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USE OF THE UNDER-WATER SPARK WITH THE HILGER SECTOR PHOTOMETER IN ULTRA-VIOLET SPECTROPHOTOMETRY

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ABSTRACT

The paper describes a device for the operation of a high-voltage electric discharge between metal terminals under distilled water and its use with the Hilger sector photometer in ultra-violet spectrophotometry.

The spark terminals are inclosed in a hard-rubber box, through which a stream of distilled water may be circulated. External adjustments are provided for the length of the spark gap and its position relative to the axis of the optical system.

The effect of the dispersion introduced by the biprism and wedges of the sector photometer is discussed in its relation to the adjustment of the spark; and some modifications in the construction of the photometer are suggested.

CONTENTS

I. PURPOSE AND SCOPE OF PAPER

The high-voltage discharge under water has been used by many investigators as a source of radiant energy in ultra-violet spectrophotometry. Its advantage over arcs and sparks in air or other gases lies in the continuity [1] and uniformity of its spectrum throughout the visible and ultra-violet regions to the limit of transmission of the quartz spectrographs commonly employed in this kind of work. The uniform continuous spectrum is most suitable for quantitative spectrophotometric measurements and enables the accurate location of sharp absorption bands.

This source has been in use at the Bureau of Standards for a number of years in the well-known method of photographic spectrophotometry employing the Hilger sector photometer with a quartz spectrograph. The theory of this method and a description of the apparatus have been given [2] in B. S. Sci. Paper No. 440 (Scientific

[1] Under certain conditions an electrical discharge through hydrogen yields a continuous spectrum, which has been used by others for absorption measurements.

[2] See also papers by Howe, Phys. Rev. (2), 8, p. 674; 1916; and by Tyndall, B. S. Tech. Paper No. 148 Appendix.

Papers of the Bureau of Standards, vol. 18, p. 121; 1922), and the reader is here assumed to be familiar with the general nature of the apparatus and its method of use.

Since the above paper was issued, however, improvements have been made in the construction and operation of the source. Various improvements in the photometric apparatus have been under consideration but, owing to the pressure of other work, have not been effected. In view of the increasing application of quantitative methods to the study of the absorptive properties of materials in the ultra-violet, it is believed that the following description of the improved source, with the accompanying discussion of the photometric apparatus, will be of interest to those contemplating the design and installation of similar equipment.

II. CONSTRUCTION OF SOURCE

In the use of the under-water spark with the Hilger sector photometer certain difficulties arise as a result of the wave-length dispersion along the axis of the spark gap, introduced by the biprism and wedge lenses of the photometer. As explained later, this necessitates a careful adjustment and rigid support of the spark terminals and the use of an adequate length of spark gap in order to obtain and maintain the desired equality between the intensities of the two beams of radiant energy emitted by the spark to the photometer.

The construction of the new source is shown in Figure 1. The spark terminals are inclosed in a hard rubber box, the inside dimensions of which are 75 by 75 by 90 mm. The upper terminal enters the box through a thick hard rubber circular rod, which projects well under the surface of the water before exposing any of the bare metal of the terminal. This is an important detail of the construction, in order to confine the high-voltage oscillatory discharge to the spark gap. When the bare metal is allowed to come in contact with the surface of the water, the discharge tends to follow the surface around to the other terminal.[3] The lower terminal of the spark gap is grounded, as is also the lower terminal of the tesla coil (*T*, fig. 1) and the whole metal support for the box. The upper terminal of the tesla coil is connected by a carefully insulated wire to the upper well-insulated terminal of the spark gap. Adjustments for the length of the gap are provided, as clearly illustrated in the figure.

The metal used for the terminals is tungsten wire approximately 2 mm in diameter. Molybdenum, brass, and other metals have also been used. The operation of the spark and the continuity of the spectrum are apparently independent of the nature of the metal.

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[3] In the original construction of the box this matter was not given careful consideration. As a result, it was later found necessary to alter the construction sufficiently to provide the proper insulation of the upper terminal before a satisfactory operation of the spark was obtained.

