Heumann found for this purest ultramarine the following formula : $2Na_2Al_2Si_2O_8 + Na_2S_2$, which, written according to my view, would be

$$
\begin{array}{cc}
2\ Si_2O_4 & Al_2O_3 \\
Al_2O_3S & 2\ Na_2O \\
& Na_2S \\
\end{array}
$$

Proportion of Oxygen + Sulphur in

Acids.		Bases.
2	:	1
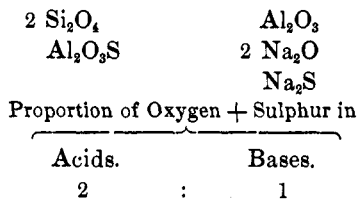
In the above formula, $2Si_2O_4.Al_2O_3.2Na_2O$ represents what I have called the silicate rest, while $Al_2O_3S.Na_2S$ is the so called color nucleus, which, when introduced into the composition of a silicate, will produce a colored compound, even if it be not colored itself.

Since the question of the constitution of ultramarine resolves itself mainly into the determination of the position of the sulphur atoms, my action in considering a certain part of the molecule separately may be justified.

New York, March 14th, 1881.

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XL.—The Rotatory Power of Commercial Glucose and Grape Sugar. A Method of Determining the Amount of Reducing Substance Present, by the Polariscope.

By Prof. H. W. Wiley.

In "the trade" the name of grape sugar is applied only to the solid product obtained from corn starch. On the other hand, the term "glucose" is given to the thick syrup made from the same material.

I shall use these words in their commercial sense.

INSTRUMENTS EMPLOYED.

I used in the following investigations two polariscopes, made by Franz Schmidt and Haensch, Berlin. The readings of these instruments, after correction for displacement, agreed well together.

The one was the instrument ordinarily used, in which the purple ray is employed, and the quartz half moons give blue and red tints.

Both of these instruments are graduated to read 100 divisions, each equal to 1 per cent. sugar with a solution containing 26.048 grms pure cane sugar in 100 c.c. In addition to this scale the half shadow has another which gives the actual angular rotation.

This is especially convenient when the specific rotatory power of a substance is to be determined. The angular rotation, however, can be calculated for the former instrument.

For if we take the specific rotatory power of cane sugar at $73.8°$, we have the following equation: $73.8 = \dfrac{\alpha \times 100}{2 \times 26.048}$ whence $\alpha = 38°.45$.

Each division on the cane sugar scale is therefore equal to $0°.3845$ angular measure.

This quantity corresponds to the transition tint. It is different for the differently colored rays. In the half shadow polariscope, an instrument particularly adapted to persons afflicted with any degree of color-blindness, the mono-chromatic light coming from the sodium-Bunsen lamp passes through a crystal of acid potassium chromate. The ray thus produced is less rotatable than the " transition tint."

When the instrument gives 100 divisions on the sugar scale, it shows an angular rotation of only $34°42' = 34°.7$. Our division, therefore, of the sugar scale, is equal to $0°.347$ angular measure.

To determine the specific rotatory power of cane sugar for the sodium-acid potassium chromate ray, we use the following equation:

$$\text{Sp. rot. pr.} = \frac{34°.7 \times 100}{2 \times 26.048} = 66°.6.$$

To determine the specific rotatory power for any other substance which has been determined for the transition tint, we multiply by the factor 0.9024.

Thus, if we take the specific rotatory power for any other substance which has been determined for the transition tint, we multiply by the factor 0.9024.

Thus, if we take the specific rotatory power of dextrine for the transition tint at $139°$, for the half shadow tint it will be, $139° \times 0.9024 = 125°.4$.

These data rest upon the accepted formula :

$$(1) \ \theta = \frac{\alpha}{\varepsilon.\ \delta.\ \lambda}$$

$$(2) \ \theta = \frac{\alpha \times v}{\lambda \times w}$$

Here α = angular rotation.

θ = specific rotatory power,

ε = amount of substance in one grm of the solution.

δ = specific gravity of solution.

λ = length of observation tube.

w = weight of substance in grms.

MATERIAL.

The glucose studied in the following examinations, was made by the Peoria Grape Sugar Company. I am under obligations to Mr. Allen, the superintendent, for many favors in connection with my work. The grape sugars were made in Buffalo.

ROTATORY POWER.

