capillary lamps gave over one hundred times as much photochemical action as a commercial lamp.

The chief reason for the high intensity (per sq. mm. of lamp surface) is the high concentration of energy. The volume of the arc in the capillary lamp is approximately 0.05 cc. as against 20 cc. in a commercial lamp. Although the volume of a commercial lamp is 400 times as great, the total input of energy is less. The dimensions of the capillary lamp are such that a much greater fraction of the radiation emitted by the lamp can be brought to the slit of a monochromator or passed into a reaction cell of ordinary dimensions.

The authors are pleased to acknowledge the help contributed by Mr. Glenn Damon and Mr. Harrison Holmes to the development of the lamp described here.

Summary

An inexpensive quartz mercury vapor lamp of high intensity has been described and tested.

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[CONTRIBUTION FROM THE LABORATORY OF PHYSICAL CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

PHOTOCHEMICAL TECHNIQUE. II. CONSTRUCTION AND TESTS OF A QUARTZ MONOCHROMATOR[1]

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Monochromatic radiation of measured intensity is necessary for the quantitative study of photochemical reactions. Separation of the different wave lengths by refraction in a monochromator offers the most effective method for obtaining this radiation but the energy flux available at any one wave length is extremely low on account of losses due to reflection, absorption, slit dimensions, etc. To minimize this handicap a more intense source of light was developed.[2] Further efforts to increase the radiation intensity by using a monochromator of large dimensions and favorable optical conditions are described in the present communication.

The subject of monochromators and of photochemical apparatus has been reviewed in detail by G. S. Forbes.[3] The dimensions and material of the prism and lenses used in the present investigation are approximately those described by Marshall and Knudson.[4] The purpose of

[1] Complete details of the dimensions and calculations may be obtained from the Ph.D. Thesis (June, 1930) of the first author, which is on file in the Library of the University of Wisconsin.

[2] Daniels and Heidt, THIS JOURNAL, **54**, 2381 (1932).

[3] Forbes, *J. Phys. Chem.*, **32**, 482 (1928).

[4] Marshall and Knudson, *ibid.*, **52**, 2304 (1930).

this article, then, is to describe and to present tests for an efficient method of mounting an optical system of fused quartz used as a monochromator. The mechanism described automatically keeps the prism at minimum deviation and in the center of the field, and provides automatic focusing. Previously this has been accomplished by means of compound prism arrangements or mirrors. Included in the tests is a study of the photo-decomposition of uranyl oxalate made prior to the publication of the classic paper of Leighton and Forbes.[5]

Description of Monochromator

Side and top views of the monochromator and accessories are shown in Figs. 1 and 2. A is a 60° fused quartz prism 12 cm. on a side and 14 cm. high. B and B'

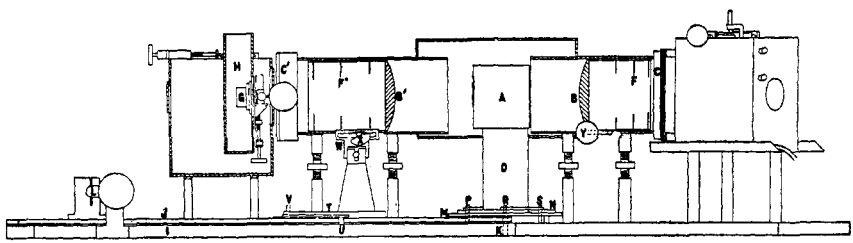
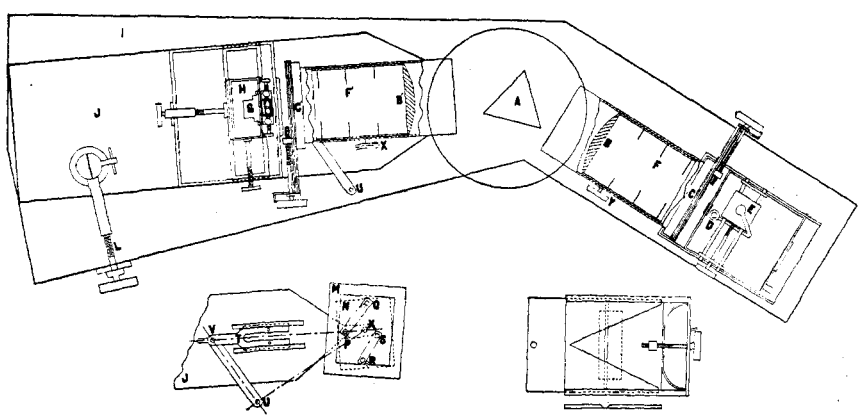


