Notes on Spectrophotometry. By R. W. DITCHBURN, B.A., Trinity College, Isaac Newton Student.

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1. *Sources of light for ultra-violet spectrophotometry.*

The source of light used as a background is an important factor in determining the convenience and accuracy of ultra-violet absorption work, etc. If a source of light of constant intensity is available, a direct comparison method can be used and it is only necessary to calibrate the plates. If the source of light is not constant in intensity, it is necessary to divide the light into two beams and use one to check the variations of intensity while the other goes through the absorbing substance or (during calibration) the reducing sector or wedge. This latter method requires much more complicated apparatus and if the variations in the source are at all large it becomes inaccurate. In addition to being constant in intensity a good background for ultra-violet absorption spectra should possess the following qualities:

(1) Most of the energy should be emitted in the form of a continuous spectrum.

(2) It is desirable to be able to use one photograph of the whole region to be investigated. For this purpose it is necessary that the variations of intensity in different parts of the spectrum should be small enough for it to be possible to arrange the exposure so that all parts of the spectrum are within the correct exposure range, i.e. it must not be necessary to over-expose any part in order to get a strong enough intensity at another wave-length.

The hydrogen continuous spectrum possesses both these qualities and is an excellent background for the region on the short wave-length side of 3200 A.U. It may be used for longer wave-lengths, but the hydrogen secondary lines are apt to prove troublesome unless a fairly large dispersion is used.

The most convenient way of producing this light is a discharge tube of the pattern invented by Lyman* (Fig. 1). The writer has found that with suitable precautions it is possible to make this tube run perfectly steadily. In the form used by the writer the tube is of soft glass and a quartz window is waxed on to one end, enabling the capillary to be viewed end on through the cylindrical electrode. A more permanent tube might be constructed of pyrex with tungsten-pyrex electrode seals and a pyrex-quartz seal enabling the quartz window to be fused on.

* *Astrophysical Journ.* 23, 181 (1906).

The diameter of the capillary should be between 2 and 3 mms. and the length between 5 and 6 cms. There is some advantage to be gained by making one of the ends larger than the other and, since the window must be placed well away from the electrode, the window end should be the larger. A bulb of about a litre capacity is attached to the tube to prevent violent changes of pressure when the tube heats up and also to reduce the fall of pressure produced by prolonged running of the discharge. The best pressure is about a millimetre of mercury, which is a little above the pressure at which the effective impedance of the tube is least. This assists in producing stability. When the current increases, the tube becomes hotter, the pressure rises and causes the current to fall, and similarly if the current falls the consequent change of pressure tends to bring it back to its former value.

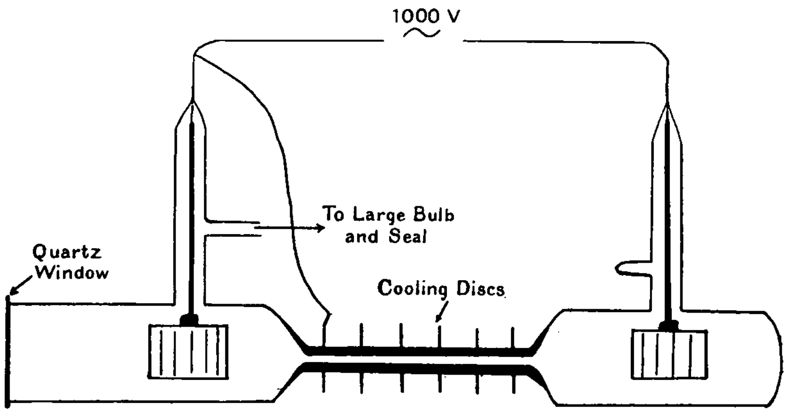

Fig. 1.