The average value of θ for the "half shadow ray" is nearly 85°. For the purple ray it is nearly 94°. It, however, varies extremely in different samples.

The following table will show the range of these variations.

TABLE I.

Showing variations of θ in different specimens of glucose and grape sugar, together with the specific gravities of the same.

No.	θ	Sp. Gr.	No.	θ	Sp. Gr.
1	91.50	1.406	11	89.36	1.416
2	91.50	1.407	12	87.73	1.422
3	98.10	1.440	13	89.77	1.417
4	79.93	1.414	14	70.84	1.463
5	75.47	1.414	15	69.40	1.463
6	83.97	1.417	16	87.67	1.412
7	82.75	1.416	17	109.99	1.427
8	86.41	1.415	18	93.17	1.431
9	84.11	1.416	19	89.75	1.409
10	87.19	1.417	20	91.31	1.421

From a study of this table it is seen that within small limits θ is independent of the specific gravity of the solution. Nos. 14 and 15 were grape sugar, and the specific gravity is much higher here than in the glucose, while the value of θ is much less.

Where the increase in density, however, is considerable, as in 3 and 17, there is also a marked increase in the value of θ, although this increase is not proportional to the increment of specific gravity. In masses of homogeneous nature and structure we should expect *a priori* that θ would always be proportional to the density of the body, *i. e.*, to the amount of optically active matter in a unit number of grammes.

It is thus seen without further argument that commercial glucoses are not optically homogeneous, even when made in the same factory and by processes which do not sensibly vary.

A further study of these optical reactions convinced me that the rotatory power of commercial glucose increased as the percentage of reducing substance diminished.

The following table shows the value of θ and the corresponding percentage of reducing matter as obtained by Fehling's solution.

TABLE II.

No.	θ	% Glucose	No.	θ	% Glucose
1	91.50	53.20	11	89.63	53.50
2	91.50	52.36	12	87.73	56.49
3	98.10	54.60	13	89.77	52.36
4	79.93	61.73	14	70.84	69.93
5	75.47	62.50	15	69.40	69.30
6	83.97	59.35	16	87.67	56.34
7	82.75	61.40	17	109.99	39.22
8	86.41	58.80	18	93.17	57.14
9	84.11	58.55	19	89.75	54.37
10	89.19	55.60	20	91.31	56.81

It will be seen by the above table that as the per cent. of reducing matter increases, the value of θ diminishes, and *vice versa*. Nos. 14 and 17 show extreme cases of this law. Nos. 3, 18 and 20, because of their high specific gravities, should not be included in the above generalization. Having thus established the law that the per cent. of reducing matter is in general inversely as the value of θ, it is next proposed to investigate the relation between these two quantities, and determine whether it is constant or variable.

From Nos. 1 and 2, of table II, it is seen that for a value of $\theta = 91.50$, the percentage of reducing matter is 52.78. Let us say for convenience in calculation that $\theta = 91.50$ corresponds to reducing substance $= 53$ per cent. Let us consider next, some of the cases in which the value of θ differs widely from 91.50. No. 17 of above table affords an example.

The difference is, $109.99 - 91.50 = 18.49$. The difference in the per cent. of reducing substance is $53 - 39.22 = 13.78$. Thus an excess of the value of θ of 18.49 corresponds to a deficit of 13.78 in the percentage of reducing matter.

Therefore a variation of each degree in the value of θ is equivalent to 0.745 in the percentage of a reducing matter. By similar calculations with the other data furnished by the table, I have found, not including Nos. 3, 18 and 20. marked by the high specific gravity, that this number lies between 75 and 78.

I will give the calculation for the first of these numbers, and compare them with the numbers obtained by analysis.

TABLE III.