Fig. 1.—Monochromator, side view.

are fused quartz lenses 15.25 cm. in diameter, each with a focal length of 35 cm. for λ795 mμ. C and C′ are slits shown in detail in Fig. 2a. The pupil C is curved to make the exit beam rectangular. D is the source of radiation previously described.[2] Fine



(b) (a)

Fig. 2.—Monochromator, top view.

adjustments placing the source on the principal axis of B are made by a screw attached to E. F and F′ are graduated elliptical diaphragms three of which are placed in each of the collimator and telescope tubes to diminish stray light. The latter are brass tubes

[5] Leighton and Forbes, THIS JOURNAL, **52**, 3139 (1930).

telescoping freely without play by means of the rack and pinion arrangements X and Y.[6] G is a thermopile mounted flush against a slit built into a vertical track in which G slides in a submarine H. Directly in front of G is mounted on H an adjustable support for reaction vessels. Fine adjustments of H, G and the support can be made in three dimensions by means of appropriate screws, not all of which are shown in the cuts. The submarine and the cells are immersed in distilled water thermostated to 0.1°. A double-convex quartz lens (not shown) 5 cm. in diameter with a focal length of 5 cm. for λ 795 mμ placed between C′ and the reaction vessel renders the light parallel when passing through the latter to the thermopile. I is the weathered and planed cast-iron base 200 cm. long. Leveling is accomplished by means of screw supports in the base, not shown. J is a steel plate on which the telescope is mounted. This plate, mounted on brass tracks, is pivoted about the intersection, K, of the principal axes of the collimator and telescope. Gross and fine adjustments of J are made by the screw, L, equipped with a split nut.

M, N, O, P, Q, R and S in Figs. 1, 2 and 2b comprise a mechanism such that (a) the prism is turned through half the angle through which the telescope is turned to keep it at the angle of minimum deviation, and (b) the center of the prism is displaced along the bisector of the angle between the axes of the collimator and telescope to keep it in the center of the field. This displacement (b) is 8.4 mm. in passing from $n_{798\ m\mu}$, 1.4534 to $n_{185\ m\mu}$, 1.5746 for fused quartz. N is a brass plate which slides on a horizontal brass plate M; a pin in N, over K, engages a slot in M. M and N have slots for the passage of pins, P and S. The position of N for a short wave length is shown by its dotted outline in Fig. 2b. O is the prism table. Its center, the center of the fixed pin in N which engages the slot in M, and a point on the perpendicular bisector of the base of the prism, A, lie on a straight line. P is a pin fixed on the principal axis of the telescope lens to J. Q is a pin fixed to N and joined to P by means of a rigid bar equipped with fine adjustments for length. R is a similar pin fixed to N and similarly joined to S. S is a pin fixed on the principal axis of the collimator lens to I. P, Q, R and S and the slot in the center of M are placed such that Q, K and R are always on a straight line in the plane of the perpendicular bisector of the base of the prism.

T, U, V, W and X in Figs. 1, 2 and 2b comprise the mechanism for automatic focusing. T is a metal fork which clears the post supports of the telescope. U is a pin fixed in I. V is a pin free to move along the axis of the telescope in a rectangular slot cut in J. The rod connecting U and V has a fine adjustment for length. W is a rack mounted on T. W rides on a cog wheel X. The turning of X actuates another wheel and rack which moves B′ in a corresponding fashion to V. X, which is mounted in a split nut, may be disengaged from the shaft driving B′ thus permitting hand adjustment. Y permits hand adjustment of B.

The whole apparatus is adjusted by hand for some definite wave length (one of the known lines of the mercury lamp); the lenses B and B′ are then set at equal distances in the tubes. The automatic adjustments are then set. Thereafter the monochromator is set for different wave lengths by turning the screws L and Y. The positions for the different wave lengths are marked on a scale under L in the floor, I, of the instrument. The lens B is set by hand at the same relative position as B′, using a depth gage.

Tests of the Monochromator.—Figure 3 is an energy distribution curve[7] of a mercury vapor capillary arc lamp[2] as determined with this monochromator. Any adjustments of the prism or lenses by hand follow-

[6] Internal surfaces are blackened with an alcoholic solution containing lamp black and shellac, which while drying is smoked thoroughly with camphor black.