It is very desirable to have the hydrogen really pure. For this purpose the tube should be run for some hours with a stream of electrolytic hydrogen passing through it, liquid air traps being placed between it and the nearest taps. This removes mercury and hydro-carbons. Lyman* found that when the discharge was run a film collected on the window. This seems to be entirely due to the presence of hydro-carbons. For this reason the window should be taken off and cleaned after the discharge has been run long enough to remove all traces of hydro-carbon. After this the tube is again run for some hours with the stream passing and then the pressure is adjusted to a little above the right value and the taps are turned off. The tube is then run for at least three hours more to get rid of the last traces of oxygen and mercury and is then sealed off. The purity

* Lyman, *loc. cit.*

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of the hydrogen is best tested by watching the relative intensity of the line and continuous spectra. When the hydrogen becomes really pure the relative intensity of the latter increases enormously.

The tube runs much more steadily with nickel electrodes than with aluminium. The electrodes should be prevented from vibrating and this is conveniently done with small glass wedges. The source of electrical supply is a 1000 volt transformer, the current being controlled by a resistance in the primary. As much as 200 milliampères may be put through the tube steadily, but with currents of more than 30 milliampères the capillary needs cooling. This is secured by wrapping with tinfoil on which may be fastened the brass radiating discs. With a current of 100 milliampères the continuous spectrum is sufficiently intense to be photographed in a low dispersion spectrograph with an exposure of a few seconds.

The tube may still run unsteadily owing to certain capacity effects. These are avoided in the case of the tube at present in use by connecting the cooler to one side of the supply. For another tube it was found to be desirable to connect a Leyden jar to the cooler instead. These capacity effects are difficult to understand, but it is fairly easy to find the right arrangement to eliminate them after a few trials.

When this has been done the tube runs steadily to better than a half per cent. If run on the town supply it is of course necessary to follow the fluctuations of the supply and keep the current through the tube constant by adjusting the resistance in the primary of the transformer. Photometric tests showed that for small changes the intensity of light produced is proportional to the current. Thus the constancy of the source is simply dependent on the effectiveness of the control of the supply voltage.

The only other constant sources of continuous ultra-violet light are the tungsten lamps and the cadmium spark used by Harrison*. The intensity of the tungsten lamp falls very rapidly in the direction of shorter wave-length. It is necessary to take several exposures to cover any considerable range of wave-length and the intensity is very feeble for wave-lengths below 2800 A.U. The source used by Harrison seems to possess most of the qualities of the hydrogen tube in the region from 3500 A.U. to 2000 A.U. The hydrogen discharge tube appears to be simpler and more convenient than the spark. Moreover, with a fluorite window, it may be used for work in the Lyman region.

2. *Reducing Sectors, etc.*

For all methods of spectrophotometry it is necessary to have some way of reducing a beam of light in a known ratio. The purpose of this section is to discuss the various devices which have

* Harrison, *Phys. Rev.* 24, 466 (1924).

been used, and to describe a form of sector which is simple in construction and possesses many advantages.

I. *Neutral Wedge Methods**. A wedge of neutral grey glass is cemented to one of clear glass. The difference between the absorption coefficient (for a given wavelength) at two planes, such as A and B, is proportional to the distance between them. If it is desired to have a small area where the absorption coefficient is constant, two grey wedges may be used, as shown in Fig. 2 *b*. The small wedge has the same angle as the other, and thus the same density gradient. The density of the combination is constant over the area of the small wedge, and is varied by moving the large wedge.

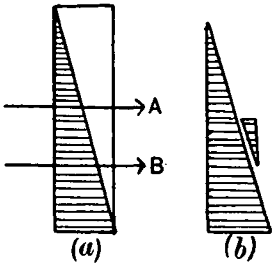

Fig. 2.

For ultra-violet work, wedges of gelatine on quartz have been investigated to λ2900 A.U. by Toy and Ghosh†. Wedges of spluttered platinum have been used by Merton‡ and by Dorgelo§. These last have not a uniform density gradient, but this can be allowed for in calibration.

The neutral wedge is very useful for many purposes (as is illustrated in the book of Dobson, Griffiths and Harrison), and it is the basis of the very interesting method of spectrophotometry devised by Merton, but it is at best a secondary standard in that it needs to be calibrated by reference to some other reducing device.

