

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.

“  $\epsilon$  = sp. gr. of the sample.

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

## EXPERIMENTS.

## I.

Reading before addition of coal.....	52° 00
After shaking with 20 grms coal.....	47° 20
Loss.....	4° 80

## II.

Reading before.....	52° 63
After adding 10 grms coal.....	50° 28
Loss.....	2° 35

## III.

Reading before.....	52° 63
After addition 4 grms ivory black.....	52° 38
Loss.....	0° 25

## IV.

Reading before.....	52° 20
After addition 4 grms ivory black.....	51° 13
Loss.....	1° 07

## V.

Reading before.....	52° 20
After addition 10 grms ivory black.....	48° 13
Loss.....	4° 07

From these figures it is certain that a glucose may lose nearly 10 per cent. of its rotatory power when shaken with animal charcoal. This is a matter of great importance when attempts are made to examine commercial syrups with the polariscope.

These syrups are usually highly colored, and require a great deal of bone black and lead acetate to make them fit for polariscopic examination. I have not yet tried the action of lead acetate on the rotatory power of glucose.

## HEATING WITH DILUTE ACIDS.

The following readings as well as those in the preceding part of this paper are divisions on the cane sugar scale.

## I

A glucose gave direct reading .....	53°.70
Heated to 68° with 10 per cent. of its volume of strong hydrochloric acid, reading.....	52°.96
Loss.....	<u>0°.74</u>

## II.

Heated same glucose for 50 minutes at 68°, reading	50°.76
Loss.....	<u>2°.94</u>

## III.

Direct reading another glucose.....	43°.36
Heated for 10 minutes at 68°, with 10 per cent. of its volume strong HCl, reading.....	43°.02
Loss.....	<u>0°.34</u>

## IV.

Heated same glucose 20 minutes at 68°, reading..	42°.36
Loss....	<u>1°.00</u>

## V.

Heated same for 30 minutes at 68°, reading.....	40°.16
Loss.....	<u>2°.86</u>

## VI.

Heated same for one hour at 68°, reading.....	39°.26
Loss .....	<u>4°.10</u>
The percentage of reducing substance in the above sample before heating with the acid was	62.50
After .....	65.58
Increase .....	<u>3.08</u>

Thus a loss of 4.10 on the cane sugar scale corresponded to a gain of 3.08 per cent. in reducing power.

## VII.

A grape sugar gave direct reading.....	40°.83
Heated with one-fifth its volume strong HCl, for 20 minutes at 68°, reading.....	31°.70
Loss.....	<u>9°.13</u>

## VIII.

A grape sugar gave direct reading . . . . .	40°.00
After heating with one-fifth volume HCl for 15 minutes at 68°, gave reading. . . . .	32°.52
Loss. . . . .	7°.48
The percentage of reducing substance in the above was:	
Before heating . . . . .	69.30
After heating. . . . .	71.50
Gain . . . . .	2.20

Thus a loss of 7.48 divisions in rotatory power corresponded only to an increase of 2.20 per cent. in reducing power.

It will be seen by inspection of the foregoing numbers that glucose and grape sugar undergo quite a degree of change when subjected to the process of inversion as it is practiced on cane sugar. This change is sufficiently great to introduce an appreciable error into the process of estimating cane sugar and glucose in mixtures.

CONVERSION OF THE WHOLE OF THE OPTICALLY ACTIVE SUBSTANCES  
IN GLUCOSE INTO PURE MONO-ROTATORY GLUCOSE.

I next made an attempt to convert the whole of the optically active substances present in glucose, into pure glucose, by prolonged heating with dilute sulphuric acid.

The conversions were made in a flask fitted with a glass tube about one meter in length. By this device, vapors arising are condensed and flow back into the flask. Thus no loss of volume takes place.

The flask was at first heated in a water bath at 100°. The conversion, however, took place so slowly by this method, that I afterwards added enough salt to the bath to raise the temperature to 104°.

The sulphuric acid employed was of 1.25 sp. gr., and was used in the proportion of 10 per cent. of the volume of the glucose solution.

The readings were made in a tube longer by one-tenth than half the length of the 200 m.m., and the result multiplied by 2.

