# Refractive Index as a Measure of Dry Substance in Saccharine Products.*

By A. Hugh Bryan.

Dry substance determinations are the most difficult determinations a a chemist has to make, and again one of the most important. In sugar materials, containing many organic substances and also inorganic salts, various reactions and changes are going on when the sample is heated in the course of making a dry substance determination. Varying degrees of heat also tend to decompose these substances. Also, the length of time of heating is a very important factor. The accepted method for sugar compounds, where accurate results are desired, is the loss of weight at 70° C. when heated in vacuum. It has been found at that temperature that levulose shows little, if any, decomposition. Sugar chemists of Germany modify that procedure by drying at 65° to 70° C. in the air until all visible water is gone, and then heat for from 2 to 4 hours at 105° C. in vacuum, it being claimed that by first drying and then heating to 105° in vacuum, no sugar is decomposed. It is a fact, however, that if one makes two determinations of moisture on the same sample at different times, it is more than likely that the results will not check. Differences of as high as 0.5% have been noted, especially where the substance under examination is high in reducing sugars. It can hardly be expected to obtain a method for determining moisture accurately without a direct determination of this by drying. Such a procedure takes time, and at its best, so far, gives only approximate results.

The refractometer was first tried in sugar work by Strohmer (Zeit Ruben Zuckerind., Vol. 21, p. 256) in 1884 and again in 1886 by Muller (Ibid. Vol. 37, p. 91). They showing that the index depended on the concentration of solution. The latter investigator gave a table for estimating the dry substance of beet juices from the refractive index. Again in 1901, Stolle published a table for the above. All of these used the old forms of instruments. Tolman and Smith,[1] using the heatable prism instrument, such as is used today, and pictured later in this paper, found

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[1]Jour. Amer. Chem. Soc. (1906), *28*, 1476.

that for equal concentrations, all sugars have about the same index of refraction. Main[1] published tables of water content from refractive index in 1907, and called attention to the accuracy of this method, as compared with the true dry substance. Since that time the literature has been full of articles on this method of determining the dry substance.

All authors, with but few exceptions, claim much for this method as a quick one and yielding comparable results. They all agree that the results so obtained are nearer the true dry substance than by obtaining the dry substance from the specific gravity. The substances dissolved along with the sugar seemingly have a closer refractive index to sugar than specific gravity.

Working on syrups of various origins, I obtained the following average figures.[2] The method for true dry substance was loss of weight in vacuum at 70° C. The table of Prinsen Geerligs, and also his corrections for temperature were used. These are given later in this paper.

### IN CASE OF MAPLE SYRUP.

Thirteen samples were examined. In only one case was the refractometer dry substance higher than the true, and in all others the true dry substance was higher. This difference ranged from 0.20% to 1.34% with an average of 0.50%.

### WITH CANE SYRUP.

Ten samples were examined. In three cases the refractometer dry substance was higher than the true by 0.16%, 0.34%, 0.62%. The other cases range from 0.24% to 0.93%, or an average difference on the whole of 0.29%.

### HONEYS.

Twenty-four samples were examined. In 2 cases the refractometer dry substance was higher than the true by 0.21% and 0.91%. In all the rest it was lower by from 1.15% to 2.52%, with an average of 1.45%. This is the greatest difference noted. One of three causes or all may account for this large difference. (1) The actual dry substance may not be right, viz., this product may not give up all of its water at 70° in vacuum, or, (2) the dextrin of the honey may change the refractive index of the

[1]Inter. Sugar J. (1907), *9*, 481.

[2]NOTE. See Jour. Amer. Chem. Soc. (1908), *30*, 1443, for a previous paper on this subject by the author.

whole, or, (3) the values given in the table for dry substance from refractive index may not be right.

### COMMERCIAL GLUCOSE.

The two samples examined show the refractive index dry substance higher by 0.27% than the real dry substance. The closeness of these readings would tend to disprove the second cause for honey.