[7] Compare with data of Harrison and Forbes, *J. Optical Soc. Am.*, **10**, 1 (1925).

ing automatic adjustment to a mercury line always caused a decrease in the energy flux through the exit slit. The upper and lower curves are for slit widths of 0.6 and 0.1 mm., respectively; the height of the slits in both cases was 20 mm. The total energy flux (ordinate) in ergs/sec. (upper curve only) passing through the exit slit was determined by means of a

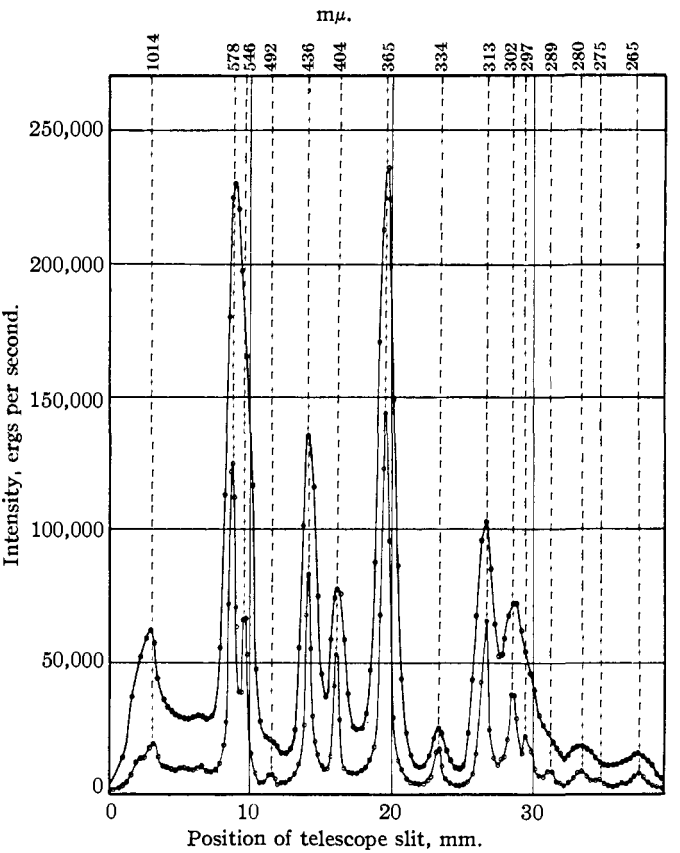


Fig. 3.—Energy distribution: upper curve, 0.6-mm. slits; lower curve, 0.1-mm. slits; capillary lamp, 200 volts, 5.5 amperes, 1100 watts; the scale of ordinates applies only to the upper curve.

large thermopile to be described later. The thermopile–galvanometer circuit and accompanying shunts was calibrated against U. S. Bureau of Standards lamp C44. The abscissa represents clockwise turns of L in terms of the distance between a fixed point on L and its split nut attached to J. The absence of λ 254 mμ due to absorption by the fused quartz should be noted. That this line and shorter wave lengths are present in the source was proved by a spectrogram.

The intensity of radiation of λ 313 mμ was compared under identical

conditions with a commercial monochromator having a prism 3 cm. high. The monochromator described here gave more than ten times as much intensity.

The degree of monochromatism obtainable with this instrument was tested (*a*) qualitatively by spectrophotometry and (*b*) quantitatively by radiometry.

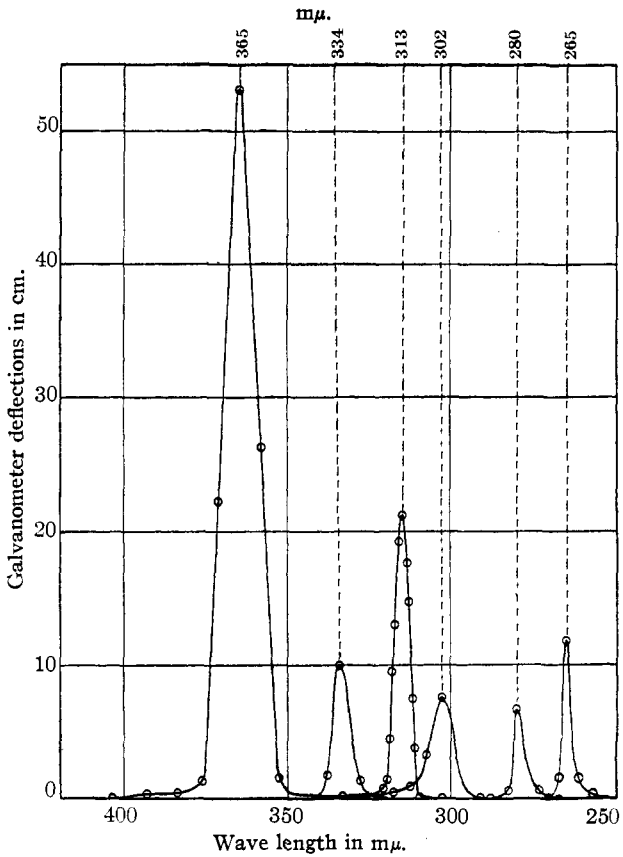


Fig. 4.—Efficiency of the monochromator as determined with a second monochromator.

