

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

PHOTOCHEMICAL TECHNIQUE. III. QUARTZ CAPILLARY ARC LAMPS OF BISMUTH, CADMIUM, LEAD, MERCURY, THALLIUM AND ZINC

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In a previous communication a simple mercury lamp¹ of high intensity was described. The object of the present investigation has been to develop similar lamps with other metals in order to make available intense light for a wider selection of wave lengths. Mercury lamps are more convenient because mercury is a liquid at room temperature, it is not oxidized, and it does not adhere to the quartz. The other metals tend to break the quartz lamps on solidifying.² It is desirable then to make a lamp so simple and so cheap for photochemical work that it can be discarded when the current is turned off at the end of an experiment.

Construction and Operation of Lamps

The lamp is shown in Fig. 1. It is made by fusing a 12-mm. section of quartz capillary, 1 mm. inside diameter and 2 mm. outside diameter, between two thin-walled quartz tubes, 2 mm. in outside diameter and 5 cm. long. Thin bulbs are blown out at these joints to localize the arc. The end-pieces may be used over and over again. The upper electrode is formed by stopping the lower end of the capillary with a pointed iron rod and gently melting down small pieces of metal to fill the whole capillary and the upper tube. Any bubbles are floated out of the molten metal. The lower electrode is cast or scraped down from a larger rod so as to fit snugly into the lower quartz tube.

It is pointed, and set so as to leave a short gap between the two electrodes. The metal at both ends of the lamp is then melted and short iron wires connected to flexible leads are inserted. The connections are insulated and rendered gas tight with de Khotinsky cement. The air space in the lower bulb serves as a spark gap, for starting the lamp, and as a reservoir into which the molten metal runs down from the capillary when the arc is struck. The pressure under which the lamp operates, and the resistance of the lamp, are largely determined by the volume of this air space.

The water jacket is indicated by dotted lines. A quartz tube about 1.2 cm. in diameter and 10 cm. long surrounds the lamp and two T tubes of Pyrex glass are attached with rubber tubes. The insulated leads protrude from the T tubes through rubber tubes closed with screw clamps. A stiff spring centers the lamp and prevents vibration. For use with a monochromator a metal tube (not shown) with a large slit is placed inside the quartz as a shield. The upper electrode is made the negative terminal.

A rapid stream of water is forced in at the bottom and the lamp L is then started by passing a spark of electricity across the air gap between the two electrodes while the

¹ Daniels and Heidt, *THIS JOURNAL*, **54**, 2381 (1932).

² Bates and Taylor added tin to a cadmium lamp to prevent breaking. *THIS JOURNAL*, **50**, 772 (1928). Smits and Frederikse used lead in quartz at high voltages. *Z. Elektrochem.*, **34**, 350 (1928). Earlier lamps are reviewed by Forbes, *J. Phys. Chem.*, **32**, 486 (1928).

circuit is closed. An induction coil N giving at least a 1-cm. spark is connected with a condenser C and spark gap S, and two adjustable spark gaps G as shown at the right in Fig. 2. The adjustable gap is made by attaching wires to a double pole switch which is adjusted for maximum efficiency with a long insulated handle. A high-resistance shunt (not shown), grounded at the center, and two 100-turn inductance coils (not shown) must be placed in the lamp circuit to protect the line against the high frequency spark discharge. The lamps must be operated on direct current and in most cases a potential of at least 150 volts seems to be necessary for starting.

In some cases the arc can be started by heating the capillary with a blast lamp; but the breakage is then very high. Dr. L. W. Morris of the Physics Department, in using these lamps, eliminated the spark circuit by connecting the two electrodes with a small fuse wire of the same metal. An initial current of high amperage through the lamp melts the metal and strikes the arc.

Adjustment of External Resistance.—The steadiness of the lamps depends to a large extent on the control of the wattage by proper adjustment of the external resistance. The wattage and the rate of external cooling determine the temperature of the lamp which in turn determines the vapor pressure of the metal. The resistance of the lamp increases as the vapor pressure increases. When the lamp is operating on a fixed line voltage with an external resistance in series the consumption of energy depends entirely on the resistance of the lamp.

The problem may be analyzed by considering the lamp and an external fixed resistance R connected in series across a fixed line voltage V . If the calculated wattage W through the lamp is plotted against the changing resistance r of the lamp, a maximum is obtained when the resistance of the lamp is equal to the external resistance.