II. *Variable Aperture Screens.* The screen is used to reduce the effective area of one of the lenses in the optical system. If the illumination were uniform over the whole area of the lens an iris diaphragm might be used. To compensate for uneven illumination a grating or gauze replaces the simpler diaphragm. The opaque and clear spaces must be quite irregularly distributed, or else the screen must be kept in irregular motion to and fro across the surface of the lens.

The calibration is made by measuring up the area of the opaque spaces. A set of about five different screens is needed, and by using these in different combinations a sufficient number of calibration points is obtained.

This method of reducing the intensity suffers from two disadvantages.

* Dobson, Griffiths and Harrison, *Photometric Photometry*, ch. I.
† Toy and Ghosh, *Phil. Mag.* 40, 775 (1920).
‡ Merton, *Proc. Roy. Soc.* A, 106, 378 (1924).
§ Dorgelo, *Phys. Zeits.* 26, 756 (1925); *Zeits. f. Phys.* 31, 827 (1925).

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(1) If the size of the spaces is too small diffraction effects become appreciable, and these cause an error which is different for different wave-lengths. If, on the other hand, the size is too large the distribution over the lens area will not be sufficiently irregular. It is very difficult to be sure that both these troubles have been avoided.

(2) The calibration (which must consist of measuring up each space) is rather a lengthy process, and it is by no means certain that the value will remain constant. If the screen consists of a set of lines ruled on a silvered surface it is very liable to collect a little dust or to become oxidised, and so change its opacity by a few per cent. Wire gauze or metal plates drilled with a number of holes are a good deal better from this point of view, but not perfectly satisfactory.

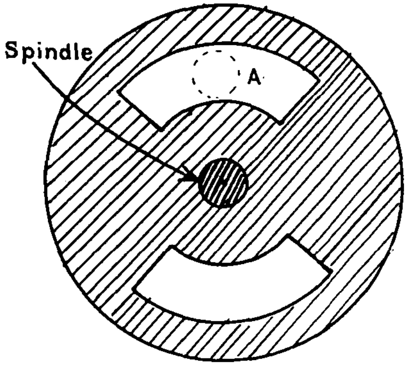

Fig. 3.

III. *Nicol Prisms.* A pair of nicol prisms is placed in the path of the beam; the intensity of the light transmitted is proportional to the square of the cosine of the angle between their principal planes. It is necessary to arrange that the light entering the spectroscope always has the same plane of polarisation.

This method is convenient for visual measurements though, as will be shown later, the angle-sensitivity is rather low. For ultra-violet work Foucault air prisms might be used since Canada Balsam is opaque. These have a small field, and cannot be used below $\lambda 2500$ A.U., since calcite begins to absorb strongly at this wave-length.

IV. *The Circumference-aperture Sector.* In this device two discs of the shape shown in Fig. 3 are fastened on the same spindle so that they can be fixed at any angle relative to each other and so that the whole system can be rotated. The light passes through the aperture A, of which the size can be varied by

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altering the angle between the discs. This device is very simple and is quite useful for finding the shape of an absorption curve (qualitatively), but it cannot be used for accurate quantitative work on account of the failure of the reciprocity law of photographic action. It is known that the effect of steady exposures is approximately proportional to It^p (where I is the intensity, t the time of exposure and p is a constant). These, however, are not steady exposures, and it is not known what the law of action is for intermittent exposures of this type. There is thus no possibility of working out a correction, and this method is more uncertain than calibrating by reducing the length of exposure.

V. *The Judd-Lewis Vane Sector**. The sector system consists of four triangular vanes, each of which has two edges at right angles. The angles of the vanes all meet in a point, so that when they are all in one plane (perpendicular to the direction of the beam) no light is allowed to pass. The vanes are capable of being rotated about their bisectors ("*m*" in Fig. 4 *a*) through a measured angle, and their shadow in the beam is in the form of a maltese cross (Fig. 4 *b*).

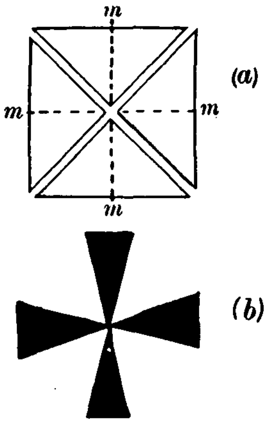

Fig. 4.

