

Without giving any more of the experiments I have conducted, I will briefly state the conclusions I have arrived at :

1st. That 10 grms of bone black will absorb from a solution of perfectly pure sugar (26.048 in 100 c.c.), sufficient sugar to weaken the saccharine strength of the solution 0.30 per cent. to 0.35 per cent.

2nd. That 10 grms of bone black will absorb sufficient sugar, and, also, other substances which effect polarized light, from a solution (26.048 in 100 c.c.) of an impure or raw sugar, so that the saccharine strength of the solution will show a loss of from 0.10 per cent. to 0.66 per cent. by the direct test, but only 0.30 to 0.35 per cent. by the inverted test.

3rd. That some perfectly dried bone blacks will absorb more sugar than others.

4th. That the greatest amount of absorption by 10 grms of any kind of prepared bone black on a solution of pure sugar (26.048 in 100 c.c.), is only sufficient to reduce the saccharine strength of the solution 0.70 per cent.

5th. Since 2 grms of bone black are quite sufficient to decolorize a filtered sugar solution which has been partly clarified and decolorized by means of tri-plumbic acetate, it can be used with safety, as the amount of sugar it will absorb would hardly effect the saccharine strength of the solution appreciably.

6th. Supposing 10 grms of bone black to reduce the saccharine strength of a solution (26.048 in 100 c.c. water) of pure sugar testing 100 per cent., exactly 0.35 per cent., then we can deduce the fact, that 1 ton of bone black will absorb 18.2 lbs. of sugar, or, bone black is capable of absorbing 0.0091168 per cent. of sugar.

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## XL.—THE PRACTICAL DETERMINATION OF THE VALUE OF THE SUGARS OF COMMERCE.

By HENRY A. MOTT, JR., PH. D., E. M.

Owing to the many constituents which enter into the composition of sugar in its "crude" or "raw" condition, and to the fluctuations in the proportions of these constituents, and, *above all*, to the difficulty in obtaining an average sample, it becomes almost an impossibility to arrive at an accurate estimate of the value of a cargo of sugar, on the small scale necessary for laboratory investigations. Still many very valuable data may be obtained in the laboratory, which,

when combined with other indications, such as the brand, the color, the depth of "foots," etc., will enable one to arrive at an approximate estimate of the real value.

The elements necessary to be known before any approximate value can be put on a given cargo are :

1st. *The number of hogsheads* from which the sample has been taken.

The taking of an average sample has to be done with great care, and considerable discretion must be exercised by the sampler, as very often a large number of hogsheads are found mixed in with a given lot of sugar, which are quite inferior in grade. In such cases it is always well to make a separate sample of the same, and to count the number of hogsheads found. Experienced samplers consider that a handful of sugar taken by means of an augur, from 20 to 50 per cent. of the number of hlds., in a given lot, and thoroughly mixed together, is a fair average of the lot. In all sugars except centrifugals, the hlds. are bored in the centre and at the foot; in centrifugals, besides being bored at the foot, the hlds. are bored about four inches from the top, to save loss of sugar. The samples weigh about sixteen pounds.

2nd. *The brand of sugar*, whether it be a centrifugal, Muscavado, molasses, clayed, Manilla, Pernambuco, Melado, domestic molasses, etc., etc.

3rd. *The color, according to the Dutch standard.* This is a very important element, as the cost of decolorizing a dark colored sugar is not to be ignored.

4th. *The presence, or absence, of excess of gum.* This can be determined by feeling the sugar. An excess of gum hinders the rapid filtration of sugar, and, also, increases the expense in decolorizing.