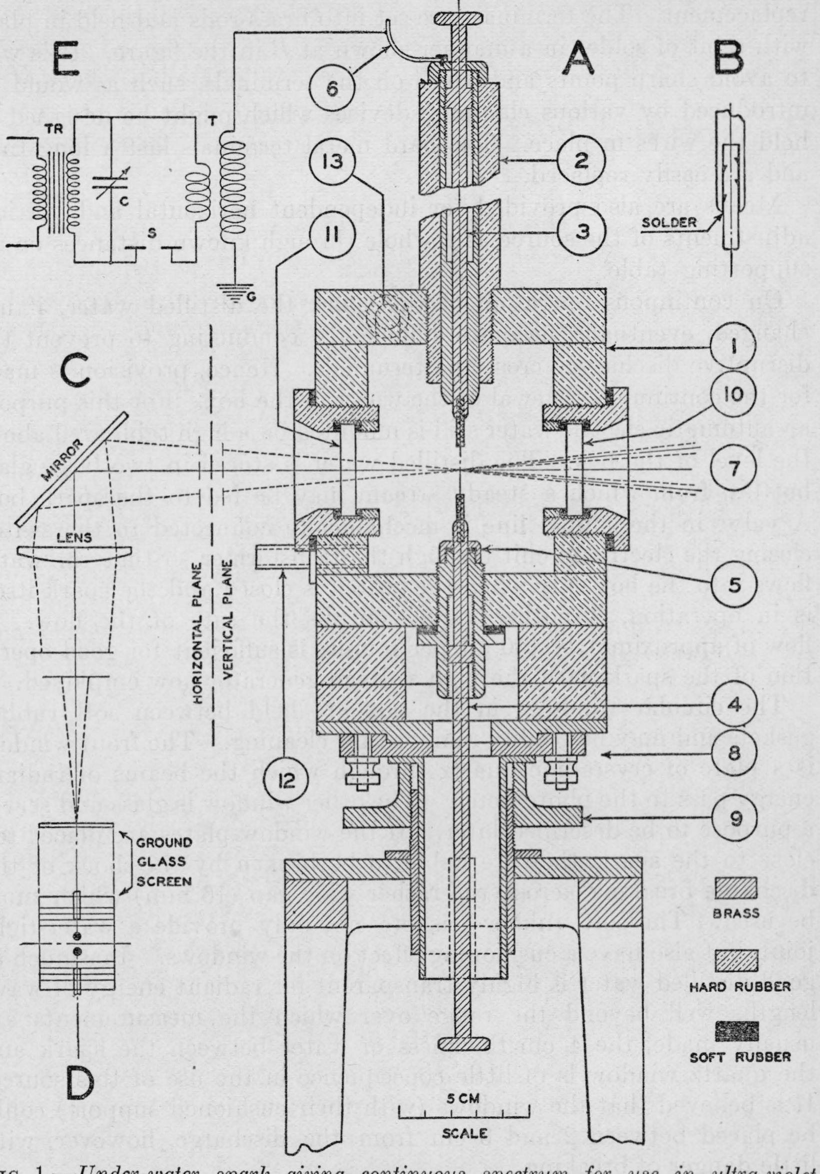

FIG. 1.—*Under-water spark giving continuous spectrum for use in ultra-violet spectrophotometry*

A, vertical median section through center of spark terminals and beams to photometer. (*1*) Hard-rubber box, inside dimensions 75 by 75 by 90 mm. Built up from sheet stock 2 cm in thickness. Plates held together by cement and metal screws. (*2*) Hard-rubber rod 3 cm in diameter. (*3*), (*4*) Brass rods carrying hard-metal terminals of spark gap and adjustable in vertical direction. (*5*) Packing box to prevent leakage of water. (*6*) Electrical connection to upper terminal. Lower terminal and metal parts of base are grounded. (*7*) Beams of radiant energy to photometer. (*8*) Provision for horizontal adjustment of spark box, in direction perpendicular to beams. (*9*) Vertical adjustment of spark box. (*10*) Crystalline quartz window. (*11*) Glass window. (*12*) Inlet for distilled water. (*13*) Overflow tube.

