XXXII.—*A New Sector Spectrophotometer.*

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IN a paper by the author on "The ultra-violet absorption spectra of blood sera" (*Proc. Roy. Soc.*, 1917, [B], **89**, 327), it was stated that the work described had been done with two sector spectrophotometers, that these were not adequate to the exacting nature of the investigation, although they were the best and most modern instruments available, and that a new photometer to the author's design was under construction. That apparatus has now been in use for several months, and the purpose of this paper is to describe it. A short account of the method of using such instruments is given in the reference mentioned above.

As was the case with the work detailed in the paper cited, the present development of the sector spectrophotometer has been generously supported by the Beit Research Fund Committee, the trustees of a fund which has been placed at the disposal of the British Homeopathic Association by Mr. Otto Beit for purposes of scientific research.

The new instrument was designed by the author in 1915 with a view to meeting the requirements of the work on blood serum. No instrument can be unnecessarily refined for this, and should it be desired to employ the method of ultra-violet absorption spectrography for clinical purposes, whether for blood serum or for any other substances, an instrument which is at once trustworthy and easy to manipulate is essential. Incidentally, an instrument which fulfils these conditions should satisfy most of the demands of scientific research and bring the practice of ultra-violet absorption spectroscopy within the range of applied chemistry. Unless or until the ideals set out are attained, absorption spectroscopy can have little more than academic significance; but perfect, easily adjustable spectrophotometers may be expected in course of time to occupy a place in the general laboratory not less important than that filled by the polarimeter or the refractometer.

Among the objects aimed at in the new design were the following:

(*a*) The utmost accuracy and refinement in the resulting spectra, because for the serum work it is required to discover with certainty very small differences of detail in the absorption curve, as explained in the paper cited.

(*b*) To work quickly as well as accurately, since it is necessary to undertake the examination of a serum at very short notice, and there is no reasonable opportunity of revising the observation, as

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the serum will usually have changed in character by the time the absorption curve is drawn; this presumes quick and perfect adjustment of the instruments.

(c) To maintain this excellent adjustment throughout an experiment, or to restore it from time to time during the progress of an observation, without the necessity of other disturbances.

(d) Precise quantitative values for the extinction coefficients, since the amplitude of the curve has important significance.

(e) To attain this high standard, and yet to be able to use the one spectrograph alternately with the photometer and for other purposes as circumstances may require.

The photograph exhibits the general appearance of the new photometer; it exposes the vanes in the upper sector, the front of the sector box having been removed; also only one platform bearing a tube carrier is shown. The arrangement of parts is displayed in the diagram.

Q represents a suitable lamp, light from which falls on the two lenses L_1 , L_2 , which render the light parallel. These pencils of light pass through the face a_1b_1 in the reflecting prism P_1 and through the face a_2b_2 in the reflecting prism P_2 in the manner shown, and are reflected approximately at right angles by the inclined faces a_1c_1 in prism P_1 and a_2c_2 in the prism P_2 , so that in each case the light follows a course parallel to the main axis of the prism to a second inclined face b_1d_1 in prism P_1 and b_2d_2 in prism P_2 , where it is reflected again at right angles.

The parallel beam reflected from b_1d_1 passes through the sector D_1 , the diaphragm O_1 , and the lens L_3 to the inclined face e_1f_1 in reflecting prism P_3 , where it is reflected at right angles along the main axis of the prism on to the inclined face g_1h_1 , where it is again reflected at right angles and passes out of the prism on to the face ki of the rhomb R placed in front of the slit S of the spectrograph, or, in the absence of the rhomb, directly on to the slit.

The pencil from b_2d_2 undergoes similar treatment, and eventually passes out of the photometer on to the face kj of the rhomb.

The rhomb may be dispensed with if the pencils of light are directed so as to fill the angles of the prisms at g_1 and g_2 , provided that one prism slightly overlaps the other, as shown in the figure, so that the prominent edge may define the line of juxtaposition. It will be seen that any stray parts of the pencils of light would be reflected or escape out of the field.

The essential part between the two prisms in either path is the sector D_1 , D_2 , capable of cutting off any desired portion of the light passing along that path.

It should be observed that the prisms and sectors are enclosed in dust-proof metal boxes provided with quartz windows.