In this graph the curve rises steeply when $r < R$, but, beyond the maximum, where $r > R$, the curve descends slowly. Differentiating the expression $W = V^2r/(r + R)^2$, and setting dW/dr equal to zero, it is

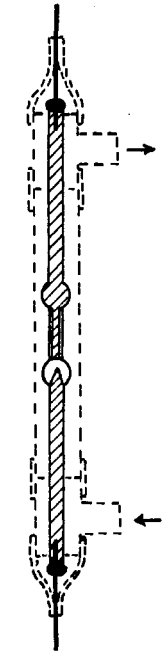


Fig. 1.—Capillary quartz lamp for solid metals. Water jacket in broken lines

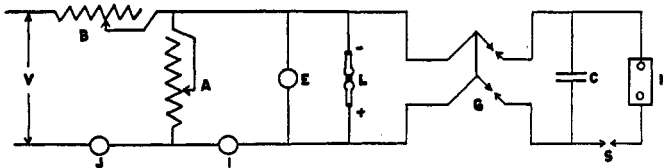


Fig. 2.—Lamp circuits: starting circuit at right; operating circuit with external resistances at left.

evident that a maximum, where W is independent of r , must be obtained when r is equal to R . When dW/dr is positive, an increase in lamp resistance increases the wattage through the lamp and, unless the cooling

system can handle this increase, the temperature, vapor pressure and resistance again increase. A regenerative process is thus set up which eventually causes the lamp to blow up, particularly in the case of the lamps of high-melting metals. When dW/dr is negative, any increase in the lamp's resistance decreases the wattage and cools the lamp and restores it to its original condition. These considerations show that the external resistance should not be greater than the resistance of the lamp for then dW/dr is positive; it may, however, be somewhat less.

The metal arc lamps described here range in lamp voltage from 60 to 400 volts depending on the air volume and on other specific factors. A 550-volt generator was used in all cases but this voltage is theoretically too high for any lamp with a voltage drop of less than 275 volts. The difficulty can be met with the help of a shunt but then the rule that R should be equal to r no longer holds. The problem was solved in the following manner, where A is the adjustable shunt resistance and B is the adjustable series resistance as shown in Fig. 2. Let S be the resistance of A and r in parallel, I , the amperage through the lamp, J the total amperage, and E the voltage drop across the lamp.

$$\text{Then} \quad E = \frac{S}{S+B} V \quad (1)$$

$$\text{but since} \quad S = \frac{Ar}{A+r} \quad E = \frac{ArV}{Ar+AB+Br} \quad (2)$$

$$\text{Also} \quad W = \frac{E^2}{r} = \frac{(AV)^2 r}{(Ar+AB+Br)^2} \quad (3)$$

$$\text{Then} \quad \frac{dW}{dr} = \frac{(AV)^2}{(Ar+AB+Br)^2} - \frac{2W(A+B)}{(Ar+AB+Br)} \quad (4)$$

$$\text{Letting} \quad \frac{dW}{dr} = 0, W_{\max.} = \frac{(AV)^2}{2(Ar+AB+Br)(A+B)} \quad (5)$$

$$\text{Equating } W \text{ and } W_{\max.} \quad \frac{Ar+AB+Br}{2(A+B)} = r \text{ and } AB = Ar+Br \quad (6)$$

This equation shows the conditions under which the lamp has reached its stable point, *i. e.*, the wattage of the lamp is independent of the resistance of the lamp when the series and shunt resistances are such that their product is equal to their sum, multiplied by the resistance of the lamp. But it cannot be used directly; it must be converted into terms which can be obtained from the voltmeter and two ammeters in the circuit.