5th. *The depth of "foots" in the hogsheads.* Overlooking and not allowing for this element, may be the cause of great loss. In Trinidad sugars, when green (or new), the foots vary from 5 to 12 inches, but generally from 6 to 8 inches. When the sugar gets old, the foots vary from 5 to 7 inches. In Martinique sugar, when green, the foots vary from 4 to 8 inches—when old, from 5 to 6 inches. The hogsheads are smaller for Martinique sugars than for Trinidads—the former only holding 1,200 to 1,300 lbs., while the latter hold from 2,000 to 2,500 lbs. In molasses sugars the foots amount to from 3 to 5 inches in the green suga., and from 0 to 3 inches in the old. In Cuba Muscavado sugars there are from 5 to 6 inches of foots in the

green, and 2 to 4 inches in the old sugar. In centrifugal sugar, in the green, from 1 to 2 inches of foots are found, and in the old, from 0 to 2 inches. The foots of a sugar will test all the way from 2 to 10 per cent. less than the sugar itself.

6th. *The general condition of cargo.* This is all important, for often the cargo is so badly damaged by water that it becomes next to an impossibility to obtain an average sample.

7th. *The per cent. of cane sugar present.*

8th. *The per cent. of impurities.*

9th. *The per cent. of dry substance, and*

10th. *The per cent. of sugar in the dry substance.*

The first five of these factors can be obtained outside of the laboratory; of the other five, only two have actually to be determined in the laboratory, which are, 1st, the percentage of cane sugar present, and 2nd, the percentage of water. From these, the other three are obtained by calculation. The processes for determining the percentage of sugar and water should, therefore, be as accurate as possible.

Many processes for the determination of sugar other than by the use of the saccharometer, have been from time to time suggested, and although some of them are quite short, and give quite accurate results, especially the process proposed by P. Casamajor, with methylic alcohol, still I think that they are not to be preferred when the saccharometer is at hand. Of the various instruments on the market it becomes important to determine the one most suitable for the examination of sugar. The best instrument, in my opinion, is the Duboseq-Soleil, which is provided with the necessary tubes and other appliances, for testing by inversion—a point neglected by the Germans, and which I consider of great importance. It has, furthermore, the advantage over many of the other instruments, that it only requires 16.35 grms of sugar to be dissolved in 100 c.c of water. A solution of 26.048 grms in 100 c.c., as required with other instruments, cannot, in the case of dark colored sugars, be sufficiently decolorized to allow a correct reading in the polariscope.

I now proceed to describe what I consider the best methods for testing a given sample for cane sugar and water :

Instead of 26.048 grms or 16.35 grms of sugar being taken, ten times this quantity should be weighed off, that is, 260.48 grms for the Ventzke, and 163.50 grms for the Laurent's or Duboseq's instrument. By taking so large a quantity of sugar, we are sure of

getting a fair average sample, which is next to impossible in the majority of raw sugars, where only 16.35 or 26.048 grms are taken. This I have frequently demonstrated by repeatedly testing the same sugar; the difference in some instances amounting to from 0.5 to 0.75 of one per cent., when the greatest possible care is used.

For the purpose of decolorizing, I use in the case of dark colored sugars 4 c.c. of a concentrated solution of chloride of sodium and 6 c.c. of a solution of tri-plumbic acetate, for every 16.35 grms of dissolved sugar. If the sugar is of a light color, much less of these reagents may be used.

To determine the fact that the use of these proportions does not influence the percentage of sugar, I have conducted a number of experiments:

16.35 grms of granulated sugar were dissolved in water, diluted to 100 c.c. and tested; result = 99.8 per cent. The same quantity was again weighed out, and the above proportions of salt and lead solution were added. The filtrate from this solution tested exactly the same, *i. e.*, 99.8 per cent. I repeated this experiment with sugars of inferior grades with identically the same results, which demonstrated that the volume occupied by the precipitate did not influence the result. Ten times the normal weight of sugar is to be dissolved in water, poured in a flask graduated to exactly 1000 grms of water, and then treated according to either one of the two following processes:

1st. The sugar may be perfectly dissolved, and then diluted to the 1000 c.c. mark, and thoroughly shaken, when 100 c.c. may be taken and decolorized with 4 c.c. of salt solution, and 6 c.c. of tri-plumbic acetate, and then tested, adding 10 per cent. to the indications obtained, or

2nd. The sugar may be perfectly dissolved, and, if very dark, 40 c.c. of salt solution may be added, and 60 c.c. of tri-plumbic acetate, and the whole diluted to the 1000 c.c. mark. If the sugar is light, a *much smaller quantity* of decolorizing reagents may be used. The mixture should be shaken thoroughly and filtered. When 100 c.c. have filtered, use 50 c.c. for inversion, and test the remainder directly in the instrument.

