

## SOME NOTES ON LAURENT POLARISCOPE READINGS.<sup>1</sup>

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FOR many years the Laurent polariscope has been the common instrument in our chemical laboratories for the measurement of optical rotation, especially in the determination of specific rotatory powers, which are the constants of calculation in polarimetric analysis.

Till comparatively recently the results obtained with the Laurent polariscopes have been accepted as expressing rotations of the plane of polarization of the D ray, or ray of standard wave-length. The light used in Laurent measurements, as is well known, is made by vaporizing common salt in a powerful Bunsen burner, and filtering the rays through a section of potassium bichromate crystal.

The *saccharimetric* scale of the Laurent polariscope is based on the *specific rotation of quartz*, which was taken as 21.667 at the standard temperature. Later measurements of the specific rotation of quartz, even some of more than twenty years ago, give a higher value—21.72 at 20°. As by common usage, the 100-point of the Laurent saccharimeter is a fixed one, equivalent to the rotation value of 21.667, an attempt has been made to reconcile this value to the original definition by stating that this expresses the rotation of quartz at 6°. Obviously, this is merely a matter of definition, the scale being based on a fixed rotation, independently of whether this be the specific rotation of quartz or not.

The Laurent instrument is little used for saccharimetry in this country, the value of the specific rotation of quartz given by the instrument being chiefly of interest as a point of reference for determining the accuracy of its measurements as expressing angular rotations of the plane of polarization of the standard yellow ray.

In 1890<sup>2</sup> Lippich published a paper designed to prove, theoretically, that errors of 0.2 per cent. or more necessarily existed in Laurent measurements. As confirmation of this, in the same paper, Lippich also published comparative measurements of the optical rotation of a standard quartz plate made on a Lippich polariscope and two of the Laurent type, the readings of which latter showed variations of forty-five to eighty-two seconds from those of the Lippich polariscope. It should be noted that, in these

<sup>1</sup> Read at the Providence meeting of the American Chemical Society.

<sup>2</sup> "Zur Theorie der Halbschattenpolarimeter," *Wien Sitzungsber* [II], 99, 695.

experiments, Lippich filtered the sodium light through both potassium bichromate and cupric chloride solutions, so that the light he used probably differed appreciably from that designed for the Laurent polariscope.

Landolt<sup>1</sup> has pointed out that the sodium light as usually employed in polariscopic measurements is not homogeneous, but is made up of light of many wave-lengths, most of them differing slightly from each other, but that such light can be considered as homogeneous light which has a wave-length of the ray which is the resultant in intensity of all the rays emitted. This ray is termed the "optical center"<sup>2</sup> of the light. In his work on optical rotation, Landolt discusses the different optical centers of light used in polarimetric measurements, but does not consider exactly the kind of light used by Laurent instruments.

In most of the more recent accepted measurements of the specific rotation of quartz the light used has been the yellow rays of the two D lines of the spectrum, separated by spectroscopic methods, either from white light or from sodium flame.

For the Lippich polariscopes, Lippich has designed a ray filter which practically absorbs all light except those rays adjacent to the D lines. This filter purifies the light of incandescent sodium chloride vapor so that its optical center is practically that of the spectrally purified light. According to Landolt, who describes the preparation of the solutions in detail, it consists of a 10-cm. absorption cell filled with a 6 per cent. solution of potassium bichromate and a 1.5 cm. cell filled with a specially prepared solution of uranyl sulphate.<sup>3</sup>

Consideration of many published rotation values obtained on Laurent polariscopes, as well as readings of the two instruments of the sugar laboratory of the Massachusetts Institute of Technology, has led us to believe that polariscopes of this type, if of French make, give readings which are concordant within one minute at least, although about 0.2 per cent. lower than those obtained with the Lippich ray filter. As long ago as 1899 one of us published this opinion.<sup>4</sup>

Quite recently we have made two series of rotation measurements of two standard quartz plates on a Laurent polariscope,

<sup>1</sup> "Optische Drehungsvermögen," p. 360.

<sup>2</sup> "Optischer Schwerpunkt."

<sup>3</sup> Lippich: *Ztschr. für Instr.*, 12, 340; Landolt: "Optische Drehungsvermögen," p. 362.

<sup>4</sup> This Journal, 21, R105 (1899).

one set with the light designed to be used by the Laurent polariscope, sodium chloride light filtered through a section of bichromate crystal; the other set, with sodium chloride light passed through a Lippich ray-filter. The instrument used was a Laurent, "large model" made about 1888 by Leon Laurent, of Paris.