(*a*) Using a carbon arc as a continuous source, slit widths of 0.6 mm. and the instrument set at λ 420 mμ, a spectrogram of the emerging light showed a blackening which covered 20 mμ (as determined by reference to the 436 and 404 mμ lines of mercury photographed on the same spectrogram) about this wave length.

Using a mercury arc as source and the monochromator under identical conditions, a spectrogram showed complete isolation of 436 or 404 mμ, depending on the setting of the monochromator. Exposures of several

seconds, however, gave spectrograms showing all the prominent lines of mercury. Similar tests applied to a commercial monochromator showed it to be less efficient than this instrument.

(*b*) The energy distribution of light emerging from the large monochromator at given settings for maximum intensity of the wave length in question is shown by the curves in Fig. 4. These curves were determined using the mercury arc[2] as source, slit widths of 0.6 mm. and a second monochromator with thermopile–galvanometer. "Purity" of the light may be obtained by estimating the area (counting squares) under these peaks be-

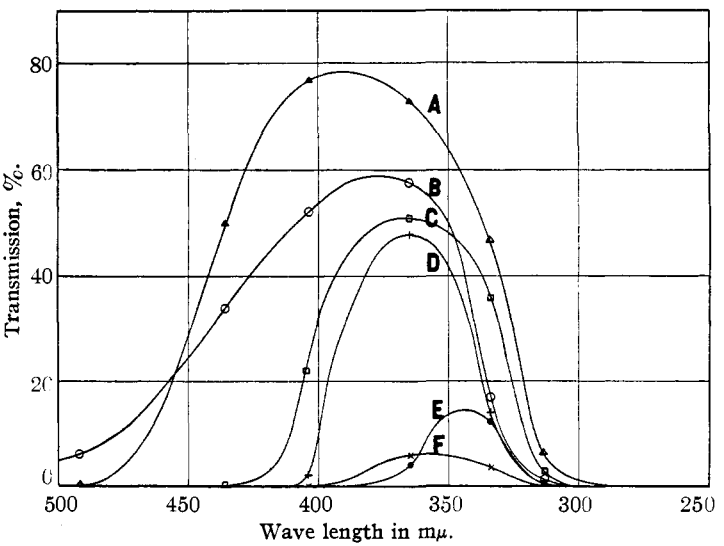


Fig. 5.—Percentage transmission of various glass filters of thicknesses stated: A, blue-purple ultra, 3.91 mm.; B, cobalt glass, 2.61 mm.; C, red-purple ultra, 4.17 mm.; D, red-purple ultra, 5.08 mm.; E, ultraviolet filter IVc, 4.57 mm.; F, ultraviolet glass, 8.91 mm.

tween definite limits. The limits, of course, depend on the energy distribution of the lamp, wave length and the width of the slits of the second monochromator. At 365 and 313 mμ 98% of the total energy recorded on the thermopile of the second monochromator fell between 353 and 375 mμ and between 310 and 320 mμ, respectively. It was gratifying, particularly since the quartz lenses and prism contained many small bubbles and some striations, to find that, although all the mercury lines were recorded on a spectrogram, the intensity of the other lines was less than 1% of the one selected by the first monochromator. Spectrograms of any one of 436, 404, 365, 334, 313 and 302 mμ emerging from the exit slit of the two monochromators in tandem (using slit widths of 0.6 mm.) showed only the wave length in question on exposures as long as ten minutes.

Comparison with Filters.—Purity [method (*b*) used] of light transmitted by certain filters is shown in Fig. 5. With the exception of B these were standard filters purchased from the Corning Glass Works. Comparison with Fig. 4 shows that the monochromator is much more effective than these filters in restricting the light to a narrow range of wave lengths.