Substituting

$$A = \frac{E}{J-I}, B = \frac{V-E}{J} \text{ and } r = \frac{E}{I} \quad (7)$$

equation (6) becomes

$$\frac{E(V-E)}{J(J-I)} = \frac{E^2}{(J-I)I} + \frac{(V-E)E}{JI} \quad (8)$$

and solving for J

$$J = \frac{2I(V-E)}{V} \quad (9)$$

V is fixed at 550 volts and E and I are read directly from a voltmeter and ammeter connected to the lamp. If, after starting, the lamp instruments read 5 amperes and 100 volts, for example, the proper value of J can be determined at once by solving equation (9).

$$J = \frac{2 \times 5 (550 - 100)}{550} = 8.2 \text{ amp.}$$

The shunt resistance A and series resistance B are then decreased simultaneously in such a way that the amperage and voltage of the lamp are not changed but the total amperage J through the whole circuit reads 8.2 amperes. This calculation and adjustment is made immediately, before the lamp has a chance to burn out. Although these conditions make $dW/dr = 0$, it has been found in practice that the lamp burns more steadily when the total amperage is slightly greater than the calculated value. When J is greater than the calculated value, dW is negative and there is a compensating effect in the circuit. J , then, may be regarded as the lower limit of the stable range.³

The shunt circuit entirely eliminated the earlier tendency of certain lamps to burn out, due to simultaneous rise of lamp resistance and wattage. In general the stabilizing effect is great enough to cause a noticeable decrease in the fluctuations of the lamp. An automatic record of the thermopile-galvanometer deflections on a single wave length showed a variation of 5.2% over a period of ten minutes, but when the circuit was properly balanced the maximum variation dropped to 3.7%. A considerable part of this variation was due to fluctuations in the dynamo and drifts in the zero point of the thermopile-galvanometer. When a mazda lamp was substituted for the arc the variation was still as great as 2.8%.

Measurement of Energy Distribution

The lamps were studied with a Hilger quartz monochromator (4 cm. prism), provided with a Coblenz linear thermopile and a Leeds and Northrup galvanometer having a sensitivity of 15 mm. per microvolt. The thermopile-galvanometer deflections were recorded photographically in a simple manner. A carrier holding photographic bromide paper, $6\frac{1}{2} \times 8\frac{1}{2}$ ", slides on a vertical track in a light-tight box at a distance of 2 meters from the galvanometer. The vertical galvanometer beam enters through an adjustable horizontal slit, thus making a small point of light on the paper. The carrier is suspended by a strong linen thread which passes over two small pulleys and down to an axle upon which it is wound in a single layer. This axle is attached directly to the wave length drum which rotates the prism. The monochromator is so constructed that twelve revolutions of the drum cover the range from 2000 to 7000 Å. and the axle is of such diameter (6 mm.) that these twelve revolutions cause the plate to drop a vertical distance equal to its own height as the thread is unwound. The galvanometer deflec-

³ The resistance of all the capillary lamps described here increases with temperature, but in some low-pressure lamps an increase in temperature and vapor pressure may lead to a decrease in resistance. In such a case the conditions would be reversed and the lamp would be more stable when dW/dr is positive. J would then be the upper limit.

tions are recorded as horizontal displacements and thus continuous curves are automatically obtained with intensities graphed against wave lengths. The rotation of the axle and drum is slowed down to approximately one revolution per minute with the help of a variable-speed motor and reducing pulleys.

The single filament galvanometer lamp is operated at slightly more than the normal current, in order to give sufficient intensity for recording. The greatest difficulty lies in the fact that in the flat hollows of the curve the beam is traveling over the paper at the rate of perhaps 1 cm. per minute but as it approaches the peaks it may be traveling at the rate of 1 cm. per second. On account of this variation in exposure time a flat developer of metol or pictol is used.

A wave length scale was prepared on a film placed in the carrier. The galvanometer and monochromator were disconnected, the drum stopped at integral wave lengths and a line was exposed by flashing on an electric light. The peaks were identified with the help of this scale by reference to Eder and Valenta's "Atlas typischer Spektren" (Österreichischen Staatsdruckerei, Wien, 1924). The identification was facilitated also by comparison with spectrograms of the lamp taken with a large Fuess quartz spectrograph which gave nearly the same dispersion as the graphs.

The capillary dimensions, which bring most of the radiation to the slit of the monochromator, combined with the large input of energy, give such high intensities that it is possible to use a monochromator with a narrow slit and still obtain adequate deflections with a thermopile and galvanometer. This method is superior to the more common method in which spectrograms are analyzed by measuring the density of the lines on the photographic plate. In the spectrographic method the blackening of the plate does not depend alone on the intensity of light; but the thermopile-galvanometer deflections obtained by the method described here are directly proportional to the intensity at all wave lengths.