### CANE MOLASSES.

Seventeen samples were examined. In 3 cases the refractometer dry substance was higher than the true by 0.16%, 0.39%, and 0.59%. In all the rest it was lower by from 0.38% to 1.53%. The average difference was 0.79%.

### BEET MOLASSES.

Fifteen samples were examined. In all cases the true dry substance was higher than the refractometer. The difference varied from 0.38% to 1.83%, with an average of 1.08%. When the original substance was diluted one-half with water, and a reading made on this, the dry substance obtained was doubled. The results showed 5 cases where the refractive index dry substance was higher than the true by from 0.25% to 0.53%. In all other cases, the true was the highest by from 0.39% to 1.62%, with an average of 0.36%. It is seen then by dilution, the average difference between the true dry substance and refractometer has dropped from 1.08% to 0.36%. The results then are nearer the true dry substance. This comes about by being able to get a clearer field and thereby a closer reading.

However, later work has shown that this dilution with water, even though it has brought the dry substance by refractometer nearer the true dry substance, introduces a serious error. When water is added to molasses there is a contraction in volume.

This contraction has been taken into account in the construction of specific gravity and refractometer table for pure sugars so that solutions of the latter, whether mixed with water or a sugar syrup, will give the correct percentage of solids either by specific gravity or refractive index.

The impurities, however, which accompany sugars in solution in molasses, have not only a different specific gravity than sugar, but also a different contraction co-efficient, so that the solution diluted with water shows a different specific gravity or refractive index than that calculated from tables for pure sugars.

To reduce these variations of contraction to the minimum, a concentrated pure sugar solution is used as a dilutant. Results obtained with some cane molasses samples show the error that is introduced by the water dilution and also the effect of the sugar dilution.

| Sample No. | Undiluted Molasses. | Diluted Half With— | |
|---|---|---|---|
| | | Water. | Sugar Sol. |
| 1 | 80.57 | 83.24 | 80.91 |
| 2 | 72.32 | 72.94 | 72.21 |
| 3 | 77.92 | 78.44 | 77.91 |
| 4 | 73.92 | 75.34 | 73.81 |
| 5 | 82.05 | 84.44 | 82.41 |

In the undiluted form all of these can be easily read. The half dilution with water is anywhere from .62% to 2.7% higher than undiluted while the half dilution with sugar solution varies from 0.0 to 0.3%.

Tischtschenko (Z. des Vereins Deut. Zuckerind., Feb. 1909. 103), calls attention to this possible error in the determination and recommends the use of a pure sugar solution. Von Lippman corroborates the results (Deut. Zuckerind., 34. 1909. 401). It therefore behooves us to use sugar solution in diluting our dark colored solution in preference to water. The formula for calculating the dry substance when using a concentrated sugar solution as a dilutant is:

$$X = \frac{(A + B) C - BD}{A}$$

in which X=% dry substance of the original sample, (A) the grams of the original substance mixed with (B) the grams of concentrated pure sugar solution, (C) the % dry substance of the mixture obtained from its refractive index, and D= the % dry substance of the pure sugar solution obtained from its refractive index. The method of procedure is simply the preparation of a concentrated granulated sugar solution and mixing in a small beaker a weighed quantity of this with a weighed quantity of the original solution or sample, and taking refractive index of the mixture.

Summarizing the average results, we find that the refractometer dry substance is higher than the true.

| | Per Cent. |
|---|---|
| The difference in case of maple syrup | 0.50 |
| The difference in case of cane syrup | 0.29 |
| The difference in case of honeys | 1.45 |
| The difference in case of glucose | 0.27 |
| The difference in case of cane molasses | 0.79 |
| The difference in case of beet molasses | 1.08 |
| The difference in case of beet molasses (half) | 0.36 |

With the exception of the honeys and possibly cane molasses, also beet molasses undiluted, the differences are well within the error of determination of water by actual drying. By half dilution, the beet molasses is brought within the limits, and where dilution with sugar solution tried this difference would be cut down considerably. Cane molasses, showing 0.79%, might be considered within the limits, as a true moisture content on this material is a difficult task. Honeys are, then, the only ones whose difference is large, but it is hoped that with the work now being carried on, the reason for this difference will be obtained and a method for procedure be established for this grade of substance. However, there is one thing to be said in regard to the refractometer, that it is possible to obtain duplicate results that are identical, and different investigators should obtain identical results, which is a condition that does not exist with the other methods for dry substance determination in use now. The refractometer method has the advantage of being quick and not losing accuracy by speed, and then only small portions are necessary for a determination.