B, showing method for the support of tungsten or other hard metal terminals in brass rods (*3*) and (*4*).

C, Lens and mirror arrangement imaging plane of spark terminals on ground-glass screen.

D, showing images on ground-glass screen of spark terminals and beam sections (for green light) in plane of spark.

E, electrical circuits for operation of spark. (*T*), Tesla transformer. (*S*), primary spark gap. (*C*), variable condenser (set of Leyden jars). (*TR*), Iron-core transformer, 110 to 20,000 volts.

A hard metal is preferable, to avoid rapid wearing and frequent replacement. The terminals are set into brass rods and held in place with a bit of solder in a manner shown at *B* in the figure. It is well to avoid sharp points and edges on the terminals, such as would be introduced by various clamping devices which might be designed to hold the wires in place. The hard metal terminals last a long time and are easily replaced.

Means are also provided for independent horizontal and vertical adjustments of the source as a whole through known distances on its supporting table.

On continuous operation of the spark the distilled water, if unchanged, eventually becomes sufficiently conducting to prevent the disruptive discharge across the terminals. Hence, provision is made for the continuous renewal of the water in the box. For this purpose an automatic electric water still is mounted on a high table well above the level of the box. The distilled water is stored in two large glass bottles, from which a steady stream may be fed to the spark box. A valve in the supply line is mechanically connected to the switch closing the electric circuit through the transformer so that the water flows into the box only when the switch is closed and the spark itself is in operation. Another valve controls the rate of the flow. A flow of approximately 150 ml per minute is sufficient for good operation of the spark with the high voltage generator now employed.

The circular windows in the box are held between soft rubber gaskets and may be readily removed for cleaning. The front window is a plate of crystalline quartz through which the beams of radiant energy pass to the photometer. The other window is glass and serves a purpose to be described later. If the window plates are placed too close to the spark, they are liable to be broken by the shock of the discharge breaking across the rather wide gap (16 mm) which must be used. The soft rubber gaskets not only provide a water-tight joint, but also have a cushioning effect on the windows. Inasmuch as good distilled water is highly transparent for radiant energy of wave lengths well beyond the range over which the measurements are usually made, the 4 cm thickness of water between the spark and the quartz window is of little consequence in the use of this source. It is believed that the windows (with their cushioned support) could be placed between 2 and 3 cm from the discharge, however, with little danger of breaking.

III. WAVE-LENGTH DISPERSION IN OPTICAL SYSTEM OF PHOTOMETER

A diagram of the optical parts of the Hilger sector photometer[4] is shown in Figure 2. Two beams of radiant energy from the spark

[4] The sector photometer here under discussion was built in the shops of the Bureau of Standards and is a duplicate of the Hilger instrument. Any small differences in construction which may exist would not materially affect the present discussion.

