CALCULATED LIGHT FACTORS.

	From (1) and (3).	From (1) and (4).	From (2) and (3).	From (2) and (4).
Quartz A	0.3458	0.3466	0.3469	0.3478
Quartz D	0.3458	0.3466	0.3467	0.3475

SUGAR LABORATORY,
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VARIATIONS OF STANDARD AMONG VENTZKE SACCHARIMETERS.[1]

BY HARRIS E. SAWYER.

Received June 27, 1904.

IT SEEMS generally to be supposed that the Ventzke saccharimeter is always standardized to read 100° on a 200 mm. column of a solution, prepared and polarized at 17.5° C., of 26.048 grams of sucrose, weighed in air, in 100 Mohr cubic centimeters. Rolfe has claimed,[2] however, that through most instruments now in use conform to this standard, certain of newer saccharimeters are graduated for the slightly stronger sugar solution produced by dissolving the old normal weight in 100 cubic centimeters; and in view of this claim it seemed advisable to the writer to ascertain what standard was adopted in the graduation of his own instrument—a Schmidt & Haensch triple-field, No. 4914—purchased about three years ago.

To this end he first polarized with great care a series of four positive quartz plates belonging to the Massachusetts Institute of Technology. These plates, which read respectively 55.30°, 62.66°, 95.99° and 100.07° on the two half-shadow instruments of the Institute,[3] gave the values 55.08°, 62.45°, 95.75° and 99.86° on the writer's instrument, the mean ratio between the two sets of values being 1.0028, whereas the theoretical ratio should be 1.0023 in case the instruments were graduated respectively for Mohr and for true cubic centimeters. Since the Institute's instruments are known to be adjusted to the Mohr cubic centimeter standard, it seemed obvious that the writer's must be intended for use with true cubic centimeter flasks. At this point, therefore, he communicated his observations to Schmidt and Haensch, in-

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[1] Read at the Providence meeting of the American Chemical Society.

[2] Review Am. Chem. Research, V, 105 (1899); This Journal, 25, 1007 (1903).

[3] The foregoing values are the means of the values given for the instruments No. 2880, Schmidt and Haensch, and No. 624, Scheibler, in the tabulation on p. 994.

quiring if this was not the case; and in due time he received their answer that "the saccharimeter, No. 4914, as all our quartz wedge polariscopes, has been graduated for the old scale—26.048 grams weighed in air with brass weights, 100 Mohr cubic centimeters, 17.5° C." In view of this reply the writer found it advisable to carry his investigation further.

It was necessary first to determine, by tests with pure sugar, what concentration of solution would, at 17.5° C., give a reading of 100° on the saccharimeter in question. Accordingly, a set of weights, a 200 mm. polariscope tube and a tenth-degree thermometer were submitted to the Bureau of Standards for correction; a sample of pure sucrose, prepared by the method of the International Commission and checked by Dr. Wiley against a pure sucrose prepared by Herzfeld, was obtained from the Bureau of Chemistry; a true 100 cc. flask, graduated by the United States Coast and Geodetic Survey, was recalibrated and found to contain within 0.01 per cent. of its indicated capacity at 17.5°; and also, since the neck of this flask was somewhat wide and its graduation mark at a distance from the bulb, another flask with a neck only 8 mm. in diameter was provided with a mark 5 mm. above the beginning of the cylindrical portion, and was calibrated with great care, being found to contain 98.18 true cubic centimeters at the temperature of the subsequent determination.

After preliminary trials, to acquire manipulative facility, two determinations of the sugar value of the saccharimeter were made.

(1) One hundred true cubic centimeter flask; 26.048 grams pure sucrose; temperature of air and solution at time of preparation and polarization, 24° C.; mean of 10 zero-point readings, —0.204°; mean of ten polarizations, 99.601°; net observed polarization, 99.805°.

(2) 98.18 true cubic centimeter flask; 25.509 grams pure sucrose; temperature of air and solution at time of preparation and polarization, 28° C.; mean of ten zero-point readings, —0.008°; mean of ten polarizations, 99.395°; net observed polarization, 99.403°.