In the graphs the emission lines are labeled and their energies in ergs per second falling on 1 sq. mm. of the thermopile, with the monochromator, are given in the accompanying tables. The energy entering the monochromator slit is much greater with the capillary lamps than with commercial mercury lamps of larger dimensions.

Calibration against a radiation lamp, C44, of the U. S. Bureau of Standards showed that the sensitivity of the thermopile and galvanometer was such that a deflection of 1 cm. was produced by 15.68 ergs of radiation per sec. per sq. mm. In the case of the most intense lines the deflections passed beyond the photographic recording-box and were determined by visual observation. In Figs. 5-8 a shunt was used which reduced the sensitivity to 29.7 ergs per sec. per sq. mm. for a deflection of 1 cm.

The slit at the thermopile was 0.22 mm. in width, 8.9 mm. in length and 1.96 sq. mm. in area. The effective slit width is shown in the circular insert in Fig. 3. It is the same for all the figures. In determining this width it was found that the image of the front slit moved across the face of the thermopile a distance of 10.5 mm. in changing from 5970 to 2570 Å., while the distance between the same wave lengths on the photographic paper, amplified by the drum movement and thread, was 98 mm. The effective slit width on the graphs was then 98/10.5 times the actual slit width. The front slit was 0.382 mm. for Figs. 3-5 and 0.254 mm. for Figs. 6-8.

For photochemical purposes the thermopile slit may be broadened, thus giving a proportional increase in intensity. In the distribution curves a narrow slit is required to show the valleys between peaks, but in photochemical work one isolated line may be focused on the center of a broader slit without overlapping. The effective slit width may be nearly as great as the distance to the adjoining peaks. With the apparatus described here it would be safe in most cases to treble the slit width to 0.66 mm. and then the total energy available may be obtained by multiplying the values in Figs. 3-8 by a

Wave length, Å.	Ergs sec. × mm. ²	
A	5552	67
B	4723	160
C	4308	17
D	4122	67
E	3888	5
F	3596	78
G	3511	74
H	3397	67
I	3068	298
J	3025	154
K	2993	138
L	2989	
M	2938	
N	2898	111
O	2864 (Hg)	64
P	2731	17
Q	2697	13
R	2628	33
S	2525	31
T	2516	
U	2490	22
V	2431	19
W	2401	13
X	2309	3
Y	2231	3

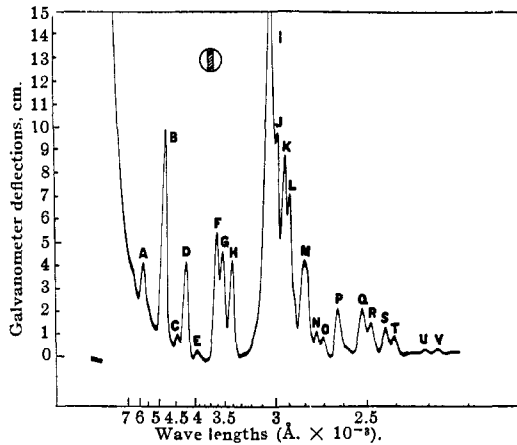


Fig. 3.—Bismuth lamp, 8 amperes, 70 volts.

Wave length, Å.	Ergs sec. × mm. ²	
A	7399	122
B	6439	1030
C	5086	950
D	4800	824
E	4678	824
F	4415	44
G	3729	49
H	3610	1010
I	3466	680
J	3404	512
K	3261	174
L	3253	
M	3133	82
N	2981	201
O	2881	108
P	2764	33
Q	2678	19
R	2329	5
S	2288	5

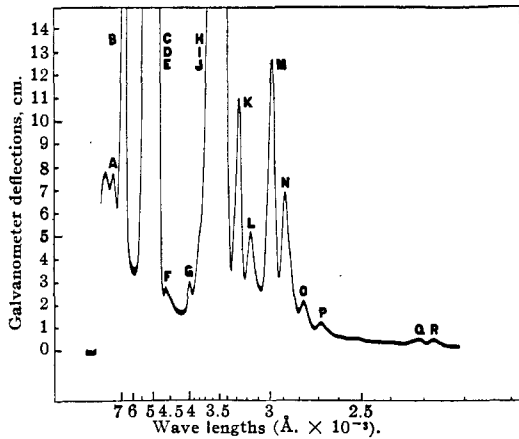


Fig. 4.—Cadmium lamp, 5.2 amperes, 110 volts.