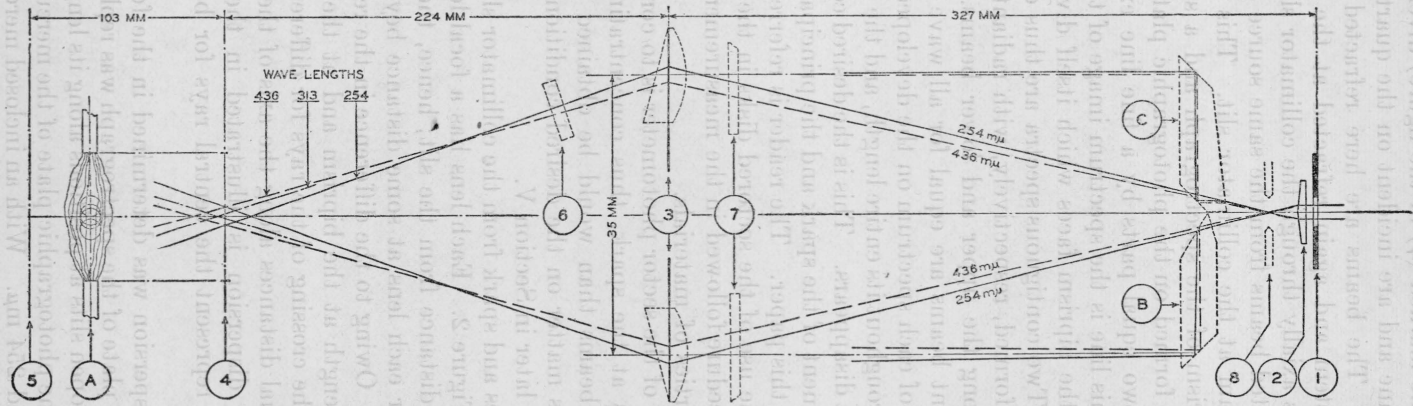

FIG. 2.—*Trace of rays through Hilger sector photometer, showing (primarily) the dispersion at the spark gap introduced by refraction at the biprism and at the wedges on the photometer lenses*

Vertical spread of beams on diagram is drawn to four times the scale of the horizontal distances; hence the dispersion is magnified four times in the diagram. Optical parts are not drawn to scale.

Description of parts: (*1*) Collimator slit of spectograph. (*2*) Biprism, made of crystalline quartz cut with optic axis perpendicular to back plane surface. (*3*) Wedge lenses of photometer. Each is a single piece of crystalline quartz cut with optic axis parallel to axis of lens. Focal lengths of lenses each approximately 16 cm. (*4*) Plane of spark gap and mean position for crossing of beams. (*5*) Approximate plane of foci of collimator slit. (*6*) Transmission sample. (*7*) Variable sectored disks. (*8*) Spark gap between aluminum terminals; used to locate wave-length positions on photographic plate.

A, vertical section through spark gap and through beams of different wave lengths. All dimensions strictly to scale, with 16 mm gap.

B, C, suggestions for redesign of photometer. See text.

(which is placed in the plane marked (*4*) in the figure) diverge from each other in a vertical plane and are incident on the quartz wedge lenses of the photometer. The beams are here refracted toward the axis of the optical system and again refracted at the inclined faces of the biprism to pass axially through the collimator slit of the spectrograph. Two separated beams from the same source are thus combined into a single beam at the collimator slit. This beam is dispersed by the quartz prism of the spectrograph and a spectrum image of the collimator slit formed on the photographic plate. The spectrum is divided into two equal parts by a fine line extending along its entire length. This line is the spectrum image of that part of the intersecting line of the biprism faces which itself divides the slit into two equal parts. Two contiguous spectra are thus obtained on the photographic plate, formed, respectively, with radiant energy entering the instrument along the upper and lower beams. When the intensities of the entrant beams are equal for all wave lengths, the blackening (or density) of each spectrum on the developed photographic plate is the same throughout its entire length, and the dividing line between the two spectra disappears. This is the desired condition to be attained in the adjustment of the spark and the principal matter for further consideration in this paper. The reader is referred to the previous publications for the use of the sectored disks in the entrant beams and the general procedure followed in the measurement of the spectral transmissive properties of materials.

The purpose of the lenses of the sector photometer is to control the cross section of the beams at the spark, thus concentrating more radiant energy into these beams than would be obtained without lenses. The bearing of this matter on the desired conditions of adjustment will be considered later in Section V.

The distances of the lenses and spark from the collimator slit of the spectrograph are given in Figure 2. Each lens has a focal length of approximately one-half its distance from the slit; hence, the conjugate focus of this slit is for each lens at some distance beyond the crossing points of the rays. Owing to the difference in the refraction of rays of different wave length at the biprism and at the wedges on the photometer lenses, the crossing of the rays for different wave length takes place at unequal distances along the axis of the optical system. This wave-length dispersion is illustrated in the figure, where the rays, as drawn, represent the central rays for beams of different wave length.