The method of making a dry substance determination is substantially this: The instrument (Fig. 1) is placed so that the light falls on the mirror (R) and this is turned on its axis to reflect the light up through the prism (B) and (A). The source of light can be daylight, but a better one is a 32 or higher candle power lamp. The tubular (D) is connected by rubber tubing to the source of water supply of constant temperature and the other tubular (E) has a rubber overflow connection. The thermometer is placed in its socket. The optical parts of the instrument are turned forward on the stand (a). By turning the catch (V) the prism B is swung open on (C) from prism (A) and a few drops of the solution to be examined is placed on the prism (A). Enough of the solution should be added so that on closing the prism (B) on (A) a part of the liquid is forced out. The optical parts are brought back into their original place.

The arm carrying the magnifying glass (L) should be down to the 1.3 end of the scale. Then by looking through the eyepiece (F), focusing the cross-hairs into plain view, the arm (L) is moved until a bright color appears in the lower half of the field. By turning the milled screw (M)

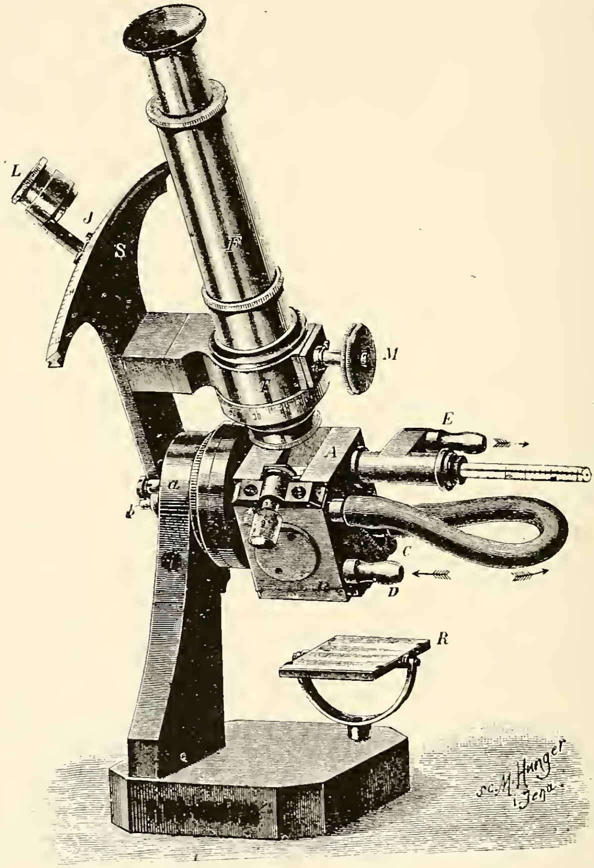


Fig. 1.

of the compensator the line of color is made more distinct; viz., there is sharpness of line dividing the light and the dark field. By moving the arm farther this line is brought up to a point where it coincides with the intersection of the cross-hairs. At this point, the index of refraction is read on the scale (J). At the same time the temperature is read on the thermometer.

The instrument should be tested first with water and its accuracy established thereby: Ref. Ind. of water at 20° being 1.3330. The substance to be examined should be at about the same temperature at which the readings are to be made. Therefore waiting a few minutes after applying the liquid to the prism, it could be considered that this is at the same temperature.

