XLV. Description of a new spectrophotometer and an optical method of calibration

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To cite this article: Prof. D. B. Brace Ph.D. (1899) XLV. Description of a new spectrophotometer and an optical method of calibration, Philosophical Magazine Series 5, 48:294, 420-430, DOI: 10.1080/14786449908621432

To link to this article: http://dx.doi.org/10.1080/14786449908621432

Published online: 08 May 2009.

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tive discharge, is the fact that $k$ is probably less for blunt than for sharp points with a given current.

The smaller the current, however, the smaller this discrepancy will be; and a small current is also likely to give rise to a smaller back-discharge error. On the other hand, the error which is due to the luminous projection from the negative point may be reduced by using a sharper point. Two points of respective diameters 0.013 cm. and (approx.) 0.001 cm. were therefore selected, and sixty observations of the $\pi$-pressure made as before with each for an average current of 990 e.s. units. Taking $k = 1.5$ the number of molecules in the diameter of a positive cluster deduced from these data was 16; that for the negative cluster 12. These numbers are consistent with the higher speed of the negative ions, besides being likely to be more reliable than those given above for the reasons just stated. Whether the use of still smaller points and currents, if it were practicable, would alter them much it is impossible to say. At least they represent the order of magnitude of the quantities concerned, and they thus afford considerable support to the theory of molecular clusters.

In conclusion I wish to express my thanks to Mr. E. H. Dixon for valuable aid during the later experiments on the estimation of $\pi$; and to my assistant, Mr. Herbert Strachan, who helped me with the greater part of the work, and to whose skill and patience much of the success of the experiments is due.

XLV. Description of a New Spectrophotometer and an Optical Method of Calibration. By Prof. D. B. Brace, Ph.D.*

To Govi, Vierordt, Crova, Cornu, Glazebrook, Wild, König, and Lummer and Brodhun, and others are due different types of spectrophotometric instruments. The arrangement adopted by Govi, Vierordt, Crova, and others of bringing the two spectra to be compared into contiguous positions by means of double slits and total-reflecting prisms fails in eliminating the dark line separating the two, and thus reduces the sensibility of the eye in determining a match, as is well known to be the case unless the bounding lines of the two fields are perfectly sharp, and vanish completely when set for a match. The same defect exists in the polarizing arrangements of Glan, Crova, Glazebrook, König, and others, where the two spectra are brought into juxtaposition by

* Communicated by the Author.
double-image prisms or extra collimators and prisms. The visibility of this bounding line reduces the sensibility at least one-half. In the arrangement of Cornu, and later of Kundt, of applying a diaphragm to the objective, similar difficulties are met with. The method first applied by Babinet, and used by Wild, Trannin, and others, of superposing the interference-bands from two sources of light after passing through polarizing-systems, in addition to the serious fatiguing effect on the eye, does not allow of the sharp contrast necessary for the highest sensibility.

In the different methods adopted by Lummer and Brodhun of causing the separating line to vanish we have one of the conditions for the greatest sensibility of the eye. If the "contrast principle" introduced by them be further utilized, we have the highest sensibility yet attained. In direct comparisons of white light this latter principle has been successfully applied; but in spectrophotometry the optical difficulties in the way of its use have prevented the obtaining of corresponding results.

In the measurement of the relative intensities we have a variety of methods, most of which involve serious cutting down in the intensity of the original source; so that for many experiments the field is too weak for the eye to make accurate comparisons. This is true of polarizing-systems and also of sectorial systems, both when used as fixed diaphragms before the objective and when made to rotate before the slit. The use of absorbing-screens or of diverging optical systems in spectrophotometry is impracticable. It has also been shown by Lummer and Murphy that the direct use of the slit-width cannot be relied upon in all parts of the spectrum when it exceeds a certain value dependent upon the dispersive power of the prism and the nature of the source. In the Lummer-Brodhun spectrophotometer, as constructed by Schmidt and Haensch, together with a direct-reading variable rotating sector, after the principle of Talbot, for varying the intensity, we have a means of comparison of the colours of the spectrum to a degree of sensibility not hitherto attained in other forms of instruments. This sensibility quite exceeds the constancy of the ordinary sources of illumination, except of incandescent filaments and pencils actuated by the same electric current. The want of a source of sufficient intensity, constancy, and uniformity throughout the spectrum is still for many comparisons, particularly in the study of absorption, a serious hindrance in spectrophotometric measurements.