The following table contains the results of my work.

Nos. 1, 2 and 3 were heated at 100°. No. 1 for 6 hours, No. 2 for 4 hours, and No. 3 for 3 hours.

Nos. 4, 5 and 6 were heated for 3 hours at 102°.

Nos. 7, 8, 9, 10, 11 and 12 were heated for 3 hours at 104°.

TABLE I.

No.	Reading before heating	% Glucose before heating	Reading after heating	% Glucose after-heating
1	52.65	53.20	25.92	81.30
2	48.40	59.35	27.14	80.00
3	48.45	58.55	26.10	80.00
4	43.50	62.50	24.72	79.00
5	50.26	55.60	24.18	82.00
6	51.50	53.50	25.38	81.14
7	52.65	52.36	25.89	83.33
8	56.53	54.60	27.36	90.10
9	51.74	52.96	26.19	82.00
10	47.70	61.40	25.36	82.64
11	49.80	58.80	26.02	84.00
12	40.83	69.93	26.07	84.80

In all cases the samples assumed a decidedly yellowish tint before the completion of the operation, interfering somewhat with the delicacy of the final readings.

No. 8 was a sample of glucose made for confectioners' use. If we exclude it we get the following general results:

1st. The percentage of reducing substance obtained is nearly 82.00.

2d. The average reading of the cane sugar scale is nearly 25.5 divisions.

3d. If the pure glucose present is mono-rotatory, the specific rotatory power  $\theta$  would be  $\theta = \frac{8^{\circ}.85 \times 100}{2 \times 8.2} = 54$  nearly.  $80^{\circ}.85$

is the angular rotation (half shadow) corresponding to 25.5 divisions of the scale, but the specific rotatory power of pure glucose for the half shadow polariscope is nearly 50. We have then here an excess of  $\theta$  equal to 4.

4th. This excess is due to the presence of optically active matter of a higher specific rotatory power than pure glucose, which has not been changed even by prolonged boiling with dilute acid. I conclude, therefore, that it is quite difficult to convert the whole of the optically active matter into pure mono-rotatory glucose.

#### EXAMINATION OF MIXTURES.

In the examination of mixtures of cane sugar and grape sugar, it is necessary first to obtain the direct reading. Afterwards the cane sugar is to be inverted, using at most not more than ten minutes for this, and keeping the temperature at  $68^{\circ}$ . It is simply necessary to heat to  $68^{\circ}$  and then quickly cool.

After inversion the temperature is carefully noted and another reading taken. Then by Clerget's table the percentage of cane sugar is calculated. This, however, will only be approximately correct.

We next calculate the whole amount of rotation produced by the approximate amount of grape sugar present. Having determined this, the reading after inversion is to be corrected for the effect of inversion on the rotatory power of the grape sugar present. The average correction, when the heating has been carried just to 68°, will be about 2 per cent. of the whole rotation due to the grape sugar. If the process of inversion is carried on for an hour, as is the practice of some, the correction may amount to 10 per cent.

If the amount of glucose present is very small, this correction can be neglected. But if the amount is large, a failure to correct will introduce an appreciable error into the result. If animal charcoal has been used, a correction must be made also for it, depending, as has been shown, upon the amount employed, and also upon some other conditions which are not yet clearly made out.

It is easy to see into how grave an error we might fall, should we attempt to intimate directly the percentage of reducing substance present in such mixtures, from its rotatory power. I have shown in a previous paper that the percentage of such reducing substance is not *directly* but *inversely* as its rotatory power.

The error would be equally as grave if the amount of the grape sugar present should be computed by using a factor supposed to represent the amount of such substance for each division of the scale. Such a method is based upon the assumption that the rotatory power of grape sugar is constant and proportional to the reducing substance present. My paper already mentioned shows that this assumption is false.

#### SYRUPS.

When we come to the syrups of commerce, the case becomes still more difficult. These syrups are glucose adulterated with so-called cane syrups, *i. e.*, with the drippings and refuse of the sugar refineries. Among the syrups which are commonly used I may mention the "Revere" and the "Continental."

A "Revere" syrup which I examined had a specific gravity of 1.425, and contained 34.5 per cent. cane sugar.