In calculating the result of the first determination, 0.02 per cent. was allowed for the expansion of the 100 cc. flask between 17.5°, the temperature of calibration, and 24°. The polariscope tube employed has, at 17.5°, a length of 200.01 mm., corresponding to 200.02 mm. at 24°, and to 200.03 mm. at 28°; and though the excess of length is very slight, it nevertheless was taken into account in the calculations.

In reducing the polarizations from 24° and 28°, the temperatures of observation, to the standard temperature of 17.5°, the factor 0.0317° V. = 1.0° C. was employed, this being the mean of the values given by the United States Coast and Geodetic Survey, Andrews, Landolt, and Wiley,[1] and in almost absolute agreement with the result of the latter investigator.

All these corrections for temperature having been applied, the values 100.00° and 99.72° were obtained, as indicating the polarizations of the writer's sugar solutions at 17.5° in a 200 mm. tube. Since the solution used in the first determination was prepared to contain 26.048 grams of sucrose in 100 true cubic centimeters, no further correction of the value 100° is necessary. In the second determination, however, the solution was of less than normal concentration, since 25.509 grams in 98.18 cc. corresponds to 25.981 grams in 100 cc. Accordingly, the value 99.72°, obtained as above in the second determination, was multiplied by $\frac{26.048}{25.981}$; and the value 99.98° was thus obtained as representing for this determination, the polarization of a solution of 26.048 grams of sucrose in 100 true cubic centimeters at 17.5°. It was thereby established that the writer's saccharimeter is, indeed, adjusted to the true cubic centimeter standard.

It now remained to be seen whether the difference between the standard of this instrument and that of those at the Institute of Technology seemed to be due to intent or to such calibration errors as may affect all graduated apparatus. That they could be due to the latter cause seemed wholly incredible, since the mean difference of the quartz plate values amounted to 0.28 per cent., whereas Landolt[2] has stated that variations in the 100° point of Schmidt and Haensch saccharimeters do not commonly amount to more than from 0.05°-0.10° V. and that they usually are smaller. Accordingly, an examination of all the compensation saccharimeters in Boston was undertaken, by means of the quartz plates already mentioned, in the hope of getting light upon this question. It was presumed that chance variations of standard would result in values for the

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[1] This Journal, **21**, 584 (1899).

[2] Landolt-Long: "Optical Rotation of Organic Substances," p. 375.

readings of the plates, which would be scattered irregularly between, and possibly beyond, those already obtained, and that the intentional existence of a double standard of graduation would be shown by the readings falling into two groups, the values within each group approximating those already given, and differing among themselves by such small amounts as Landolt's statement would lead one to expect.

It is well known to polariscopists that, in consequence of the variation of the specific rotary power of quartz with changing temperature, it is necessary to leave plates and wedge-compensations to come to temperature-equilibrium, if concordant results are to be obtained in such an examination as is here described. Accordingly, the greatest possible care was taken to maintain such equilibrium during all of the writer's observations; and no results are included in the following tabulation save those which are considered to be essentially free of temperature error.

The number of observations made upon any individual instrument has varied according to circumstances. In general, any value given in the table represents from 5 to 10 zero-point readings and as many polarizations; in many cases a single value represents from 25 to 30 such readings, and in some cases from 50 to 60.

On the writer's own instrument many series of readings were made with almost identical results; thus, on the A plate the means of three series, taken at intervals of several weeks, were respectively 62.44°, 62.45° and 62.46°, the probable error of each mean being ±0.02°. On other instruments of the same type—Lippich polarizer, triple field—fewer readings were made, but on account of the great sensitiveness of these modern polariscopes the mean errors were not perceptibly greater. With the older half-shade instruments, having the Jellet polarizer, the mean errors were slightly greater, amounting to ±0.03° or 0.04°; and with the color instruments examined, the mean errors affecting the tabulated results are in the vicinity of ±0.06° to 0.08°; but with the latter instruments great patience was required to attain such a degree of accuracy in reading.

It is now obvious, on consideration of the tabulated values, that the saccharimeters examined by the writer must be grouped in two classes.

COMPARISON OF QUARTZ WEDGE SACCHARIMETERS.