The sector system is placed in a part of the path where the light is parallel. It consists of four vanes, V_1, V_2, V_3, V_4 , as shown in the side elevations in the figure. Each vane has two edges at right angles, and when the four vanes are disposed to one another in one plane, so that the four angles meet at a point, the system is closed and no light can pass. This arrangement is represented in the upper path in the figure. The common point of the four angles is on the optic axis, to which the plane is at right angles. Each vane can be turned by means of suitable mechanism about its bisectors, m_1, m_2, m_3, m_4 . When all the vanes are turned simultaneously through an angle of 90° about their respective bisectors, light can pass in the direction of the optic axis without any interruption except that caused by the slight obstruction due to the thickness of the material of the vanes, as shown in the figure for the lower path. By turning the vanes through any other given angle about their bisectors, a known proportion of the light may be allowed to pass. Each of the four vanes is carried on a wheel, by means of a spindle which coincides with the bisector of the vane and also forms the axle of the wheel. These wheels are mounted on the outside of the walls of the box enclosing the sector at right angles to one another, and fit into one another by bevelled cogs. They move simultaneously, and the fitting is so close that back-lash is reduced to an insignificant minimum. The amount of rotation of the vanes is measured by a pointer, I , mounted on the front wheel and moved against an arc graduated in half degrees from 0 to 90.

A diaphragm or stop, O_1, O_2 , is placed in front of each sector to reduce the section of the beam of light to suitable dimensions, say 9 mm. in diameter when the observation tubes or cells have a lumen of 12 mm.

In order to correct the error caused by the obstruction due to the thickness of the material of the vanes, their edges are reduced to knife edges, and the thickness along the bisector is graduated from the minimum at its extremity at the optic axis to what is necessary, say 1 mm., at a distance of 10 mm. The two sides of each vane are equally made, and each of the four surfaces is plane or concave. Hence a section through a vane at right angles to its bisector has the form of a rhombus having two very obtuse and two very acute angles; also a section which includes the bisector has the form of an isosceles triangle.

It follows that when the sector system is open, as shown in the lower path in the figure, the obstruction or shadow produced by

each vane has the form of a geometrical sector of known dimensions, and therefore the sectional area of the pencil of light passing through the sector system is reduced by four times the area of one small sector shadow; also, each of the four apertures has the form of a geometrical sector.

Compensation for this reduction in area is made by employing for the path in which the light is to be of whole, or 100 per cent. intensity, that is, for the path in which the substance under observation is placed, a diaphragm the aperture of which is appropriately larger than that of the diaphragm in the other path. In the author's instrument, the diameter of the larger aperture is 9.3 mm. and that of the smaller 9.0 mm. These diaphragms are loose and may be used with either sector, according to whether it is desired to use the upper or lower sector.

The only limitation to this arrangement is that the sectors do not operate for those angles which are included by the small angle covered by the thickness of the vanes. In the author's instrument this is 2.6° , so that the range of operation is from 2.6° to 90° .

The lenses L_3 , L_4 , placed between the sectors and the second set of prisms, focus the light on the slit, the focus being that for light of a wave-length of about 3000.

The edge of the rhomb is placed close to the slit, so that the two pencils of light when they emerge from either side of it into the slit may be at the focus of the collimating lens; the line of juxtaposition between the two spectra is thus very clearly defined without the least overlapping or intervening space, with the result that the lines in the two spectra, whether visual or photographic, can be compared for their relative intensities at the best advantage.

The cell containing the substance under observation is placed in the parallel beam of light between the sector and the central lens; room is provided for tubes up to 100 mm. in length, and tubes of this length were used successfully in an investigation relating to Lambert's law. As the pencil of light is 9.3 mm. in diameter, it is desirable for long tubes that the lumen of the tube should be at least 12 mm. in diameter, so as to avoid serious reflection from the inner walls of the tube. When the lumen is small and the layer of substance thin, it may be placed in the convergent beam immediately in front of the prism P_3 , as shown at w , and a still smaller cell might be interposed between the prism P_3 and the face ki of the rhomb, but only with due regard to existing conditions. Inasmuch as the system in the lower path of light is identical with that in the upper, the cell may be placed in the lower with equal advantage, or, as explained later, cells may be placed in both beams simultaneously.

