advisable to use the refactometer right through the factory, as it has been shown there is really no difficulty in getting a clear reading with undiluted molasses. I do not think we should accept the so-called buyers' pyknometer method. One might almost say that with very viscous mill molasses you can get any figure you wish, depending entirely on the character of the molasses and the method of treatment. For instance the figure of 66° Brix for a molasses which gives something like 85° with 50% dilution cannot be called satisfactory. I don't know whether Mr. Blacklock has been dealing entirely with Refinery molasses, but I should say there would be far less difficulty with that than with some of the low grade mill products.

Mr. BIJOUX: I don't think it would be possible for us all at present to take refractometer readings owing to a shortage of instruments. It would be preferable if you were to obtain the weight per unit volume of the molasses by filling a litre flask with the substance and weighing same.

Mr. HAYES: You will still have to get over the difficulty of de-aerating the molasses. Once you get over that the method is satisfactory, the whole difficulty is to get rid of the entrained air.

CHAIRMAN: I notice that in methods No. 1 and 3 the molasses is heated to 80° for half an hour, cooled overnight and skimmed. In discussing No. 3 the disadvantage of heating is mentioned owing to the possibility of decomposition, but in method No. 1 that disadvantage is not mentioned, and the method is spoken of as a highly satisfactory one.

Mr. HAYES: With the refractometer method on undiluted molasses the sample was heated to 80°C. and treated in exactly the same way as with the pyknometer method so that we could get a direct comparison. At the same time we did a further series of samples without heating. In every case the heated sample showed a slightly higher refractometer figure than the unheated, although this difference was not consistent by any means. The sole reason for heating was to reveal any relation which might exist between refractometer and pyknometer figures. The refractometer results from the unheated sample and the sample heated and placed vacuum are as follows:—

	Unheated	Heated and Vacuum
2	76.45	77.20
4	83.39	83.32
6	79.48	80.78
8	80.99	81.12
17	77.73	78.89
18	80.67	80.80

CHAIRMAN: Is there not a possible way of approaching this question by making up artificial solutions containing approximately the constituents of molasses, in which you know exactly what you are putting in, and then trying out these various methods? If there is no drawback against the scheme it is one which might well be tried.

Mr. HAYES: I have no doubt this could be done if the exact composition of the molasses was obtained, but I think it would be very difficult to obtain a synthetic molasses. Mr. Deer has mentioned a method for obtaining accurately the weight per unit volume of molasses by mixing with oil of a known specific gravity. We have not tried this method as yet but it may lead to something.

Mr. BECHARD: The crux of the whole thing is this method of buying on the pyknometer method that the buyers have forced on us. I note what is said here under the pyknometer method (reads). I would like a little more assurance on this point. The main thing here points to the fact that in filling up the pyknometer there is considerable danger of including air. This was pointed out at a meeting with the buyers' analyst and he agreed it could not be guaranteed that in filling the pyknometer you did not occlude some further air. In view of the fact that this paper shows conclusively that the undiluted pyknometer method gives most discordant results and results which are highly unsatisfactory, it is up to the Sugar Industry to approach the buyers and point out that some satisfactory method of testing should be obtained, and try and get at a standard which would be more satisfactory. This paper tends to show that no possible method that is accurate can be devised, so it must be a method that would be a sort of via media as between buyers and sellers. It would have to be a method to give concordant results.

Mr. HAYES: What Mr. Bechard has just said brings us to the fixing of an arbitrary standard, which I mentioned in the paper. If we do that, the standard will have to be rigidly adhered to. The paper was written to show that according to our findings there is no fixed relationship between the various analytical methods. Another point Mr. Bechard mentioned was the entraining of air while the pyknometer is being filled. I don't think there is very much danger of this. Of course there is the possibility, but duplicate tests did not show very much difference with the same molasses, so that the difficulty lies with the entrained air which is already present in the sample, and not with that which may get in while filling the pyknometer. If the pyknometer is made according to the methods laid down, and filled with the funnel and glass rod, there is not much danger of air bubbles being trapped. Occasionally, right in the neck of the flask, you will get an air bubble caught, but on standing a while it will rise to the surface. I might say that the use of vacuum was most useful in showing the extent to which air could cause difficulty. We would take a molasses apparently free from air and on filling the special pyknometer and connecting it with the vacuum line the whole sample would froth up and bubbles appear.

Mr. BECHARD: There is of course another method of finding the actual volume. That method has been developed by Van't Hof at the Experiment Station at Java. He has applied it in bagasse to find the actual dry solids in bagasse. He used the pulsometer. By varying the pressure on the substance of which the volume has to be measured he finds the quantity of air that has either contracted or expanded under the varying tests. I don't know whether that has occurred to you.

Mr. HAYES: No, we have not come across that method in our work.

Dr. HEDLEY: I would like to congratulate Mr. Hayes on reading this paper. It is his maiden effort and I think he has done it well! I think the way he has answered the questions shows he knows his subject, and he has certainly done the work in the Experiment Station greatly to his credit, and I should like to say so before you all. (Loud applause).