The elaborateness and expense of such an outfit practically excludes it from general use in colour measurements. The
instrument and method of measurement to be described show that quite as great, if not greater, sensibility and greater facility in making comparisons are attainable with a much simpler form. The two chief factors of this system are the peculiar prism used and the method of obtaining the intensities free from the errors heretofore involved in the readings of the slit.

Fig. 1.

The compound prism (fig. 1) is made up of two equal rectangular prisms A D B and A D C polished on their three faces, and so cut that when placed with their longer sides in contact the whole forms an equilateral prism with three polished faces. It is evident that two rays of the same colour, red say, incident at the same angle and in the same plane will pass out and form parallel rays $a_r$ if one pass through the prism and the other be totally reflected at $d$ by the face A D. If the incident rays be of a higher frequency, violet say, they will also pass out forming parallel rays $a_v$. Thus two systems of incident parallel rays of white light will form, on emergence, two spectra with corresponding rays exactly parallel, and hence of the same dispersion. If $c$ passes through the face A D and $b$ is reflected, we shall have in a similar way the rays $a_v'$ and $a_r'$ forming similar spectra, but in inverse order to the first spectra. This arrangement immediately enables us to realize all the conditions essential for the highest sensibility, by obtaining two fields with delimitations which are perfectly sharp, and vanish when set for a match.
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This is obtained by a similar method to that adopted by Lummer and Brodhun. One of the prisms (fig. 2), as A D C, is silvered over the face A D and the silvering then carefully removed except a strip S S parallel to A D. The edges of the strip S S must be as sharp and as regular as possible. The two prisms are then carefully cemented together with a substance of as nearly as possible the same index of refraction as the glass.

Light entering the prism A D C by the face D C and striking S S is then almost totally reflected internally, and passes out through the face A C. This occurs up to the edges, where the rays pass abruptly on through the prism A D B by regular refraction. Those rays which enter the prism A D B by the face B D pass on directly through the entire compound prism except those which encounter the strip S S; these are reflected and pass out of the face A B. We have thus an abrupt transition between the two sources of light, so that a perfect continuity in the field obtains when the setting is made for a match.

In order to make comparisons with light as nearly monochromatic as possible, glass of great dispersive power should be used, and this requires a cementing-fluid of corresponding refractive index. The glass selected is that from the factory of Messrs. Schott and Co., Jena, Catalogue type No. O 102, Dense Silicate Flint. \( n_D = 1.6527 \), mean dispersion C to F, 0.01950. Canada balsam may be used as the cement, but much better results have been obtained with alpha-monom bromonaphthaline, \( n_D = 1.6582 \) at 20° C. This fluid is very transparent, particularly in the blue and violet, and has so nearly the same index as the glass that there is little internal reflexion at the surface A D. It does not attack the silver strip, and, while rather volatile, can be easily cemented in at the edges by insoluble material such as gelatine, shellac, &c., making it fairly permanent. If necessary, the prism may be readily taken apart, cleaned, and refilled a number of times without injury to the faces or the silvering.

In order to adjust the instrument for use the collimator T (fig. 3), the prism P, and the telescope R are placed to give minimum deviation for sodium light, the cross-hairs of the eyepiece coinciding with the centre of one of the sodium lines. The collimator T is then screened and T′ adjusted so
that the cross-hairs bisect the sodium line. The two spectra are then found to be exactly superimposed throughout their extent. On removing the eyepiece and inserting in its stead Fig. 3.