The table gives the result of the measurements as well as the saccharimetric readings of the two quartz plates, on the saccharimeters of the Institute laboratory, which are graduated in the standard Ventzke scale for use of Mohr flasks, and their readings also on a triple-shade saccharimeter of the United States Department of Agriculture, which latter readings were made by Dr. Wiley in 1898, and obviously are on the true cubic centimeter scale.

The saccharimetric readings of "Quartz A" plate show that, within a small error, it is a millimeter in thickness.<sup>1</sup> On this account it is interesting to note that the value given with the ordinary light used with the Laurent polariscope is practically that obtained for the specific rotation of quartz by the *earlier* investigators, while that given by the Lippich light closely approximates to the *modern* value.<sup>2</sup> The results, as a whole, have led us to believe that the difference in values obtained by the Lippich and Laurent measurements are not due to the imperfections of the Laurent instrument, but to the kind of light used, at least up to the precision required in chemical laboratory measurements, or 0.1 per cent. of the values obtained.

The greater convenience of the Laurent polariscope, owing to its end-point adjustment being independent of the position of the polarizer for the regulation of the light intensity, as well as the advantage of the bichromate section over the Lippich ray-filter, which absorbs a large percentage of light and soon deteriorates, owing to the oxidation of the uranium solution, makes the Laurent more advantageous than the Lippich for general laboratory measurements. Our results show that Laurent measurements can be converted to the standard of spectrally purified light by increasing their value 0.2 per cent. The tabulated light factors calculated from the different rotation and saccharimetric values

<sup>1</sup> Landolt: "Optische Drehungsvermögen" (First Edition), p. 162. The plate was always placed in the instruments in a definite axial position, but we have been unable to detect any difference in its readings in different positions.

<sup>2</sup> Landolt: "Optische Drehungsvermögen," p. 130.

will, it is hoped, explain some of the different values which are given indiscriminately, and, in fact, without proper explanation in the various publications dealing with optical rotation.

It may be unnecessary to point out that Rimbach,<sup>1</sup> Landolt,<sup>2</sup> and others have shown that the light factor of a quartz-wedge saccharimeter may vary with the nature of the substance measured. This is on account of the difference in the rotary dispersion of quartz and the solution measured, the result being that all the rays of the spectrum whose planes are rotated by the solution are not restored exactly to their original angular positions by a section of oppositely rotating quartz of one definite thickness. Hence no position of the quartz compensation wedges will exactly restore the original light effect of the end-point when the solution is placed in the instrument, and a more or less parti-colored field is given in shadow saccharimeters. If the dispersion difference is slight, this can be obviated and an evenly tinted field obtained by absorbing the rays of the blue end of the spectrum by means of a ray filter of bichromate solution, or somewhat less effectively, but more conveniently by means of a piece of brown (carbon) tinted glass. The ray filter, however, in the case of the quartz-wedge saccharimeter, merely assists in obtaining a more precise end-point. The light factor, as determined by a solution of commercial glucose, for instance, will differ appreciably from that obtained with quartz. Even cane-sugar solutions differ sufficiently from quartz in rotary dispersion to give light factors of slightly different value.

Hence, it is imperative, in stating that the light factor of a saccharimeter is a certain value, that reference should be made (1) to the exact nature of the light used in the rotation readings; (2) the saccharimetric standard of the scale of the quartz-wedge instrument; (3) the nature of the substance measured; and (4), obviously, the temperature at which the comparisons are made. It would seem as if these conditions of measurement ought to be well known, but they are singularly ignored in statements in publications on the subject, to the confusion of most readers.

## READINGS AT 20°.

	(1) Sacch. read- ings, orig. Ventzke scale.	(2) Sacch. read- ings, true cc. scale.	(3) Laurent read- ings, orig. light.	(4) Laurent read- ings, Lippich Ray-filter.
Quartz A . . . . .	62.66	62.45	21.667	21.719
Quartz D . . . . .	96.02	95.77	33.200	33.284

<sup>1</sup> *Ber. d. chem. Ges.*, 27, 2282

<sup>2</sup> *Ibid.*, 21, 191.

## 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

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## VARIATIONS OF STANDARD AMONG VENTZKE SACCHARIMETERS.<sup>1</sup>

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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,<sup>2</sup> 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,<sup>3</sup> 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-

<sup>1</sup> Read at the Providence meeting of the American Chemical Society.

<sup>2</sup> Review Am. Chem. Research, V, 105 (1899); This Journal, 25, 1007 (1903).

<sup>3</sup> 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.