The magnitude of the dispersion was determined in the following manner: The photographic plate of the spectrograph was replaced by a piece of cardboard having open slits at positions along its length corresponding to positions on the photographic plate of the mercury lines of wave lengths 436, 313, and 254 mμ. With an inclosed mercury arc

lamp mounted behind the cardboard plate, a homogeneous beam of radiant energy of either wave length 436, 313, or 254 mμ could be sent in a reversed direction through the spectrograph and sectored disk photometer. By inserting and exposing strips of photographic plate in the beams at various distances from the biprism to the spark the separation of these beams was recorded for each of the three wave lengths. For the sake of clearness in the representation, the magnitude of the dispersion has been quadrupled in the diagram relative to the other dimensions given therein. Actually, the distance between the two central rays for wave lengths 254 and 436 mμ is approximately 3 mm in the plane of the spark, and the axial distance between the crossing points for these rays is approximately 28 mm.

When the spark is placed at a position along the axis corresponding to the crossing of rays of a wave length in the neighborhood of 300 mμ, both beams to the spectrograph for this same wave length are then taking radiant energy from the same area of the spark. For longer and shorter wave lengths, however, it is obvious that each beam collects its radiant energy from different areas of the spark. The discharge is not continuous, of course, but consists of a rapid succession of sparks following different paths across the terminals and presenting an appearance (due to the persistence of vision) much the same as represented at *A* in the figure. An equality of the intensities of the two beams to the spectrograph for wave lengths in the far ultra-violet or visible spectral regions must depend, therefore, on the proper averaging of the discharges through the separated sections of each beam.

IV. ADJUSTMENT OF SPARK

The best average position of the spark on the axis of the system is at the crossing of the rays for a wave length somewhat shorter than 313 mμ. It is obvious that the terminals of the gap should also be placed in the plane of dispersion (vertical). To obtain an equality of the intensities of the two beams for all wave lengths; it is necessary to use a sufficient length of spark and to accurately maintain the positions of the terminals relative to the axis of the system and the plane of dispersion for the two beams. The greater the length of gap that may be used the less sensitive will be the adjustments. This is apparent from a consideration of the diagram of the spark at *A* in Figure 2; for as the individual sparks wander over the faces of the terminals, or persist for a time at any one point of either terminal, the chance of obtaining a time-averaged equality of the discharges through the separated sections of each beam is greater when the terminals are farther removed from the corresponding sections of the beams. As might be expected, the vertical adjustment of the spark is more sensitive than either horizontal adjustment. These adjustments can be made quite stable and permanent with the apparatus herein

employed when a 16 mm gap is used. The stability of the adjustments is increased very appreciably when the gap is increased from 14 to 16 mm. This gap is about the limit that can be used, however, with the high-voltage generator at present installed. It is believed that still better results would be obtained with a slightly larger gap and a more powerful generator of higher voltage. An excess voltage for the spark and greater capacity in the primary oscillatory circuit would undoubtedly lead to steadier operation of the under-water spark and avoid the necessity for a high degree of purity in the water.

The desired position of the spark gap on the axis of the optical system is known from the diagram of Figure 2, after a correction is applied for the small refraction of the beams in passing from air to water. This adjustment need not be accurate, however. A glass lens and silvered-glass mirror are permanently mounted as shown at *C* in Figure 1, with the spark terminals and a ground glass screen placed in conjugate planes of the lens. These planes are selected to give approximately unit magnification. When an incandescent lamp is set up at the photographic plate end of the spectrograph, in proper position to send a beam of green or blue-green light in reverse direction through the instrument, a cross section of the two beams in the plane of the spark terminals may then be seen on the ground glass along with an image (unmagnified) of the terminals. The picture presented to the eye is illustrated at *D* in Figure 1. By means of the horizontal and vertical adjustments provided for the spark box, the spark terminals may be readily lined up in the plane of dispersion at the spark and the length of the gap adjusted from time to time as the terminals gradually wear away. If a sufficient length of gap is used, this adjustment will be accurate enough to give the desired result; but if for any reason a shorter gap must be used, it may be necessary to take a series of exposures on the photographic plate, each for a slightly different vertical or horizontal position of the spark, and the best position chosen by an examination of the developed plate.