an ocular slit usually about 2 millim. high and 0.5 to 1 millim. wide, and observing the prism directly with the eye, a circular field crossed by a horizontal band is seen, which latter vanishes, giving a uniform tint over the entire aperture, when the intensities of the two sources are properly adjusted by varying the slits. When the telescope R is shifted continuously through an angle of about 6°, the field appears lighted up uniformly with all the spectral colours in succession. The slightest fluctuation in the light or disturbance of the instrument manifests itself at once in the outlining of the horizontal strip. The advantage of a single prism in obtaining the same effect as with a prism and the cube of Lummer-Brodhun is evident in the simplicity of adjustment and the elimination of optical defects arising from a greater number of reflecting and refracting surfaces, only one prismatic refraction occurring after the rays leave the silvered strip. The symmetry of the optical system allows the use of the ordinary spectroscope and spectrometer as a spectrophotometer by the addition of an extra collimator.

Method of Calibration.

One of the serious difficulties in spectrophotometry is in determining the relative intensities of the sources. The direct use of the method of varying the distance is too cumbersome for colour-work, while the composition of the light may be changed by admixture from extraneous sources. The direct use of Nicol and other polarizing prisms during
observation reduces the intensity too much to allow of accurate settings in many experiments. The same may be said of the variable rotating sector in direct observations. The loss of light is at least one-half by the last two methods, and generally much more. As Lummer and Murphy have shown, the direct reading of the width of the slit cannot be taken as a measure of the relative intensities, errors of several per cent. arising in different parts of the spectrum, depending on the slope of the luminosity curve. This fact makes the method of Vierordt with a double slit defective. It is only with very narrow slits and large dispersion that the direct readings can be taken; and even in this case the true zero of the slit cannot be accurately determined, and is subject to variation by the deterioration of the edges.

However, either of the above methods—varying the distance of the radiant or using Nicol prisms, or placing a rotating sector between the source and the slit—may serve to obtain the true optical value of the slit for different widths and colours. This method of optical calibration eliminates all the errors of the screw and irregularities and lack of parallelism of the edges of the slit, and corrects the variations in the slope of the luminosity curve. With this calibration, comparisons can be made far more rapidly, and as accurately as with the direct use of the rotating sector, which Lummer and Brodhun have shown to be the most reliable method. Usually with each setting this sector must be stopped and read, a tedious but accurate process. In order that such a sector may be capable of variation and adjustment while running, to obtain a match, elaborate and careful construction is required. A simple disk, however, divided into several sectors, say six to eight, may be used to determine the optical values of the slit—which should be bilateral—in corresponding ratios; and the intermediate values may be found by interpolation, and thus eliminate any further use of the disk, the screw-readings being used thereafter directly, with the corrections of the calibration.

A simple cardboard disk, mounted on a whirling-table or motor, with its circumference divided into any convenient number of parts—eight for example—and slotted out to different depths between different radii, as shown in fig. 4, and then slid forward between the source and the slit, so that
the different sectors may cover the slit in these successive positions, will vary the intensity of light at the ocular slit in ratios depending on the angle of these sectors. Suppose, for example, the disk is placed before the slit of T, fig. 3—which may be unilateral—a match having first been obtained and the bilateral slit of T' read. When it is rotated a new adjustment of the slit of T' is made until a match is again obtained. This gives a position representing seven-eighths the full optical value of the slit. This may then be repeated for the other sectors of different angles, obtaining readings for six-eighths, five-eighths, down to one-eighth the optical value of the full slit. We have, then, a series of optical values of the slit in terms of the first or of any other, and found by knowing the ratio of the angles of the corresponding sectors. With these data we may interpolate to find the optical values of the slit widths for any other measurement. By shifting the telescope R we obtain calibrations for the specific colours whose comparison we wish to make, these being free from the numerous errors entering into the general optical system. We may also obtain intermediate values by varying the slit of T and repeating the process. We can then remove the disk and place our source to be compared before the same slit, and make all further measurements in terms of our calibrated bilateral slit. The width of the slit of T being once set should not be disturbed during one series of measurements, after which it may be varied and a new series made.

After the calibration the bilateral slit should in no case be closed, and in making a setting the screw should always be turned in the same direction. This calibration assumes a constancy in the radiant before T', but the error arising from the luminosity curve is small in most cases, and as further the form of this curve does not change materially over considerable variations in the intensity of the source, such, for example, as filaments or pencils brought to incandescence by the electric current, no sensible error enters into the calibration from this cause.