Wave length, Å.	Ergs sec. × mm. ²	
A	7229	398
B	6002	202
C	5006	175
D	4386	48
E	4168	33
F	4082	487
G	4057	
H	3740	520
I	3684	
J	3640	
K	3221	64
L	3151	80
M	2873	122
N	2833	214
O	2802	
P	2698	36
Q	2663	107
R	2614	68
S	2577	56
T	2476	24
U	2444	28
V	2394	33
W	2333	3

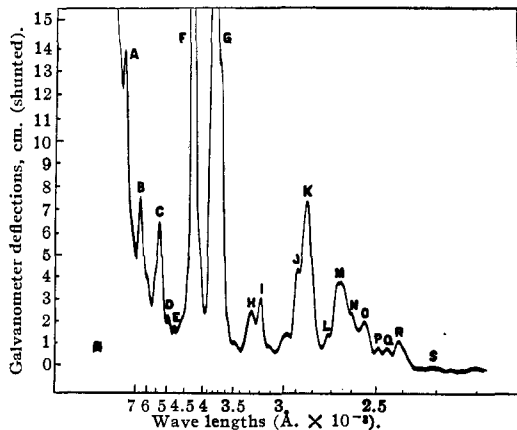


Fig. 5.—Lead lamp, 5.4 amperes, 100 volts.

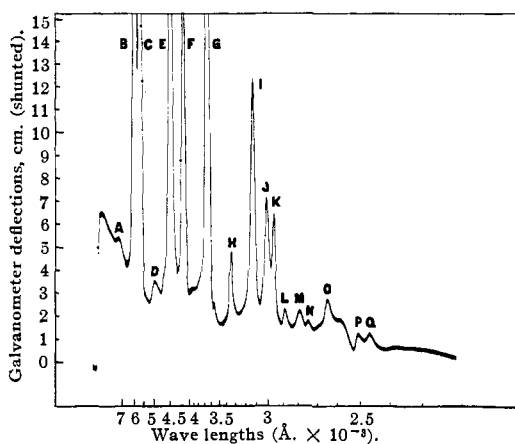


Fig. 6.—Mercury lamp, 2 amperes, 350 volts.

Wave length, Å.	Ergs sec. × mm. ²
A 6907	166
B 5790	1125
B 5789	
C 5461	1285
D 4916	107
E 4359	962
F 4047	546
G 3650	843
H 3341	145
I 3131	371
J 3023	214
K 2967	193
L 2894	71
M 2804	68
N 2753	53
O 2652	80
P 2536	36
Q 2482	36

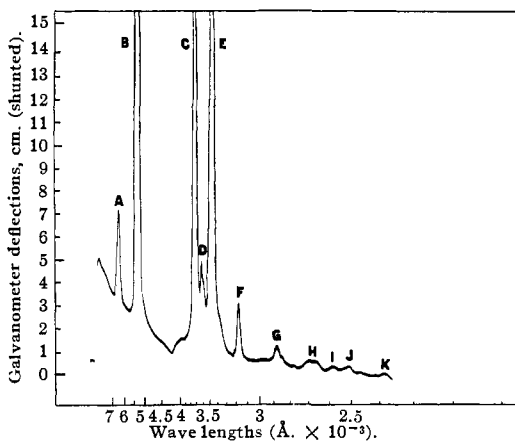


Fig. 7.—Thallium lamp, 9 amperes, 100 volts.

Wave length, Å.	Ergs sec. × mm. ²
A 6550	199
B 5351	1390
C 3776	600
D 3650 (Hg)	137
E 3519	655
F 3230	83
G 2922	33
H 2768	15
H 2709	
I 2609	9
J 2580	12
K 2380	6

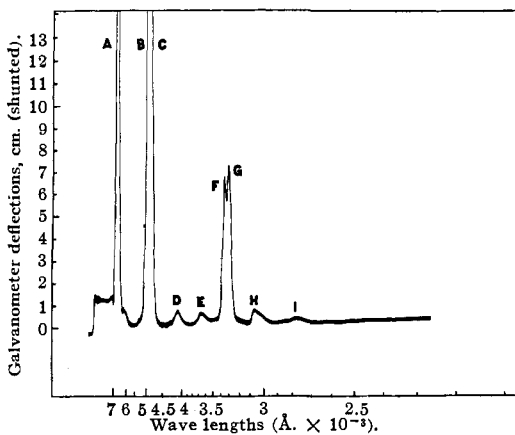


Fig. 8.—Zinc lamp, 6 amperes, 100 volts.