Tables have been prepared for converting the refractometer readings to dry substance or per cent. of moisture. To some of these previous reference has been made. Hugh Main, in the International Sugar Journal of 1907, Vol. 9, page 481, gives a table covering this. The readings are to be made at 20° C. Geerligs has published a table also for dry substance from the refractive index. The temperature of the reading is 28° C. and he has also prepared a table for corrections for other temperatures than 28°. These are now given:

*Geerlig's Table for Dry Substance in Sugar-House Products by Abbè Refractometer, at 28° C.*

(Intern. Sugar J., *10*, 69-70.)

| Index. | Per Cent. Dry Substance. | Decimals. | |
|---|---|---|---|
| 1.3335 | 1 | 0.0001 = 0.05 | 0.0010 = 0.75 |
| 1.3349 | 2 | 0.0002 = 0.1 | 0.0011 = 0.8 |
| 1.3364 | 3 | 0.0003 = 0.2 | 0.0012 = 0.8 |
| 1.3379 | 4 | 0.0004 = 0.25 | 0.0013 = 0.85 |
| 1.3394 | 5 | 0.0005 = 0.3 | 0.0014 = 0.9 |
| 1.3409 | 6 | 0.0006 = 0.4 | 0.0015 = 1.0 |
| 1.3424 | 7 | 0.0007 = 0.5 | |
| 1.3439 | 8 | 0.0008 = 0.6 | |
| 1.3454 | 9 | 0.0009 = 0.7 | |
| 1.3469 | 10 | | |
| 1.3484 | 11 | 0.0001 = 0.05 | |
| 1.3500 | 12 | 0.0002 = 0.1 | |
| 1.3516 | 13 | 0.0003 = 0.2 | |
| 1.3530 | 14 | 0.0004 = 0.25 | |
| 1.3546 | 15 | 0.0005 = 0.3 | |
| 1.3562 | 16 | 0.0006 = 0.4 | |
| 1.3578 | 17 | 0.0007 = 0.45 | |
| 1.3594 | 18 | 0.0008 = 0.5 | |
| 1.3611 | 19 | 0.0009 = 0.6 | |
| 1.3627 | 20 | 0.0010 = 0.65 | |
| 1.3644 | 21 | 0.0011 = 0.7 | |
| 1.3661 | 22 | 0.0012 = 0.75 | |
| 1.3678 | 23 | 0.0013 = 0.8 | |
| 1.3695 | 24 | 0.0014 = 0.85 | |
| 1.3712 | 25 | 0.0015 = 0.9 | |
| 1.3729 | 26 | 0.0016 = 0.95 | |
| 1.3746 | 27 | 0.0001 = 0.05 | 0.0012 = 0.6 |
| 1.3764 | 28 | 0.0002 = 0.1 | 0.0013 = 0.65 |
| 1.3782 | 29 | 0.0003 = 0.15 | 0.0014 = 0.7 |
| 1.3800 | 30 | 0.0004 = 0.2 | 0.0015 = 0.75 |
| 1.3818 | 31 | 0.0005 = 0.25 | 0.0016 = 0.8 |
| 1.3836 | 32 | 0.0006 = 0.3 | 0.0017 = 0.85 |
| 1.3854 | 33 | 0.0007 = 0.35 | 0.0018 = 0.9 |
| 1.3872 | 34 | 0.0008 = 0.4 | 0.0019 = 0.95 |
| 1.3890 | 35 | 0.0009 = 0.45 | 0.0020 = 1.0 |
| 1.3909 | 36 | 0.0010 = 0.5 | 0.0021 = 1.0 |
| 1.3928 | 37 | 0.0011 = 0.55 | |
| 1.3947 | 38 | | |
| 1.3966 | 39 | | |
| 1.3984 | 40 | | |
| 1.4003 | 41 | | |
| 1.4023 | 42 | 0.0001 = 0.05 | 0.0012 = 0.6 |
| 1.4043 | 43 | 0.0002 = 0.1 | 0.0013 = 0.65 |
| 1.4063 | 44 | 0.0003 = 0.15 | 0.0014 = 0.7 |
| 1.4083 | 45 | 0.0004 = 0.2 | 0.0015 = 0.75 |