When the inclination of the curve of luminosity does not alter rapidly, as in the case of filaments, corrections for colours not calibrated may be interpolated from the calibration curves of adjacent colours. However, with the collimator slit of 25 millim. width or less, and a dispersive power equal to that of the flint-glass above mentioned, the corrections due to the form of the luminosity curve are less than the error of observation when the standardized slit is bilateral as described above. In this case we only need to determine the optical values for two readings of the slit corresponding, say, to the
full intensity and to one half of this, to find any intermediate values from the screw-readings, by simple proportionality, assuming the screw itself to be accurate. Except in serious disarrangement of the instrument this calibration can be relied upon in all future measurements, even when new incandescent lamps are used before the standardized slit of T'.

Description of the Instrument.

Fig. 5 shows the complete spectrophotometer as constructed by Schmidt and Haensch, of Berlin, one-seventh actual size. The two collimators, T and T', and the telescope, R, are mounted in one plane. The collimator T carries a unilateral slit and is fixed rigidly on a radius of the ring Q. The collimator T' carries a bilateral slit, which is calibrated and used in making the settings, and is mounted on a radial arm movable about the axis of the instrument and having a micrometer screw N', and may be clamped to the ring Q. Set screws may displace the screw N'. The telescope R is also mounted on a radial arm so that its axis passes through the axis of the instrument. It can be clamped to the ring Q, and carries a micrometer screw, N, and a vernier for reading the divided arc, M, concentric with the axis of
rotation of \( R \). This last may be omitted and a micrometer screw with graduated head used, the ring \( Q \) being dispensed with entirely. This telescope is also provided with a variable ocular slit over which may slide the ocular \( E \). The compound prism \( P \) is mounted on a plate above the axis of the instrument which passes through the prism at the intersection of the axis of the telescope with a line drawn perpendicular to this axis from the vertex of the prism next to \( T' \), which is the radiant axis of colour. This plate has a slight movement at right angles to the axis, for purposes of adjustment, and is capable of being screwed permanently to the body of the instrument. The axis of the telescope should also pass through a point in the adjacent face of the prism at half its height and one-fourth the distance across the face from the vertical angle formed by the two half-prisms, to the angle adjacent to \( T' \). The axis of each of the collimators should lie at the same height as the axis of the telescope, and should intersect the back face half-way between the adjacent vertical angle and the dividing plane of the prism. Each half of this back face then receives, symmetrically, the rays from the collimator to which it is adjacent; and the telescope receives the combined rays from that half of the front face to which it is adjacent. The silvered strip between the two half-prisms may be seen within the prism \( P \). This strip is deposited upon the right half of the compound prism, so that reflection takes place on the side next to the glass upon which it is deposited, so as to insure a better surface and less oxidation. It is essential that the lines bounding this strip be sharp and parallel to each other, and in a plane normal to the refracting edge of the prism which is adjacent to \( T' \), in order to avoid diffraction.

The total-reflecting prisms are mounted on the slits of \( T \) and \( T' \), so that the instrument may be used for spectroscopic work and also as a modified form of Crova's or of Vierordt's spectrophotometer, by inserting the eyepiece \( E \) and examining the two contiguous spectra either from \( T \) and \( T' \), or from one of them, using the total-reflecting prism.

With this instrument the setting for minimum deviation for sodium light is first made with the collimator \( T \). The prism \( P \) is then fastened permanently, and the telescope \( R \) clamped, and the collimator \( T' \) then adjusted until the image of the slit is bisected by the cross-hairs. \( T' \) is then clamped permanently. The divided arc \( M \) may then be adjusted to zero, corresponding to the sodium line. It is then calibrated for the different Fraunhofer lines or for different wave-lengths of light. The eyepiece \( E \) is then removed, and the ocular slit adjusted so as
and an Optical Method of Calibration.