Wave length, Å.	Ergs sec. × mm. ²
A 6362	511
B 4811	644
C 4722	623
C 4680	
D 4062 (Pb)	27
E 3684 (Pb)	21
F 3346	202
G 3303	217
G 3282	
H 3072	21
H 3036	
H 3018	
I 2801	6
I 2771	
I 2757	

factor of 5.9 sq. mm. A large monochromator, already described,⁴ gives about ten times the radiation intensity per sq. mm. recorded here and the slit height is 20 mm. With such an instrument, using a slit 0.66 mm. wide, the values given in Figs. 3-8 may be multiplied by a factor of 133. The intensities may be still further increased by increasing the wattage through the lamp.

In comparing the different lamps it must be remembered that the voltage and amperage vary greatly with different lamps depending on the air space and on other specific factors. It is difficult to make two lamps with just the same characteristics but the relative intensities of the different lines are roughly constant. In some cases a film of silicate is formed on the inside of the lamp which diminishes the intensity of the ultraviolet lines more than the lines in the visible. Many of the lamps operated successfully for ten hours or more. Further investigation is necessary to determine whether some metals at the high operating temperature of the lamps (above the melting point of quartz) are able to reduce the silica itself. In some cases the purification of the metal and the exclusion of oxygen tended to prevent the deterioration. The lamps may be filled with nitrogen or other inert gas by making a tiny hole in one electrode and subjecting to alternate evacuation and filling with the inert gas.

Characteristics of the Different Lamps

Bismuth.—The bismuth lamp described in Fig. 3 proved to be simple to make and operate. It ran smoothly without extensive deterioration of the quartz. It is excellent for the production of ultraviolet light, having many strong, easily separable lines, and giving measurable intensities down to 2271 Å. The most intense line is at 3068-3025 but prominent, well isolated lines occur also at 4723, 4122, 3511, 2898 and 2628. A spectrogram showed that the 3068 line is reversed, *i. e.*, light of exactly 3068 Å. is absorbed by the un-ionized bismuth vapor in the lamp.

Cadmium.—The cadmium lamp described in Fig. 4 is particularly useful as a source of red light, the line at 6439 Å. being very intense and well isolated. There are three intense lines at 5086, 4678 and 4415, and another group at 3610, 3466 and 3404. The lines at 3261, 3133 and at 2981 are intense and well isolated. The cadmium lamp however tends to form an inner film (probably of cadmium silicate) which absorbs the ultraviolet radiation after running for a short time. The visible light is not seriously reduced. The electrodes must be pure and they must not be overheated in making the lamp because they oxidize quickly. Moisture seems to accelerate the formation of the glass film. Inasmuch as some lamps last considerably longer than others it was thought that oxygen might be the limiting factor in the deterioration but nitrogen-filled lamps did not seem to be much better.

Lead.—The lead lamp described in Fig. 5 gives a spectrum which is rich in ultraviolet. The most intense region is at 3740-3640 Å. Well isolated lines are found at 2833-2802 and at 2663. The violet line at 4062-4057 is intense and well isolated. Reversals are noted in the spectrogram at 2833, 2802, 2663, 2614, 2577, 2476, 2444 and 2394.

⁴ Heidt and Daniels, *THIS JOURNAL*, 54, 2384 (1932).

The lead must be pure as the film inside the lamp which forms rapidly with impure lead is opaque.

Mercury.—The mercury lamp is too well known to warrant a discussion. It is shown in Fig. 6 so that it may be used as a reference in estimating the behavior of the lamps of the other metals, when the behavior of a mercury lamp with a certain photochemical set-up is known. Its construction and operation are simpler¹ and the lamp may be used over again after being stopped.