The new instrument is characterised chiefly by its sectors; these are distinguished both in their construction and in the principles upon which they operate. In comparison and contrast with other sectors, they accommodate the whole beam of light, and not merely half, as is the case with some others; this enables exposures to be reduced to one-half in order to produce a photograph of the same intensity; the exposures being continuous, calibration of the photographic plate is avoided; the direct function of the new sectors is to cut down the intensity of the light, and not to do so indirectly by altering the exposure, as is the case with the Hilger instrument; the sector is still, which is a great convenience. The whole aperture of the sector system is made up of four sector-shaped apertures arranged diagonally about the optic axis, that is, they are disposed at an angle of 45° to the vertical. This has the advantage of utilising all parts of the circular beam of light in proper proportion, whatever the magnitude of the effective aperture at the moment. In this it differs from the iris and other forms of stop or sector, which reduce the intensity of the light by cutting down the light from the periphery of the beam inwards, or by cutting it down in some other way which assumes that every part of the field is equally illuminated. Under the conditions of ordinary practice, this assumption lacks sufficient justification where precise photometry is required.

The size of the sector aperture is measured in terms of the angle which it forms at the optic axis. The angle 45° represents an aperture of 100 per cent., and the angle formed at the optic axis by the shadow cast by one half of a vane in any given position is ϕ . Hence the sector aperture is proportional to $45^\circ - \phi$. This method of measuring the size of the aperture is exceedingly convenient both for simplicity of calculation from the angle θ , which is read on the graduated arc, and for the fact that apertures of any odd value may be produced at will. This will become evident from the following explanation of the manner of calculation.

When the vane acb in the figure (α) (front elevation) is turned through an angle θ , as measured by the graduated arc, so as to take up the position ecf , each half of the vane ec or cf creates a sector-shaped shadow in a beam of light in the direction of the arrow; $e'd'$ is a projection of ed . It is shown again in the figure (β) in side elevation, where $e'd'$ is the projection of ed . If the beam of light were rectangular in section, the shadow would be triangular in shape ($e'd'o$) and proportional in area to $\sin \theta$, since ed , which subtends the angle θ , is equal to e_1d_1 , which subtends the angle ϕ at the optic axis, O , for ed' and $d'o$ are equal, since they form the right angle in the isosceles triangle $ed'o$; therefore $ed'/ed' =$

$e'd'/d'o$, that is, $\sin \theta = \tan \phi$, whence θ being known, ϕ may be found directly from the tables.

The beam of light, however, is circular in section; hence the area of any sector in the circle is proportional to the angle which it contains, that is, to ϕ for the shadow and $45^\circ - \phi$ for the sector aperture.

Only one-eighth of the whole circular aperture has been considered, but it will be seen on cancelling common factors that the whole aperture at any moment is measured by $45^\circ - \phi$, where 45° is taken to represent the fully open sector. It is convenient to express the apertures as percentages of the whole aperture, that is, as $\frac{(45 - \phi)100}{45}$. The percentage apertures and values for $\log I/I'$

corresponding with each half-degree on the graduated arc have been calculated by Miss Gartha Thompson, to whom the author is indebted for valuable assistance throughout the inquiry. Examples are given in the following table:

θ .	Sin θ or tan ϕ .	ϕ .	$45 - \phi$.	Sector aperture, per cent. $\frac{(45 - \phi) 100}{45}$	Log I/I' , $\log \frac{45}{45 - \phi}$.
				45	
10	0.1736482	9.85108	35.14892	78.11	0.1073
25	0.4226183	22.90981	22.09019	49.08	0.3091
40	0.6427876	32.73241	12.26759	27.27	0.5644
40.5	0.6494480	33.00163	11.99837	26.67	0.5740
41	0.6560590	33.27239	11.72760	26.07	0.5839
55	0.8191520	39.32269	5.67731	12.62	0.8991
70	0.9396926	43.21918	1.78082	3.958	1.4026
80	0.9848078	44.56143	0.43857	0.975	2.0111
80.5	0.9862856	44.60441	0.39559	0.870	2.0559
81	0.9876883	44.64512	0.35488	0.789	2.1031
85	0.9961947	44.89078	0.10922	0.243	2.6150
85.5	0.9969173	44.91155	0.08845	0.197	2.7065
88	0.9993908	44.98255	0.01745	0.0388	3.4114

It is evident that the values in the table can be applied to graduating the arc on the instrument so that it may read directly in terms of $\log I/I'$, as has been done with other instruments. This is convenient where it is intended to use the instrument for routine work only, but for versatile research, and especially where it is desired occasionally to elaborate a particular part of an absorption curve, the freedom conferred by the ordinary scale and tables will be appreciated. There is, however, no difficulty in providing both scales on the same arc.