I consider it necessary to invert the sugar, as numerous experiments have demonstrated that the other substances present which affect polarized light, and which are supposed to neutralize each other, do not do so at all, except in very pure sugars, where they only exist in small quantities. The test for cane sugar, as given by the

direct test, I find in some cases too low ; in others, entirely too high. The process for inversion is very simple : to the 50 c.c. of filtrate, in a small flask, add 5 c.c. of HCl (containing 5 per cent. of  $\text{SnCl}_4$ ), and shake thoroughly ; then heat in a water bath to  $68^\circ \text{C}$ . It is best to allow the solution time to cool down to about  $30^\circ \text{C}$ . It can then be tested in the instrument after noting the temperature. Add this test to the direct test, and refer to Clerget's table.\*

Granulated sugar tested . . . . . 99.90 *direct*.

Inverted it tested . . . . . 30-28° C.

$$99.90 \div 30 = 129.9 \text{ at } 28^\circ \text{C.}$$

$$129.90 = 99.90 \% \text{ sugar (130.0} = 100 \% \text{ at } 28^\circ \text{C).}$$

The following are a number of tests which I made with the utmost care, regarding the 0° of the instrument, every time an observation was made :

BRAND OF SUGAR.	NO. DUTCH STANDARD.	DIRECT.	CORRECTED.	DIFFERENCE IN FAVOR OF CORRECTED TEST.
Muscavado . . . . .	11	87.10	88.25	+ 1.15%
Molasses . . . . .	6	84.00	85.50	+ 1.50%
Muscavado . . . . .	8	84.00	83.50	- 0.50%
Centrifugal . . . . .	8	93.00	94.25	+ 1.25%
Centrifugal . . . . .	8	89.00	89.75	+ 0.75%
Molasses . . . . .	7	84.30	86.60	+ 2.30%
Syrup (refined) . . . . .		39.30	41.60	+ 2.30%
Black Strap . . . . .		46.00	46.40	+ 0.40%
Centrifugal . . . . .	10	95.00	94.75	- 0.25%
Refined "C" . . . . .		85.20	85.00	- 0.20%
Centrifugal . . . . .	10	94.00	93.50	- 0.50%
Centrifugal . . . . .	7	90.40	89.00	- 1.40%
Centrifugal . . . . .	7	93.00	91.50	- 1.50%
Centrifugal . . . . .	7	91.00	90.00	- 1.00%
Centrifugal . . . . .	7	91.10	90.40	- 0.70%
Guadaloupe . . . . .	10	87.00	86.10	- 0.90%
Guadaloupe . . . . .	6	78.50	79.40	+ 0.90%
Refined "C" . . . . .		86.30	87.00	+ 0.70%

By examining these tests it will be seen that the difference by inversion is from - 1.5 to + 2.3 per cent. That is to say, a sugar testing 93 per cent. by the direct test, when inverted only tested 91.5 per cent., owing to the presence, in excess, of glucose, which turned the plane of polarization in the same direction as cane sugar. Another sugar, testing directly only 84.3 per cent., inverted tested

\* Which can be found in Ure's Dictionary of Arts, Manuf. and Mines.

86.6 per cent. This example shows that the true per cent. of cane sugar was prevented from manifesting itself, owing to the presence of excess of levulose and gum, which turned the plane in the opposite direction.

From these experiments it is clearly shown how necessary it is to invert a sugar before the true per cent. of cane sugar can be obtained.