V. SUGGESTIONS FOR IMPROVEMENT OF PHOTOMETRIC SYSTEM

In the preceding sections the construction of the present equipment is described along with a discussion of certain conditions to be fulfilled in its operation. Some modifications in the construction will now be considered, by means of which the required conditions of operation may be realized in an easier and more satisfactory manner. With due consideration for the essential requirements to be met in the optical system, many of the difficulties experienced with this photographic method may be avoided. The particular combination of lenses and dispersion in the present apparatus is inconsistent with these requirements. In the following discussion we are chiefly con-

cerned with the cross section of the beams at the spark and with the linear wave-length dispersion along its (vertical) axis. It is assumed that the wedge lenses are properly adjusted, so that the central rays, as represented in Figure 2, intersect on the central axis of the photometric system.

As a first consideration, let the focal lengths of the photometer lenses be increased so that the conjugate foci of the collimator slit fall at considerably greater distances from the axis of the spark, and the cross sections of the beams at the spark are as represented in Figure 3, *B*, for some wave length in the visible or far ultra-violet. Let the spark terminals be placed so that the entire discharge takes place through the common overlapping sections of each beam. Then, under this condition, each individual spark must send an equal quantity of radiant energy along each beam to the spectrograph. The absolute position of the spark terminals now ceases to be a matter

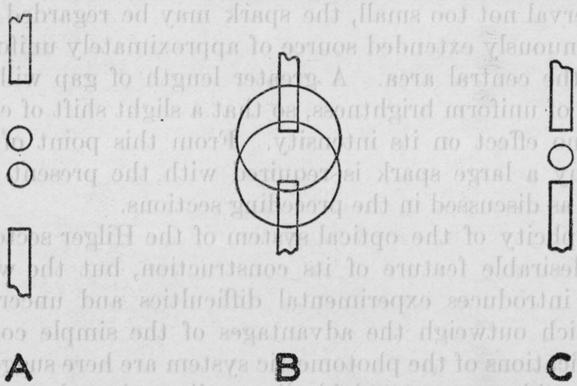

FIG. 3.—*Vertical section through beams at spark gap, corresponding to different constructions of the photometric system*

for careful adjustment. They need only be maintained within the overlapping sections of the beams.

With this arrangement, however, the spectrum obtained on the photographic plate would not be strictly continuous, for radiant energy emitted by the portions of the spark within 3 or 4 mm of the terminals contains some characteristic lines of the metal superposed on the otherwise continuous spectrum; but this would not be a serious disadvantage if the total spark length is not too small. The chief disadvantage of this arrangement would lie in the decreased intensity of radiant energy entering the spectrograph along each beam. To make the most efficient use of the source, its area should completely cover the cross section of the beam.

A more effective means of obtaining the desired ease and permanence of the adjustment is to eliminate the linear wave-length dispersion along the axis of the spark. Then the separated sections

shown in Figures 2, *A*, and 3, *A* (also 3, *B*) would coincide for all wave lengths as illustrated at *C* in Figure 3, and the best focal length of the photometer lenses would be such as to bring the conjugate foci of the collimator slit slightly beyond the plane of the spark. A shorter spark gap could then be used, thus concentrating the discharge through the coincident sections of the beams, with a maximum gain in their time-averaged intensity. As in the arrangement represented by Figure 3, *B*, an accurate adjustment of the spark terminals would not be required. Furthermore, with the shorter spark, a lower voltage would be sufficient for its operation, and by use of a higher voltage primary transformer (*T*, fig. 1) the inefficient Tesla coil could be eliminated. It would be well to use a somewhat larger spark, however, than is indicated in Figure 3, *C*, in order to provide for slight displacements or changes in convergence when a sample is introduced into either beam. When the individual discharges are averaged over a time interval not too small, the spark may be regarded as a somewhat continuously extended source of approximately uniform brightness over the central area. A greater length of gap will provide a larger area of uniform brightness, so that a slight shift of either beam will have no effect on its intensity. From this point of view it is evident why a large spark is required with the present equipment (fig. 3, *A*), as discussed in the preceding sections.