Thallium.—The thallium lamp has a simple spectrum as shown in Fig. 7. Greater intensity was obtained with the 5351 line of thallium than with any other lamp. The lines at 5351, 3776 and 3519 are very intense and well isolated. A weaker line at 3230 is also suitable for photochemical use. The metal is rather expensive and it oxidizes readily. A spectrogram showed the black central lines of reversal at 3776, 3519, 2922 and 2768.

Zinc.—The zinc lamp shown in Fig. 8 gives three excellent lines for photochemical work. The red line at 6362 Å. is even more isolated than the red line of cadmium, and the lines at 4811–4680 and at 3346–3303 are intense and unusually well isolated. The lamp is not seriously affected by the formation of inside coatings. One lamp was still operating satisfactorily when it had to be turned off after operating for fifteen hours.

Miscellaneous.—Lamps of silver, copper and aluminum were tried, but without success. Tin gives a number of ultraviolet lines but an air-filled tin lamp was unsuccessful, burning out in about five minutes. Antimony in an air-filled lamp attacked the quartz and lasted only a few minutes; but another, nitrogen-filled lamp lasted for more than ten hours. Antimony has practically no lines in the visible but many in the ultraviolet, especially below 3000 Å. The lines are too close for convenient isolation with a monochromator but the lamp might be useful for general ultraviolet radiation.

A lamp was constructed with the eutectic alloy of bismuth and lead. A spectrogram showed all the lines of both metals. Alloy lamps may be convenient for getting lower melting points and for general radiation, but they are not satisfactory for isolating intense lines because the lines are too close together and because the energy of the lamp is distributed among many lines, leaving individual ones weaker.

The authors are glad to acknowledge the support of the Research Committee of the University of Wisconsin in purchasing a dynamo which was isolated to give constant current while the measurements were made.

Summary

1. A quartz capillary lamp has been developed for metals other than mercury. The lamps can be used only once but they are comparatively inexpensive.

2. A circuit is described for starting the lamps by sparking.
3. The distribution of energy in capillary arcs of bismuth, cadmium, lead, mercury, thallium and zinc has been determined.
4. A photographic method is described for recording the thermopile-galvanometer deflections.
5. Intense sources of light, comparable with those of the constricted mercury arc, can be obtained for several additional wave lengths.
6. When an external resistance is used the potential drop across the lamp should be at least half the line voltage. When this condition cannot be met a shunt is used, and a method for adjusting to maximum constancy is described.

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[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY OF PRINCETON UNIVERSITY]

APPLICATIONS OF CERIC SULFATE IN VOLUMETRIC ANALYSIS.

X. THE DETERMINATION OF ANTIMONY AND ARSENIC^{1,2}

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Introduction.—Conflicting evidence has been reported by Rathsburg³ and by Willard and Young,⁴ respectively, regarding the oxidation of trivalent antimony by ceric sulfate. In some preliminary work⁵ our own conclusions differed somewhat from those of Willard and Young,⁴ who stated that the oxidation was too slow to be practical at room temperature without the addition of a catalyst. The further work presented in this paper supports the conclusion of Rathsburg³ that the reaction is sufficiently rapid at room temperature in solutions containing *high concentrations of hydrochloric acid* (one-sixth to one-third by volume of acid of sp. gr. 1.19). Rathsburg stated that antimony could be titrated in the presence of arsenic under these conditions. The author has found that the results for antimony tend to become erratic when the concentration of arsenious acid is roughly equivalent to that of the antimony. If the initial volume per cent. of hydrochloric acid is below 40, simultaneous oxidation of arsenic is apt to occur. When the amount of antimony exceeds that of the arsenic the results here presented show that it is possible to determine both antimony and arsenic in a single potentiometric titration with ceric sulfate. After the end-point of the oxidation of the antimony, iodine monochloride

¹ Presented at the Eighty-third meeting of the American Chemical Society, New Orleans, La., 1932.

² For previous papers of this series, see *THIS JOURNAL*, **50**, (a) 755, (b) 1675 (1928); **51**, (c) 1128, (d) 1449 (1929); **52**, (e) 1443, (f) 2347 (1930); **53**, (g) 1283, (h) 2561 (1931).

³ Rathsburg, *Ber.*, **61**, 1664 (1928).

⁴ Willard and Young, *THIS JOURNAL*, **50**, 1376 (1928).

⁵ Furman and Wallace, unpublished, 1928.