Maker.	Type.	Serial No.	C Plate.	A plate.	D plate.	E plate.
S and H	color	1159	....	62.46	95.68	99.85
"	"	1435	55.09	62.49	95.78	99.83
"	half shade J..	3258	....	62.40	....	99.80
"	" " "..	3443	....	62.36	....	99.76
"	" " L..	3010	....	62.50	....	99.85
"	" " "..	3041	....	62.48	....	....
"	" " "..	4720	....	62.45	....	99.87
"	" " "..	4914	55.08	62.45	95.75	99.86
"	" " "..	5045	....	62.52	...	99.88
"	" " "..	3923	55.11	62.45	95.77	99.84
"	" " "..	5862	....	62.47	....	99.83
"	color	1885	....	62.68	....	100.09
"	half shade J..	2540	....	62.68	....	100.11
"	" " "..	2880	55.32	62.66	96.02	100.06
Scheibler	" " "..	624	55.28	62.66	95.96	100.08
Peters	" " "..	103199	....	62.61	....	100.03

J signifies Jellet polarizer.
L " Lippich polarizer.

Taking as the basis of comparison the values of the E plate, which are nearest the 100° point, we see that the two older color instruments and the modern shadow instruments of Schmidt and Haensch must be classed together—the lowest value being 99.76°, the highest 99.88°, and the mean 99.837°. In a second class are included one of the later Schmidt and Haensch color instruments and two of their earlier half-shades, together with an old Scheibler and a modern Peters. The values of the plate on these instruments range from 100.03° to 100.11°, the mean being 100.076°. The ratio between these means is 1.0024, instead of 1.0023, as required by theory between instruments graduated for the Mohr and for the true cubic centimeter.[1]

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[1] The writer calls attention to the fact that while the mean E plate values for the two classes of saccharimeters are separated by an interval of 0.24° V. and show the ratio 1.0024, the interval between the mean A plate values 62.46 and 62.66 is 0.20°, and the ratio 1.0032. Strict proportionality would demand that the latter interval should be slightly less, and the ratio lower. That this is not the case, has no bearing on the subject of this communication, since the standard of the saccharimeter is determined by the value of the 100° point of its scale. Indeed, the introduction of the values of the lower plates in the foregoing tabulation is non-essential, although they have a certain confirmatory value. But while this is the case and while some variations from proportionality are to be expected throughout every scale, the fact that many instruments show divergences in the same direction is worthy of note and may have some significance. Accordingly, the values of the lower plates are given, so far as they have been determined ; and a study of their relations to the E plate values is being carried forward.

If, now, it be granted that the difference between the saccharimeters of these two classes is intentional—that certain of them were meant to be used with sugar solutions prepared in Mohr cubic centimeter flasks, and the others in conjunction with true cubic centimeter flasks—the writer's observations agree entirely with Landolt's statements. In the one class the extreme variation in the readings of the E plate on ten saccharimeters is 0.12° V.; in the other class, including five instruments, it is still smaller, only 0.08°.

If, on the other hand, it be denied that the instruments were graduated for two distinct standards, Schmidt and Haensch are confronted by an extreme variation of 0.35° V. at the 100° point among thirteen of their instruments—a variation far greater than any careful instrument-maker would ever have permitted. And furthermore, we have to explain the fact that between the readings of instruments Nos. 5045 and 2880, respectively 99.88° and 100.06°, there is a gap of 0.18°, to bridge which no instrument has been found.

It seems, therefore, as if there must exist a double standard of graduation among the saccharimeters of Schmidt and Haensch;—as if their earlier instruments were graduated for the true cubic centimeter, as if in time this standard had been abandoned for the more convenient and more popular Mohr cubic centimeter, and finally, as if the latter in turn had been abandoned in consideration of the growing feeling against the double standard of graduation for volumetric flasks. In view of the fact that 0.23 per cent. may make, at times, a material difference in the results of a saccharimetric determination, it seems desirable that the attention of chemists should be called to the foregoing facts.

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THE ANALYSIS OF PORTLAND CEMENT.

BY BERTRAM BLOUNT.

Received May 16, 1904.

A YEAR or two ago the New York Section of the Society of Chemical Industry suggested the establishment of a standard method for the analysis of Portland cement. Samples of cement were distributed to various chemists to be analyzed according to