To the determination of the water in sugars I have devoted considerable attention, and have made hundreds of comparative tests which have demonstrated the falsity of the indications of the areometer. A large number of sugars which, by more exact processes, showed the presence of  $1\frac{1}{2}$  to 2 per cent. of water, showed by the areometer method from 0.5 to 0.7 per cent. less than no water at all. It is not reasonable to suppose that the indications of an areometer could be worth anything when applied to a pure sugar, and then be correct when applied to impure sugars of *varying* percentage of soluble impurities, if to the indication there is added a theoretical correction which is not based upon the actual facts of the case, but on supposition only. The following experiment will illustrate the various processes :

A centrifugal sugar gave, according to the "water areometer," allowing $\frac{1}{2}\%$ of impurities as error due to the salts present.....	— 1.89%
The Balling areometer, allowing $\frac{2}{3}\%$ correction of temperature, gave.....	+ 1.30%
Scheibler's areometer (corrected) gave.....	+ 1.00%
Drying in air-bath gave.....	+ 2.30%
"    over sulphuric acid gave.....	+ 2.30%
"    in vacuo gave.....	+ 2.10%

Another sugar gave 4.5 per cent. water by drying in air-bath over sulphuric acid, and in vacuo, whilst the areometer, according to one method, gave only 0.9 per cent., and by the other, 1.5 per cent. water. With a little practice I consider it possible to tell within one per cent. the amount of water in any sample of sugar, by feeling the same, and more reliance can be placed in this method than it is possible to place in the areometer method. There can be no question, but that for the rapid determination of water, drying in vacuo is the most reliable method.

Having now determined the several factors, let us proceed to the determination of the value. The following example will serve for illustration :

BRAND OF SUGAR.....	Muscavado.
SAMPLES TAKEN FROM.....	25% of hhds.
DEPTH OF FOOT.....	4 inches.
CONDITION OF CARGO.....	Good.
COLOR OF SUGAR.....	No. 12, D. S.
GUM.....	Not excessive.
CORRECTED PER CENT. OF CANE SUGAR.....	90.00%
WATER.....	4.00%
DRY SUBSTANCE.....	96.00%
SUGAR IN DRY SUBSTANCE.....	93.75%

A cargo of raw sugar, such as is described in the above example, was, on the 10th of November, 1879, worth 9 cents per pound.

If all the factors remained the same except the color, which we will suppose No. 8 instead of 12, the sugar would then have lost one-quarter of a cent, and would be worth only  $8\frac{3}{4}$  cents, that is to say, for four shades of color an allowance must be made of at least  $\frac{1}{4}$  of one cent. If all the factors remained the same in the 1st example except the per cent. of cane sugar, which we will change to 85 per cent. instead of 90 per cent, the value then will be only  $8\frac{1}{2}$  or  $8\frac{3}{4}$  cents. This allows in Muscavado sugars  $\frac{1}{8}$  of a cent for every degree or per cent.

To find out the influence the foots have on the value of sugar, let us take, for example, 100 hhds. of a Muscavado sugar testing 85 per cent., the foots testing 75 per cent. A hhd. of Muscavado sugar is 36 inches in height, and holds about 1,600 lbs. If the foot is only 4 inches, then we will find that about  $\frac{1}{4}$  of the sugar is foot. The sugar will stand then :

Sugar 85%.....	1422.23 lbs. =	1208.89 lbs. cane sugar.
75%.....	177.77 lbs. =	132.23 lbs. " "
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	1600.00 lbs. =	1341.12 lbs. cane sugar.

If all the sugar tested 85 per cent., we should find

1600 lbs. $\times$ 85 per cent.....	1360.00 lbs. sugar
Actually present.....	1341.12 " "
Loss of cane sugar on one hhd.....	18.88 " "
" " " 100 hhds.....	1888.00 " "

1888 lbs. of sugar at  $8\frac{3}{4}$  cents \$162.84. The loss then on 100 hhds. of sugar, if calculation were not made for 4 inches of foots, would be \$162.84. Supposing the foots to be 8 inches instead of 4,

the loss would be \$325.68 ; this is, therefore, an important factor to consider. It is safe to allow for every inch of foot, in excess, at least  $\frac{1}{8}$  of a cent. per pound ; so for 4 inches extra  $\frac{1}{2}$  of a cent should be allowed.