No.	Variation of Θ	% Glucose by 0.75 Factor.	% Glucose by Fehling's Sol.
1	0.00	53.00	53.20
2	0.00	53.00	52.36
3	—12.08	62.06	61.73
4	—16.03	65.03	62.50
5	— 7.53	58.64	59.35
6	— 8.75	59.57	61.40
7	— 5.07	56.81	58.80
8	— 7.44	58.58	58.55
9	— 4.30	56.21	56.60
10	— 2.14	54.62	53.50
11	— 3.77	55.82	56.49
12	— 1.73	54.29	56.18
13	—20.66	58.32	69.93
14	—22.10	69.56	69.30
15	— 3.83	55.88	56.09
16	+18.49	39.14	39.22
17	— 1.75	54.32	54.05
18	— 0.19	53.14	56.81
19	+ 6.60	47.15	54.60
20	+ 1.66	51.75	57.14

In the above table, Nos. 18, 19 and 20 are the three specimens with high specific gravity. We will, therefore, exclude them from the discussion. In the other numbers the percentage of reducing matter, as calculated from the reading of the polariscope, falls short of the amount obtained by the alkaline copper test ten times, and by an average of 1.018. It exceeds that amount seven times, with an average of 0.75. We thus see that the polariscope will enable us to compute the reducing matter present in a glucose with a probable error of less than one per cent. This is quite accurate enough for practical purposes.

Perhaps a larger number of determinations should be made before constructing a formula for determining the amount of reducing substance in a "straight" glucose. The following formulæ, however, are given provisionally, subject to some slight correction deived from more extended data.

We may have three cases:

$$\text{1st. The value of } \theta = 91.50$$
$$\text{2d. \quad`` \qquad `` \qquad `` \quad `` } < 91.50$$
$$\text{3d. \quad`` \qquad `` \qquad `` \quad `` } > 91.50$$

In the first case the percentage of reducing substance in a glucose, if not far from 1.410 sp. gr., will be nearly 53.

In the second case the required percentage may be found by the following formula, in which $a =$ difference between the value of θ and 91.50, and $g =$ per cent. reducing required—

$$g = 53 + 0.75 \, a \text{ or } 0.78 \, a.$$

In the third case we have

$$g = 53 - 0.75 \, a \text{ or } 0.78 \, a.$$

In order to make the principle of more general application, I have modified the calculations so as to apply the formula directly to the cane sugar scale of the instrument.

To this end, for instruments using 26.048 grammes for 100 divisions, it is convenient to use only 10 grms of the glucose. If 26.048 grms are employed, the neutral point is thrown entirely beyond the limit of the scale. Ten grammes is the quantity which has been employed in the following table.

The average reading of the sugar scale for ten grammes is about 50.

In the following table will be found the results of the experiments.

TABLE IV.

No.	Scale.	% Reducing Substance by Calculation.	% Same by Cu. test.	Difference.
1	52.65	53.43	53.20	+0.23
2	52.65	53.43	52.36	+1.07
3	46.07	61.66	61.73	—0.07
4	43.05	64.90	62.50	+2.40
5	48.04	58.75	59.35	—0.60
6	47.70	59.63	61.40	—1.77
7	49.80	57.00	58.80	—1.80
8	48.45	58.56	58.55	+0.01
9	50.26	56.45	55.60	+0.85
10	51.50	54.88	53.50	+1.30
11	50.57	56.04	56.49	—0.45
12	51.74	54.58	56.18	—1.60
13	40.83	68.21	69.93	—1.72
14	40.00	69.25	69.80	—0.05
15	50.53	56.09	56.34	—0.27
16	63.80	39.50	39.22	+0.28
17	51.73	54.37	54.05	+0.32
18	52.63	53.46	56.81	
19	56.53	48.59	54.60	
20	53.70	52.10	57.14	

The above calculations were made from the following data.

Starting with Nos. 1 and 2, and discarding small fractions, we find that 53 divisions of the cane sugar scale correspond to 53 per cent. of reducing matter nearly.

By a method of calculation entirely similar to that employed in determining the reducing matter from the fluctuations of θ, I have found that a variation of one degree in the sugar scale corresponds to an inverse variation of nearly 1.25 per cent. of reducing substance.

We may have as in the previous calculation three cases.

$$\text{1st. The reading of the scale} = 53$$
$$\text{2d. } \text{``} \quad \text{``} \quad \text{``} \quad \text{``} > 53$$
$$\text{3d. } \text{``} \quad \text{``} \quad \text{``} \quad \text{``} < 53$$

In the first case $53 = 58$ per cent. nearly.

In the second case, placing a for the reading of the scale, we have

$$g = 53 - (a-53)\ 1.25$$

In the third case we have

$$g = 53 + (53-a)\ 1.25$$

In seven of the first seventeen cases the percentage of reducing substance calculated by the above formula, exceeded that given by the copper test, and by a mean amount of 0.539.