The sector system is placed in a parallel beam of light with its centre as near as possible to the axis of the optical system. The area of the beam is thus reduced in a known ratio. The intensity of the beam will be reduced in the same ratio, provided that the mean intensity over the shadowed part of the beam is equal to that over the clear part. In view of the form of the shadow this condition will in general be fulfilled, but if the source is an arc or spark capable of wandering far from the axis of the optical system an appreciable error might be involved. The sector possesses the advantage of having the whole aperture available (and not half, as in most sectors). This advantage is however completely outweighed by the mechanical difficulties of the device. These make it useless for general purposes.

VI. *The Radial-aperture Sector.*

We shall now describe a radial-aperture sector which was made for the writer by Messrs Bellingham and Stanley, and has been in use for the past year.

* Judd-Lewis, *Trans. Chem. Soc.* 1919, 312; *Journ. Roy. Soc. of Arts*, 1921, 206.

This sector consists essentially of two discs A and B, in each of which there is a semicircular hole. The discs have a common centre C, being mounted on the same large hollow spindle D. A can be rotated relative to B and fixed in any position. A is divided into degrees, and B carries a vernier so that the angle LCM can be read to a tenth of a degree. The sector system is placed in a parallel beam of light, and C is fixed as accurately as possible on the axis of the optical system. The reduction of area and of intensity is similar to that produced by the Judd-Lewis sector, but the radial aperture sector may be rotated to eliminate the effects of non-uniformity over the area of the beam. It has always been found necessary to carry out this rotation. When the centre of the

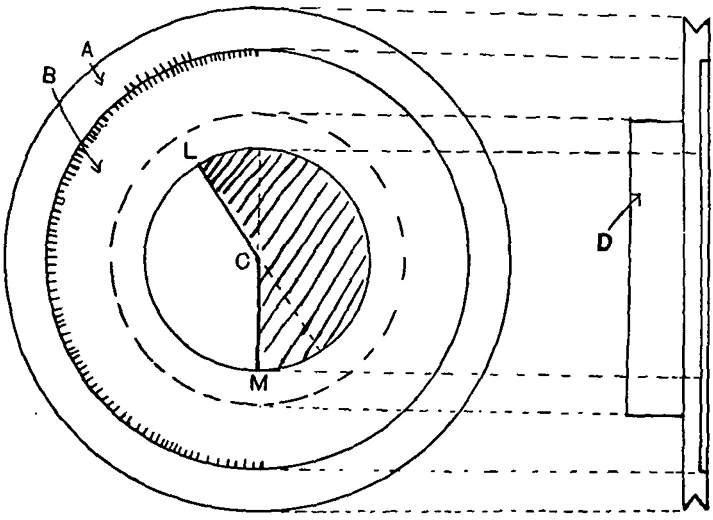

Fig. 5.

sector has apparently been set on the optical axis, it is found on looking into the spectroscope that quite large changes of intensity are produced when the sector is turned. Great care is needed in making a final adjustment so that no perceptible difference could be seen on rotating the sector.

Dr Skinner has pointed out to me that the difficulty of this adjustment may be avoided when it is possible to place the sector in one focal plane of the lens which condenses the light on to the slit of the spectrograph. When the sector is not quite accurately set on the axis of the optical system, intermittency is really produced by movement of the image of the sector which, in general, is partially focussed on the slit of the spectrograph. With the above arrangement, however, the image of the sector is at infinity and is thus completely out of focus on the slit of the spectrograph. It is desirable to employ this arrangement when using any of the aperture-reducing devices described in Sections II and IV.

In comparison with the Judd-Lewis instrument this sector has the disadvantages that only one half of the field is available, and that it has only one aperture instead of four symmetrically placed openings. It has, on the other hand, the advantage of being much simpler in construction (which means that less reliance is placed on the workmanship and that it is less costly). Moreover it may be rotated when this is desirable.