To obtain homogeneous light when white light is placed before the collimators. If it is too narrow (less than 0.5 millim.) diffraction takes place, and if too wide—it should not exceed 1 mm.—the light is no longer homogeneous over the field of view. The objective of $R$ is usually stopped to about 15 millim. The field should then be perfectly circular and crossed in the centre by a horizontal band 5 millim. wide. In the calibration of the bilateral slit of $T'$, the rotating disk is placed immediately in front of the slit of $T$, its axis being in the plane of the axes of $T$ and $T'$, so that its radii cross the vertical slit at right angles. The disk may then be moved forward or backward by only a small amount to bring different sectors over it. The pitch of the screw should preferably be 25 millim. and a total motion of 2 millim. will be sufficient, the working width of both slits being usually not greater than 1 millim. The radiant is, in general, an incandescent lamp with a ground-glass plate before the slit. With careful adjustment the instrument has given for the mean colours of the spectrum readings differing by less than 0.5 per cent. from a mean of ten readings, or a mean error of less than 25 per cent. for one setting, or double the sensibility heretofore obtained. This is largely brought about by the fact that adjustment is easier, and there is only one refraction instead of three as in the Lummer-Brodhun form; the boundary is sharper and vanishes more completely. The question of a suitable source has, however, been a serious difficulty, particularly one of sufficient intensity to make comparisons of large absorptions in the blue and violet. All the various forms of gas-burners have been found to be too constant. Specially constructed lamps with flat wide filaments or with close spirals, together with frosted globes and plates, have given almost as great a constancy and sensibility in the case of high absorption, as obtained above with unobstructed rays and under more favourable circumstances. Large variations in the voltage do not seem to affect the slit calibration, which remains constant under varying conditions. The rotating disk can be easily constructed from bristol board and mounted for the purpose of calibration, which is readily made; or a pair of mounted nicols may serve the purpose equally well. If these simple means are not at hand, the distance of the radiant from a frosted glass before the unilateral slit may be used.*

* The firm of Schmidt and Haensch of Berlin will be able to supply this instrument with some modifications for about 500 marks. They are also able to furnish one of their larger spectrometers fitted with an additional collimator, which makes a spectrophotometer superior to the
The optical principle involved in this compound prism, of obtaining a comparison viewing-screen with vanishing line in the dispersive prism itself, may be extended to other forms of instruments, such, for example, as Helmholtz's colour-mixing apparatus with two collimating telescopes containing Rochon prisms. Experimental results of this nature are reserved for future publication.

University of Nebraska,
July 29, 1899.

XLVI. On the Theory of the Electrolytic Solution-Pressure.
By R. A. Lehfeldt, D.Sc.*

The electromotive force between a metal and an electrolyte depends on the concentration, in the latter, of the ions of the same kind as the former; and it is easy to show in certain cases, on an irreproachable basis of thermodynamic reasoning, that variation of the electromotive force is proportional to that of the logarithm of the concentration. Thus, supposing the electrolyte to be a binary univalent salt (e.g. KCl) and completely dissociated, then if C be its concentration (gm. mol. per cub. centim.), the E.M.F. of the contact may be expressed in the form

\[ E = -\frac{RT}{e} \log_e C + \text{const.}, \]

where \( R \) = gas constant, \( T \) = temperature, \( e \) = quantity of electricity associated with one gram equivalent; or, if we prefer to use instead of \( C \) the osmotic pressure \( P \) produced by the metallic ions,

\[ E = -\frac{RT}{e} \log_e P + \text{const.}, \]

where the only difference is in the value of the constant. So far no assumptions are required except those usually implied in the thermodynamic treatment of solutions with the aid of semipermeable membranes.

Form here shown. Certificates of calibration might be furnished with the instrument, but it should be borne in mind that the curve of luminosity depends on subjective conditions, and a calibration by one individual might differ from that of another, particularly if the eye of one is trichromatic and that of the other dichromatic or monochromatic. However, the calibration curves of different observers have been found to be the same, which agrees with the results of König, who has shown that the slope of the curve is approximately the same in these different cases.

* Communicated by the Author; read before the British Association, Sept. 20, 1899.