In ten of them it fell short, and by a mean amount of 0.938. This method, therefore, can be relied upon to give results which do not vary from the copper test except by a small amount.

Not much more in the way of accuracy can be claimed for the copper test itself.

In Nos. 18, 19 and 20 we have again the cases where the high specific gravities vitiate the results of the calculation.

CORRECTION FOR SPECIFIC GRAVITY.

I next proceeded to find out a method for correcting the reading of the polariscope for variations, caused by changes in the specific gravity of the specimens. First I determined the percentage of water in glucose of different specific gravities ; following are the results:

I.

Sp. gr.	=	1.440
Weight taken	=	5.515, in Pt. dish.
Loss	=	0.35, at 170°, 2 hours.
% H_2O	=	$0.35 \div 5.515 = 6.37$.

II.

Sp. gr.	=	1.431
Weight taken	=	5.86
Loss	=	0.53. 170°, 2 hours.
% H_2O	=	0.53 ÷ 5.86 = 9.05

III.

Sp. gr.	=	1.409
Weight taken	=	4.038
Loss	=	0.622, 170°, 3 hours.
% H_2O	=	15.40

IV.

Sp. gr.	=	1.416
Weight taken	=	4.425
Loss	=	0.525. 170°, 2 hours.
% H_2O	=	11.93

V.

Sp. gr.	=	1.417
Weight taken	=	8.639
Loss	=	1.091, 170°, 3 hours.
% H_2O	=	12.70

VI.

SOLID GRAPE SUGAR.

Sp. gr.	=	1.463
Weight taken	=	7.215, 170°, 3 hours.
Loss	=	0.61
% H_2O	=	9.29

These data are scarcely sufficient to establish a rule for correction for variations in specific gravity, but it appears from them that the formulæ will not vary much from the following:

The rule, 53 divisions = 53 per cent., seems applicable to samples in which the percentage of H_2O is 12 to 14, and of which the sp. gr. is from 1.409 to 1.414. For each variation of 0.001 in the specific gravity, the percentage of H_2O varies about 0.3.

Thus if we take the two extreme cases, viz.: 6.37 and 15.14 per cent. of H_2O, we find the corresponding specific gravities to be 1.440 and 1.409, a difference of 0.031.

The difference in the percentage of water is 9.03. The quotient of 0.0903 ÷ 0.031 = 3 nearly.

Let us apply these data to the correction of Nos. 18, 19 and 20 in table IV. I give below these numbers and also their corrections

TABLE V.

No.	Scale.	% Reducing Substance by Calculation.	Same Corrected	Same by Cu. Sol.
18	52.63	53.46	55.83	56.81
19	56.53	48.59	55.17	54.60
20	53.70	52.10	56.55	51.14

The above corrections were based on the supposition that 53 divisions of the scale correspond to 53 per cent. reducing matter, when the sp. gr. $=$ 1.409, and the percentage of water 15.

We may therefore construct the following provisional formulæ for estimating the correction to be applied to the reading of the scale when the sp. gr. of the specimen varies much from 1.409.

Let $a =$ reading of scale.
" $a' =$ corrected reading.
" $\varepsilon =$ sp. gr. of the sample.

Then $a' = a - 3a(\varepsilon - 1.409)$, when the sp. gr. is greater than 1.409, and $a' = a + 3a(1.409 - \varepsilon)$, when ε is less than 1.409.

I next propose to undertake some investigations to show the nature and number of the optically active principles present in glucose.

XLI.—The Effect of Heating with Dilute Acids and Treating with Animal Charcoal, on the Rotatory Power of Glucose; with Notes on the Estimation of Cane Sugar and Glucose in Mixture.

By Prof. H. W. Wiley.

Shaking dilute solutions of glucose or grape sugar with animal charcoal produces a slimy precipitate.

I use the words *glucose* and *grape sugar* in their commercial sense. By *glucose* I mean the thick syrup made from corn starch, and by *grape sugar* the solid product made from the same substance ; by pure glucose I mean the substance present capable of reducing the alkaline copper solution. I will not take time here to discuss the propriety of these names nor the exact nature of the substances present. I have made some experiments to determine the effect of animal charcoal on the rotatory power of glucose of commerce.

Following are some of the results obtained.

In each case 10 grms of the substance were taken and made up to 100 c.c. The observation tube was 200 m.m. in length.