For technical purposes and routine work it may be desirable to have an instrument which need not be rotated. For this purpose it is necessary to have several symmetrical openings. The radial aperture sector may be modified in the following way. Two metal plates are accurately cut in the shape shown in the diagram and mounted on a large hollow spindle. By fixing them at different angles relative to one another the beam may be cut down in any desired ratio. In this way three symmetrically placed openings are obtained. By suitably cutting the plates any number of symmetrically placed openings may be obtained. If more openings than one are used, however, each of them will have to be proportionately narrower for a given intensity. This means that diffraction effects will be greater and also (as will be shown later) that the angle-sensitivity will be reduced in proportion to the number of openings. For purposes where it is not desired to rotate the sector, the three-aperture type is probably the best. It should be noted that even this type, while not so simple in construction as the single-aperture type, is considerably simpler than the vane sector and can be rotated if necessary.

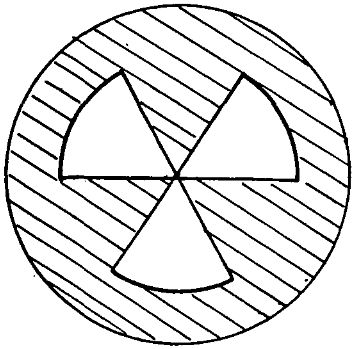

Fig. 6.

Angle Sensitivities.

In several of the methods described above the reduced intensity is calculated from the measured value of an angle. In comparing the instruments it is interesting to see how the intensity changes with the angle in each case. We may define S by the following equation:

$$\frac{1}{S}=\frac{1}{I}\frac{dI}{d\theta} \quad \text{.........................(1)},$$

where I is the fraction of the maximum intensity which is trans-

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mitted when the measured angle is θ (zero angle being that where no light is transmitted). S measures the accuracy with which it is possible to measure the absorption coefficient of a substance which transmits the same fraction of the incident light. Or, looking at it from a slightly different point of view, S measures the rate of change of density of an equivalent absorbing screen; for

$$D = \log_{10} \frac{1}{I} = k \log_e I$$

$\left(\text{where } k = \frac{-1}{2{\cdot}3}\right)$,

$$\frac{1}{S} = \frac{d}{d\theta} (\log I)$$

$$= k \frac{d}{d\theta} (D) \qquad \text{.........................(2).}$$

We shall refer to S as the "angle-sensitivity," and proceed to compare its values for the different instruments.

We first write down the relations between I and θ:

(A) *For the Nicol prisms,*

$$I = \sin^2 \theta \qquad \text{.........................(3);}$$

(B) *For the Judd-Lewis vane sector*,*

$$I = \frac{\pi - 4 \tan^{-1} (\cos \theta)}{\pi} \qquad \text{.................(4);}$$

(C) *For the Radial-aperture sector,*

$$I = \frac{n\theta}{\pi} \qquad \text{.........................(5),}$$

where n is the number of openings available.

For the circumference-aperture sector the relation is the same as for the radial-aperture sector with two openings.

From these we obtain for S,

(A) *For the Nicol prisms,*

$$S = \tfrac{1}{2} \tan \theta,$$

$$S = \tfrac{1}{2} \sqrt{\frac{I}{1+I}} \qquad \text{.......................(6);}$$

(C) *For the Radial-aperture sector,*

$$S = \theta,$$

$$S = \frac{\pi I}{n} \qquad \text{............................(7).}$$

(Thus S is inversely proportional to n, the number of openings.)

* Judd-Lewis, *Trans. Chem. Soc.* 1919, 316.

(B) The expression for S is rather complicated in the case of the vane sector, and the values of S are best obtained by calculating pairs of neighbouring values for I.