| Index. | Per Cent. Dry Substance. | Decimals. | |
|---|---|---|---|
| 1.4104 | 46 | 0.0005 = 0.25 | 0.0016 = 0.8 |
| 1.4124 | 47 | 0.0006 = 0.3 | 0.0017 = 0.85 |
| 1.4145 | 48 | 0.0007 = 0.35 | 0.0018 = 0.9 |
| 1.4166 | 49 | 0.0008 = 0.4 | 0.0019 = 0.95 |
| 1.4186 | 50 | 0.0009 = 0.45 | 0.0020 = 1.0 |
| 1.4207 | 51 | 0.0010 = 0.5 | 0.0021 = 1.0 |
| 1.4228 | 52 | 0.0011 = 0.55 | |
| 1.4249 | 53 | | |
| 1.4270 | 54 | | |
| 1.4292 | 55 | 0.0001 = 0.05 | 0.0013 = 0.55 |
| 1.4314 | 56 | 0.0002 = 0.1 | 0.0014 = 0.6 |
| 1.4337 | 57 | 0.0003 = 0.1 | 0.0015 = 0.65 |
| 1.4359 | 58 | 0.0004 = 0.15 | 0.0016 = 0.7 |
| 1.4382 | 59 | 0.0005 = 0.2 | 0.0017 = 0.75 |
| 1.4405 | 60 | 0.0006 = 0.25 | 0.0018 = 0.8 |
| 1.4428 | 61 | 0.0007 = 0.3 | 0.0019 = 0.85 |
| 1.4451 | 62 | 0.0008 = 0.35 | 0.0020 = 0.9 |
| 1.4474 | 63 | 0.0009 = 0.4 | 0.0021 = 0.9 |
| 1.4497 | 64 | 0.0010 = 0.45 | 0.0022 = 0.95 |
| 1.4520 | 65 | 0.0011 = 0.5 | 0.0023 = 1.0 |
| 1.4543 | 66 | 0.0012 = 0.5 | 0.0024 = 1.0 |
| 1.4567 | 67 | | |
| 1.4591 | 68 | | |
| 1.4615 | 69 | | |
| 1.4639 | 70 | | |
| 1.4663 | 71 | | |
| 1.4687 | 72 | | |
| 1.4711 | 73 | 0.0001 = 0.0 | 0.0015 = 0.55 |
| 1.4736 | 74 | 0.0002 = 0.05 | 0.0016 = 0.6 |
| 1.4761 | 75 | 0.0003 = 0.1 | 0.0017 = 0.65 |
| 1.4786 | 76 | 0.0004 = 0.15 | 0.0018 = 0.65 |
| 1.4811 | 77 | 0.0005 = 0.2 | 0.0019 = 0.7 |
| 1.4836 | 78 | 0.0006 = 0.2 | 0.0020 = 0.75 |
| 1.4862 | 79 | 0.0007 = 0.25 | 0.0021 = 0.8 |
| 1.4888 | 80 | 0.0008 = 0.3 | 0.0022 = 0.8 |
| 1.4914 | 81 | 0.0009 = 0.35 | 0.0023 = 0.85 |
| 1.4940 | 82 | 0.0010 = 0.35 | 0.0024 = 0.9 |
| 1.4966 | 83 | 0.0011 = 0.4 | 0.0025 = 0.9 |
| 1.4992 | 84 | 0.0012 = 0.45 | 0.0026 = 0.95 |
| 1.5019 | 85 | 0.0013 = 0.5 | 0.0027 = 1.0 |
| 1.5046 | 86 | 0.0014 = 0.5 | 0.0028 = 1.0 |
| 1.5073 | 87 | | |
| 1.5100 | 88 | | |
| 1.5127 | 89 | | |
| 1.5155 | 90 | | |