The effect produced by the size of the shadow cast by the vane being a function of the sine of the angle through which the vane has been turned is significant. From the above figures, it will be

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seen that the difference in the sector aperture produced by a constant difference of 15° in θ decreases continuously, thus:

								Per cent.
Between 10° and 25°	the aperture decreases by (78.11—49.08)							29.03
" 25° "	40°	"	"	"	"	"	(49.08—27.27)	21.81
" 55° "	70°	"	"	"	"	"	(12.62—3.96)	8.66
" 70° "	85°	"	"	"	"	"	(3.96—0.24)	3.72

Again, for half-degree intervals in θ :

Between 20° and 20.5°	the aperture decreases by (58.03—57.09)							0.94
" 40° "	40.5°	"	"	"	"	"	(27.27—26.67)	0.60
" 80° "	80.5°	"	"	"	"	"	(0.975—0.879)	0.096
" 85° "	85.5°	"	"	"	"	"	(0.243—0.197)	0.047

For any of the apertures of small size, it is evident, therefore, that a movement of the pointer on the arc over one or more divisions alters the size of the aperture by only a small fraction, so that any probable error in construction or manipulation can have no detectable effect on the measurement of the size of the aperture.

The possibility of regulating the size of the small apertures with such precision is a valuable advantage, since it is with these that much of the more important and delicate work is done.

In an investigation of uric acid, undertaken to see if it obeyed Lambert's law, it was proved that the results for all the small apertures down to 0.29 per cent. (reading 84.5° on the graduated arc and giving the value 2.53 for $\log I/I'$) harmonised perfectly with those found for the larger apertures. The still smaller ones were not quite so true, owing to a slight imperfection in the setting of the vanes, but this can be avoided in reproducing the instrument.

The instrument is absolute in all its measurements. That it is not only so, but that it is also precise, follows from the examination of a standard piece of glass which was supplied by Messrs. Adam Hilger with their photometer for calibration purposes. The figures obtained are tabulated below. The two sets of values for $\log I/I'$ are as follows: (a) those obtained by the new photometer; (b) the figures given by Hilger:

Wave-length.	(a).	(b).
2751	0.281	0.278
2636	0.665	0.610
2564	0.919	0.888
2478	1.318	1.330
2435	1.605	1.608
2389	1.970	1.940

Of the two methods, the one with the new photometer has the advantage of being direct and of not depending on the assumption

that photometry in the ultra-violet is uniform with that in the visible region and on the use of accessory apparatus, as in the method published by Hilger. In any case, the two series of results are sufficiently similar to one another to call for a discussion as to which is the more accurate expression of the phenomena.

Considerable advantage is gained by having two sectors which are equal in all respects, as in the new photometer. As already stated, the substance can be placed in the first and second paths alternately, so that any slight imperfections in the sectors or in any part of the optical train will express themselves in opposite senses in the two series of spectra; also the work will be confirmed and experimental error corrected at the same time. The mean of the two closely concordant results must be a very near approximation to the truth.

Further, opportunity is provided for eliminating the effect of the solvent directly. Most of the solvents, alcohol, for example, give feeble absorption spectra which spoil the accuracy of the extinction coefficients of the dissolved substance under investigation. It is not altogether satisfactory to correct the absorption constants of the solution by subtracting those due to the solvent, which have been ascertained separately, and in any case it is laborious to do so; for example, it is not safe to assume that a standard curve for absolutely pure alcohol applies to commercially pure spirit. Indeed, some of the impurities commonly occurring in rectified spirit are strongly absorbent of ultra-violet light. It is better to place in the one path a tube of the solution, and in front of the constant sector a similar tube filled with the same solvent as that used in making the solution. It is a good plan to have a tube of the given solvent in each of the two paths when adjusting the instrument, and then to replace the solvent in one of them by the solution in question. It is perhaps unnecessary to do so, but it lends a sense of satisfaction, while it adds little or nothing to the experimental work. It is certain that the differences then observed in the two spectra are due entirely to the substance in the dissolved state, and hence its absorption curve can be derived directly. There is, however, the possibility of the absorption spectrum being modified by the association of the solute with the solvent, but that is a matter for other inquiry in each particular case and does not affect either the general truth of the proposition or the operation of the instrument.

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