The Photodecomposition of Uranyl Oxalate.—The photolysis of oxalic acid at 313 mμ and at room temperature in the presence of uranyl salts affords a more direct test of the efficiency of this monochromator in the study of photochemical reactions. Materials used were of C. P. quality and when purchased as such were not subjected to further purification. Uranyl sulfate and oxalate were made from C. P. uranyl nitrate. Experimental procedure was essentially the same as that of Leighton and Forbes.[5] Several details require mention. Two photolyses were carried out simultaneously by using a two-compartment rectangular cell with quartz plates front and back. It was mounted flush against the exit slit, C′, on a platform (Figs. 1 and 2) which could be moved perpendicular to the axis of the

TABLE I

$[UO_2C_2O_4]$	$[H_2C_2O_4]$	% 313 mμ absorbed	Depth of cell in cm.	Time of photolysis in minutes	Quanta absorbed $\times 10^{-18}$	Molecules $H_2C_2O_4$ decomposed $\times 10^{-18}$	Quantum yield, gross
0.0005	0.0045	72	2.0	60	17.9	9.0	0.51
.0005	.0045	72	2.0	45	11.8	6.6	.56
.0005	.0045	72	2.0	60	8.4	6.2	.74
.0005	.0045	72	2.0	60	10.0	7.4	.75
.0005	.0045	72	2.0	60	12.5	8.1	.64
						Average	.64
.0017	.0330	86	1.0	60	16.0	7.2	.45
.0017	.0330	86	1.0	45	11.2	5.3	.47
.0017	.0330	86	1.0	30	7.7	3.4	.44
						Average	.46
.0017[a]	.0330	86	1.0	45	6.2	3.3	.53
$[UO_2SO_4]$							
.0017	.0330	86	1.0	60	15.1	7.8	.51
.0017	.0330	86	1.0	60	15.8	9.3	.59
.0017	.0330	86	1.0	45	11.0	7.1	.65
.0017	.0330	86	1.0	45	11.0	6.8	.62
.0017	.0330	86	1.0	90	21.8	12.1	.56
.0017	.0330	86	1.0	30	8.1	5.0	.61
						Average	.59
$[UO_2(NO_3)_2]$							
.0017	.0330	86	1.0	30	7.5	3.7	.50
.0017	.0330	86	1.0	60	16.2	10.5	.65
.0017	.0330	86	1.0	90	25.8	14.3	.55
.0017	.0330	86	1.0	45	12.4	6.4	.51
						Average	.53

[a] $MgSO_4$ is 1 Molar.

telescope lens. Solutions in each compartment were photolyzed alternately for ten-minute intervals. Energy flux transmitted by the solution was measured at three-minute intervals by a thermopile, G (a Coblentz twenty junction silver–bismuth thermopile, 20 mm. × 1 mm.), placed directly behind the reaction cell. The maximum change in per cent. absorption by the solution during photolysis was always less than 2%, usually less than 1%.

Results of this part of the investigation are presented in Table I. Concentrations are given in moles per liter. These results show that the anion of the uranyl sensitizer has little effect on the quantum yield—the oxalate, sulfate and nitrate giving nearly the same results. Even the addition of magnesium sulfate in high concentrations has little effect on the gross quantum yield.

Leighton and Forbes[5] report gross quantum yields for 0.01 *m* uranyl sulfate in 0.05 *m* oxalic acid of 0.545, 0.53, 0.57, 0.595 and 0.57, giving an average value of 0.561. The good agreement between the two researches gives confidence not only in the monochromator described here, but in the general reliability of quantitative photochemical measurements.

The authors desire to acknowledge the help given by a du Pont Fellowship held by the first named author during the progress of this work.

They desire also to thank Mr. J. H. Hanson for the careful machine work involved in the building of the monochromator.

Summary

1. A monochromator for the investigation of photochemical reactions in the ultraviolet has been described. An automatic device, not using a reflecting mirror or a compound prism arrangement, keeps the 60° prism at minimum deviation and in the center of the field. Another device keeps the telescope automatically in focus.

2. Radiation of over 100,000 ergs per second from the prominent lines of a capillary mercury vapor lamp are obtainable with this monochromator.

3. "Purity" of monochromatic light obtainable from the monochromator has been tested in several ways, and compared with that of filters. Approximately 98% of the radiation at any wave length setting falls within a range of 10 to 20 mμ.

4. In the presence of uranyl sulfate, 0.59 molecule of oxalic acid is photochemically decomposed for each quantum absorbed at 313 mμ and at 27 ± 2°. This result is in close agreement with that of Leighton and Forbes. Uranyl sulfate, nitrate and oxalate used as sensitizers give practically the same results.

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