The values of S for the different instruments are shown as functions of I in the accompanying graph (Fig. 7). The graph shows that, for intensities of ten per cent. and less, the angle-sensitivities of the Judd-Lewis and the radial-aperture sectors (with

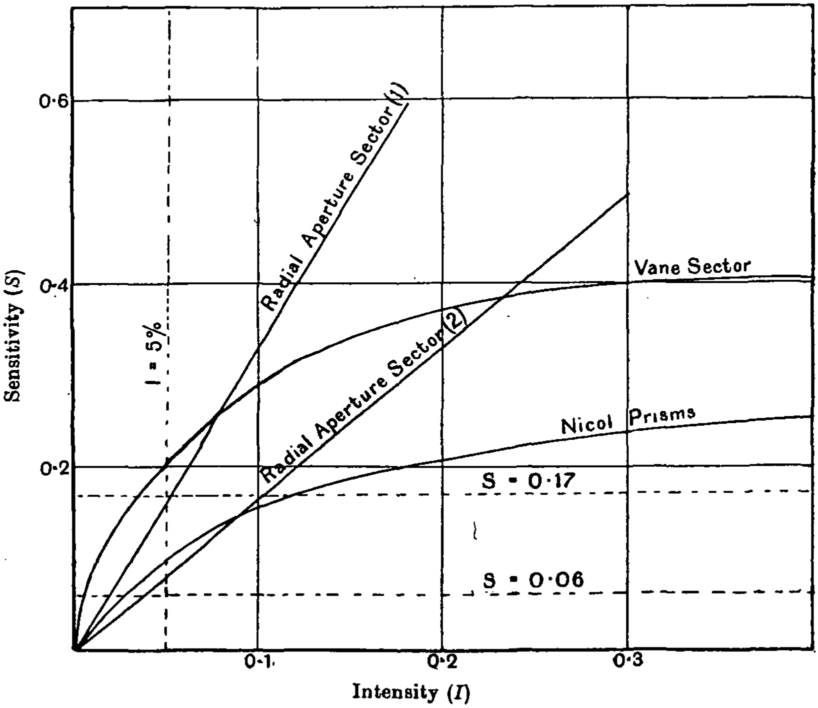

Fig. 7.

one opening) are about equal. The angle-sensitivity of the nicols in this region is about the same as that of the radial-aperture sector with two openings, i.e. half that of the radial-aperture sector with one opening. For intensities of over ten per cent. the radial-aperture sector with one opening has a far greater angle-sensitivity than any other device.

In general it is necessary to be able to measure I to one per cent. in order to have the error of the sector of the same order as other experimental errors.

Since $S = Id\theta/dI$ and we must have $dI/I \not> 1/100$, we require $S \not< \cdot 17$ if angle readings are correct to one-tenth of a degree, and $S \not< \cdot 06$ if angle readings are correct to one-thirtieth of a degree. From the graph we have

$$S \not< \cdot 17$$

for the Vane sector when	$I \not< \cdot 04$
„ „ Radial-aperture sector (1 opening)	$I \not< \cdot 06$
„ „ Radial-aperture sector (2 openings)	$I \not< \cdot 11$
„ „ Nicols	$I \not< \cdot 12$

and $S \not< \cdot 06$

for the Vane sector when	$I \not< \cdot 007$
„ „ Radial-aperture sector (1 opening)	$I \not< \cdot 02$
„ „ Radial-aperture sector (2 openings)	$I \not< \cdot 04$
„ „ Nicols	$I \not< \cdot 03$.

In general it is not desirable to use this type of device to effect a reduction to less than about five or ten per cent. of the original intensity. In the case of the sectors, diffraction effects become appreciable when the openings are too narrow. In the case of the nicols, errors due to obliquity of part of the light may enter. If a greater reduction is desired it is better to use a wedge and calibrate it in position by reference to the sector or the nicols. We thus see that an accuracy of one per cent. in I is required for values of I of ·05 and greater. For this purpose it is necessary to know θ to one-tenth of a degree for the vane sector and the radial-aperture sector (with one opening). For the nicols and the radial-aperture sectors with two or three openings it is necessary to read the angle to one-thirtieth of a degree in order to reach this accuracy.

If it is desired to be able to vary I by one per cent. it is necessary to have verniers reading to one-tenth or one-thirtieth of a degree. But if, as is usual, it is only necessary to know I to this degree of accuracy for a set of values spaced at about ten per cent. intervals, the scale need only be divided into degrees, provided that the setting is made with the above accuracy.