A "Continental" syrup had a sp. gr. of 1.415 and 35.7 per cent. cane sugar. It also contained of inverted sugar 32.64 per cent.

It is easy to see how the admixture of such syrups with glucose tend to demoralize the results of the alkaline copper test and mystify the readings of the polariscope.

No wonder that heretofore such egregious blunders have been committed in these examinations. It is only when they are made with a full knowledge of the optical peculiarities of the commercial glucose itself, and of the composition of the cane syrup employed, while at the same time attention is paid to the changes produced by inversion and classification, that they can be relied upon as correct.

#### OBSERVATION TUBES.

In the polariscopic observation of inverted sugars, I use a copper tube silver plated inside and out. I find the most convenient length to be 110 m.m.

This enables the readings to be made without the trouble of neutralizing the acid.

The silver plating of the tube is not necessary, but it makes the working with it a little cleaner. Pure copper can be used without any danger whatever of the acid acting on it.

I use a tube of thin copper and of small diameter. Such a tube, when filled, quickly takes the temperature of the surrounding air. A few c.c. will fill one of these tubes. I have found by experiment, that when such a tube is filled with a liquid several degrees above or below the temperature of the air, in twenty minutes it will differ by less than half a degree from the temperature.

If an ordinary glass tube is employed, it is quite difficult to say how much time will be required to restore the equilibrium of temperature. My experiments show that it will require from two to three times as long.

I also provide this tube with a metallic jacket very conveniently made of a piece of zinc tubing. This jacket is a little less in diameter than the metallic caps of the tube, and is of such a length that when the caps are screwed on, the jacket fits against a shoulder turned on them.

The joint is made water-tight by using a rubber packing. This jacket is furnished with three open rings, fitted with short tubes. That in the center carries a thermometer, and those at each end serve as supply or exit tubes for any liquid which we may wish to pass through the jacket. By simply drilling a hole in the trough of the polariscope for the exit tube, the whole apparatus can be placed at once in position.

If now you wish to make a reading at a temperature say of  $88^{\circ}$ , it is done in the following way. A large flask or tank placed at one side and above the polariscope, and holding several liters of water, is heated to a temperature of about  $92^{\circ}$ . By a rubber tube, this is

connected, on the principle of a syphon, with the observation tube and its jacket. By means of a pinch cock attached to the exit tube, the hot water is allowed to flow through the jacket until the thermometer shows the temperature desired. It is hardly necessary to say that the observation tube must be filled at a temperature near that at which the reading is to be made, to prevent expansion. If we desire to make a reading at  $0^{\circ}$ , corresponding to  $44^{\circ}$  to the left, Clerget, we replace the water by alcohol which is cooled by a salt and ice bath to  $-3^{\circ}$  or  $-4^{\circ}$ .

The apparatus is then used as before. We have thus a means of making readings at any desired temperature without having to mutilate the polariscope, as is done by fitting it with a water bath. I will say, however, that a judicious use of Clerget's principle renders readings at a given temperature unnecessary. They are, however, useful in certain complex mixtures by doing away with certain calculations.

I propose next to extend my investigations to candies and other confections in which glucose enters as an ingredient.

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## Reports on American and Foreign Patents Relating to Chemistry.

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### American Patents.

Condensed from the Official Gazette of the U. S. Patent Office, by ARNO BEHR.

Oct. 5, 1880.

232,889.—*Apparatus for extracting metal from ores.* THURSTON G. HALL.

232,922.—*Manufacture of Soap.* LOUIS BASTET.

A compound of soap and mineral oil, with or without the addition of boric acid.

232,974.—*Vulcanized plastic compound.* ALFRED B. and CHARLES JENKINS.

Use infusorial earth as an admixture to ordinary vulcanized india-rubber.

232,991.—*Method and Apparatus for obtaining ammonia.* HANS P. LORENZEN.

See German Patent, p. 302.

232,995.—*Process and apparatus for preparing saccharate of lime and obtaining sugar.* HENRY A. J. MANOURY.

This process has been sufficiently described in the current literature. It is patented in France and Germany since 1877, and extensively adopted in Europe for the recovery of sugar from beet-root molasses.