It is necessary to know the per cent. of cane sugar in the dry substance, as of two sugars testing 90 per cent., the one containing only water, as impurity, would be the most valuable, as it is easier to remove water than other impurities. Again, as sugar, to a very great extent, is hygroscopic, the low test of a sugar may be due to water absorbed by the sugar from the atmosphere. I have known a number of instances where a sugar would test from one to two per cent. lower if sampled on a damp day, than it would on a clear, dry day. The high test of a sugar may also be due to the evaporation of water in the natural drying of sugar in a warm room. It is best, therefore, to base calculations of value on the cane sugar in the dry substance. It is necessary to consider the per cent. of impurities present, as the amount of sugar it is possible to get out of a given cargo depends on this factor. Of course, the care exercised in refining, etc., exerts its influence. Supposing, however, there was no other element to consider except the impurities, then, taking a sugar of the following composition,

Cane sugar.....	85.00%
Water.....	4.00%
Inverted sugar.....	3.20%
Organic substances.....	6.10%
Ash.....	1.70%
	100.00%

we will find, according to the experience of the best refiners in this country, that, as one per cent. of impurities prevent the crystallization of one per cent. of sugar, we will obtain—

Cane sugar.....	85.00%
Less impurities.....	11.00%
	74.00%
Crystallizable sugar.....	74.00%
Molasses.....	26.00%
	100.00%



The French method deducts from the per cent. of cane sugar five times the ashes, plus the per cent. of inverted sugar. By this method the problem stands :

Cane sugar.....	85.00%
Ashes $\times 5$ + inverted sugar.....	}
$1.7 \times 5 + 3.2 = 11.7$ .....	} = 11.70%
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Crystallizable sugar.....	73.30%
Molasses.....	26.70%
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100.00%	
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The brand of the sugar makes some difference in value ; for example, a centrifugal sugar of the same color, test and other factors being the same, is preferred to the extent of about  $\frac{1}{16}$  to  $\frac{1}{8}$  of a cent. For each degree or per cent. of a centrifugal sugar, about  $\frac{1}{16}$  of a cent is allowed, so that a centrifugal sugar testing 90 per cent., worth 9 cents, would be worth  $9\frac{1}{2}$  cents if it tested 95 per cent., other factors remaining the same.

## XLI.—ON THE PREPARATION OF METHYLENE CHLORIDE, AND DIOXYETHYL-METHYLENE.

BY WM. H. GREENE, M. D.

With the exception of the diethyl ether of methylene glycol, all of the oxyethyl substitution compounds of methane have already been described. Ortho-formic ether,  $\text{CH}(\text{OC}_2\text{H}_5)_3$ , was studied by Kay and Williamson, and is generally known as Kay's ether. Ortho-carbonic ether,  $\text{C}(\text{OC}_2\text{H}_5)_4$ , was discovered and described by H. Bassett. Methyl-ethyl ether has long been known.

By a reaction similar to that by which these ethers are formed, I have isolated dioxyethyl-methylene, the reaction between sodium ethylate and methylene chloride taking place as indicated by theory.

The chief difficulty lies in the preparation of pure methylene chloride. The process described by Perkin, and depending upon the reduction of chloroform by zinc and ammonia, yields only small quantities of methylene chloride, and the direct chlorination of methyl chloride gives equally unsatisfactory results. The method which, after numerous experiments, I have found to answer best, consists in the reduction of an alcoholic solution of chloroform by zinc and hydrochloric acid.

The zinc and chloroform (mixed with several times its volume of alcohol) are placed in a flask connected with a suitable condensing