The simplicity of the optical system of the Hilger sector photometer is a desirable feature of its construction, but the wave-length dispersion introduces experimental difficulties and uncertainties in its use which outweigh the advantages of the simple construction. Two modifications of the photometric system are here suggested, each of which avoids any appreciable linear dispersion along the axis of the spark by the use of rhombs to obtain the desired separation of the two beams from the spark to the spectrograph.

One method of use of the rhombs is illustrated at *B* in Figure 2. The angular dispersion introduced at the biprism is unchanged by passage through the rhomb, but if the wedge on the lens at (*3*) is cut down to approximately half its present angle an equal but opposite angular dispersion is introduced into the system which practically annuls the linear dispersion along the axis of the spark. A proper choice of angles and distances could be made to give a practically achromatic system, as far as conditions at the spark are concerned. With this system it would be advantageous to place the sectored disks on the spark side of the wedge lenses, leaving a distance of 20 to 25 cm between the rhomb and the wedge lens for the insertion of the sample. If a parallel beam through the sample is desired, an additional lens could be conveniently mounted on the rhomb support. The advantages of this construction would undoubtedly fully warrant the insertion of the additional optical parts.

An alternative suggestion is indicated by the use of a different type of rhomb at *C* (fig. 2). In this case the angular dispersion introduced by the biprism is annulled at the entrance surface of the rhomb, leaving only a slight and negligible separation of the two rays as represented in the figure. The rays could then be brought to the spark by a similar use of rhombs. This optical system would be quite similar to that employed in the Lewis sector photometer.[5]

It may be noted that each of the suggested modifications of the Hilger sector photometer preserves the convenient biprism and wave-length spark arrangement as shown at (*8*) in the figure. The biprism is unexcelled for the production of a fine disappearing line between the two contiguous spectra on the photographic plate. This, in turn, is an advantage in the accurate reading of the plates. It is important that the entire optical system of the photometer (including the biprism) be firmly mounted on a single metal base.

In both modified designs suggested above either the Lewis vane-sector method or the Hilger rotating sectored-disk method could be used equally well for the necessary control of the relative intensities of the two beams in the spectrophotometric procedure. In the first method the exposure of the photographic plate is continuous (with time), and the intensity of the beam may be decreased directly by decreasing the area of its cross section. In the second method, on the other hand, the intensity of the beam is not altered directly, but, by the use of the rotating sectored disk, the total time of exposure is decreased by intermittently cutting off the beam. The question hence arises regarding the blackening produced on the photographic plate by equal products of intensity and exposure time, when the exposure is continuous in the one case and intermittent in the other. The reader is referred to the papers previously cited and to more recent papers by Baly, Morton, and Riding,[6] and by Ley and Volbert,[7] for a description and experimental comparison of the two photometric methods. These comparisons do not show any discrepancies between the two methods which are greater than other experimental uncertainties in the measurements. The sectored disks are simpler and more accurate from a mechanical standpoint. They may easily be made large enough and with sufficient accuracy to avoid significant errors in the setting of the angular openings to values as low as 1 per cent.

WASHINGTON, June 6, 1928.

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[5] J. Chem. Soc. Lon. Trans., **115**, p. 312; 1919.
[6] Roy. Soc. Proc., **113**, p. 709; 1927.
[7] Zeit. f. Phys. Chem., **130**, p. 308; 1927.