*Table of Corrections for the Temperature.*

| Temperature of the Prisms in ° C. | Dry Substance. | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | 0 | 5 | 10 | 15 | 20 | 25 | 30 | 40 | 50 | 60 | 70 | 80 | 90 |
| | Subtract. | | | | | | | | | | | | |
| 20 | 0.53 | 0.54 | 0.55 | 0.56 | 0.57 | 0.58 | 0.60 | 0.62 | 0.64 | 0.62 | 0.61 | 0.60 | 0.58 |
| 21 | 0.46 | 0.47 | 0.48 | 0.49 | 0.50 | 0.51 | 0.52 | 0.54 | 0.56 | 0.54 | 0.53 | 0.52 | 0.50 |
| 22 | 0.40 | 0.41 | 0.42 | 0.42 | 0.43 | 0.44 | 0.45 | 0.47 | 0.48 | 0.47 | 0.46 | 0.45 | 0.44 |
| 23 | 0.33 | 0.33 | 0.34 | 0.35 | 0.36 | 0.37 | 0.38 | 0.39 | 0.40 | 0.39 | 0.38 | 0.38 | 0.38 |
| 24 | 0.26 | 0.26 | 0.27 | 0.28 | 0.28 | 0.29 | 0.30 | 0.31 | 0.32 | 0.31 | 0.31 | 0.30 | 0.30 |
| 25 | 0 20 | 0.20 | 0.21 | 0.21 | 0.22 | 0.22 | 0.23 | 0.23 | 0.24 | 0.23 | 0.23 | 0.23 | 0.22 |
| 26 | 0.12 | 0.12 | 0.13 | 0.14 | 0.14 | 0.14 | 0.15 | 0.15 | 0.16 | 0.16 | 0.16 | 0.15 | 0.14 |
| 27 | 0.07 | 0.07 | 0.07 | 0.07 | 0.07 | 0.07 | 0.08 | 0.08 | 0.08 | 0.08 | 0.08 | 0.08 | 0.07 |
| | Add. | | | | | | | | | | | | |
| 29 | 0.07 | 0.07 | 0.07 | 0.07 | 0.07 | 0.07 | 0.08 | 0.08 | 0.08 | 0.08 | 0.08 | 0.08 | 0.07 |
| 30 | 0.12 | 0.12 | 0.13 | 0.14 | 0.14 | 0.14 | 0.15 | 0.15 | 0.16 | 0.16 | 0.16 | 0.15 | 0.14 |
| 31 | 0.20 | 0.20 | 0.21 | 0.21 | 0.22 | 0.22 | 0.23 | 0.23 | 0.24 | 0.23 | 0.23 | 0.23 | 0.22 |
| 32 | 0.26 | 0.26 | 0.27 | 0.28 | 0.28 | 0.29 | 0.30 | 0.31 | 0.32 | 0.31 | 0.31 | 0.30 | 0.30 |
| 33 | 0.33 | 0.33 | 0.34 | 0.35 | 0.36 | 0.37 | 0.38 | 0.39 | 0.40 | 0.39 | 0.38 | 0.38 | 0.38 |
| 34 | 0.40 | 0.41 | 0.42 | 0.42 | 0.43 | 0.44 | 0.45 | 0.47 | 0 48 | 0.47 | 0.46 | 0.45 | 0.44 |
| 35 | 0.46 | 0.47 | 0.48 | 0.49 | 0.50 | 0.51 | 0.52 | 0.51 | 0.56 | 0.54 | 0.53 | 0.52 | 0.50 |

*Example:* Desired, the dry substance of a sample whose refractive index is 1.4589 taken at 26° temperature. The nearest index is 1.4567, which equals 67% then 1.4589 minus 1.4567 (the nearest value in the table lower than it) =.0022. In the decimal column opposite look for .0022 and one finds a value of 0.95. So the reading is 67.95 but at a temperature of 26° (from the table of corrections) .16 must be subtracted or the correct dry substance would be 67.79. In like manner the dry substance of a sample with a refractive index of 1.5021 at 28° C. would be 85.05, and one of 1.3802 at 28° would be 30.1, and one of 1.3655 at 33° C. would be 22.06.

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