

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

**AUTOMATICALLY CONSTANT MONOCHROMATIC
ILLUMINATION FROM A SPARK SOURCE**

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If a prism monochromator is illuminated by a big spark, erosion of electrodes changes the gap length and the position of the discharge, likewise the intensity behind the exit slit. Thin electrodes, zinc or cadmium especially, become overheated and burn away rapidly. Thick blunt electrodes conduct away the heat faster, but the spark travels erratically over their ends so that wide slits must be used, and monochromatism suffers, especially at greater wave lengths. E. Warburg,¹ also Beckmann and Dickinson,² used thick electrodes tapered at the ends, and kept the gap constant by hand while watching the spark's image on a screen. Harrison and Hesthal³ regulated both gap length and primary impedance. The disadvantages of manual regulation increase with the duration of the run, the noise of the spark, and the degree of constancy required.

While investigating the quantum yield of uranyl oxalate and of other photolyses, we developed a spark automatically constant in length and position, over long periods. The apparatus (Fig. 1) is suitable for a wide range of physical and photochemical experiments. Two square metallic bars 400 mm. \times 25 mm. \times 25 mm. are squared in a shaper. Flexible woven metallic bands connect them directly to a condenser. They rest in rectangular troughs T at right angles. The posts P are insulated from the baseboard by vulcanite blocks. The upper trough is cut away at G to expose the lower edge of the upper bar. The ends of the troughs are raised or lowered by turning the milled heads until the bars are horizontal, and their separation, along their common diagonal, is 2 mm. By far the shortest path for the spark lies along this one line. The heat is rapidly dissipated by conduction, and radiation from the bars and trough. Blasts of air provided by two vacuum cleaners in tandem converge from the jets J upon the gap at G to blow back the corona. A ventilated housing conducts away oxide fumes. Threaded rods, R, ending in insulating links I, pass through sleeves rotated by worm gears W, retracting the bars. The optimum speed increases with the energy of the spark and the volatility of the metal. Our zinc bars traveled 250 mm. per hour—one and one-half hours net service for each of the four pairs of edges. When a pair of edges is used up, the current is interrupted, the oxide crusts are detached, the threaded rods returned to their original positions, and the bars started with

¹ E. Warburg, *Sitzb. preuss. Akad. Wiss.*, 746 (1911).

² Beckmann and Dickinson, *THIS JOURNAL*, 52, 124 (1930).

³ Harrison and Hesthal, *J. Opt. Soc. Am.*, 8, 472 (1924).

a fresh pair of edges adjacent. Depth of erosion on the upper edge is very constant at 1.2 mm. for zinc and 0.5 mm. for aluminum, on the lower edge about two-thirds as much. To form the slit (not shown) transite jaws, rigidly supported, converge from opposite edges of the collimating lens upon the spark gap. The beveled edges are parallel, 10 mm. high and 9 mm. from the spark; the corners approach the zinc bars within 3 mm. Two other air-blasts (not shown) prevent vaporized metal from collecting on the jaws and short-circuiting the spark.

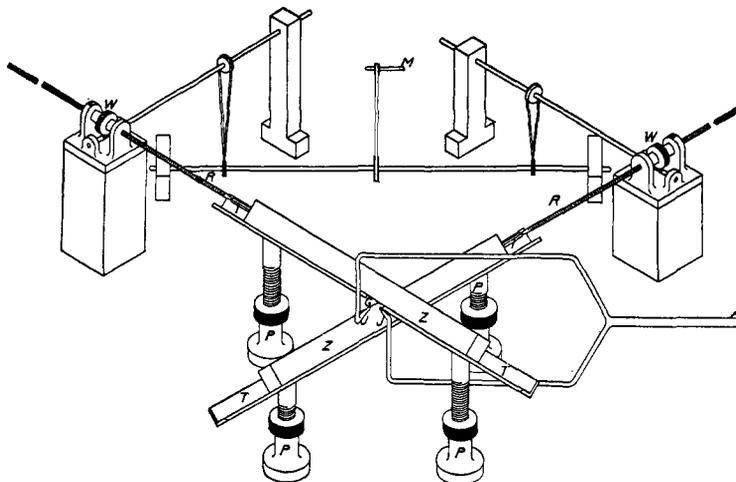


Fig. 1.—Spark source for automatically constant illumination.

A 5-kw. oil transformer operated on 35 amperes and 110 volts under control of a voltage regulator. Unfortunately circumstances precluded use of greater energies. A heavy duty mica condenser, 0.04 mf., proved to have the optimum capacity. The gap voltage was 6500 ± 500 .

The monochromator, in a separate housing, had 80 mm. crystal quartz lenses of focal length 125 mm. at $210 \text{ m}\mu$, corrected to diminish spherical aberration. Our large fused quartz prism was too opaque at this wave length, so a Cornu prism 60 mm. on each edge was substituted. The collimator slit was uniformly 0.8 mm., the exit slit 2.7 mm. Without a collimator slit, lines $5 \text{ m}\mu$ apart are not resolved, but intensity is about three times greater.

The thermopile-galvanometer system, its calibration, and the method of integrating the light energy of the divergent beam behind the exit slit have been described.⁴

Table 1 shows the constancy of energy behind the 2.7-mm. exit slit, covering the ZnII lines at $\lambda 206 \text{ m}\mu$ and $\lambda 210 \text{ m}\mu$. These were sharply resolved from $\lambda 202 \text{ m}\mu$ and $\lambda 214 \text{ m}\mu$, and could have been used indepen-

⁴ Leighton and Forbes, *THIS JOURNAL*, **52**, 3139 (1930).

dently of each other by halving the width of the exit slit. Each of the four parts of the table applies to one pair of edges. The experiment ran continuously for eight hours. Each value of S represents the sum of nine galvanometer deflections, read with the linear thermopile in nine positions 1 mm. apart and 8 mm. behind the slit. Each deflection was figured from three galvanometer swings. These sums, S , in spite of omission of several minor corrections, are very closely proportional to total ergs per second in the emergent beam. In each case D_m gives the maximum deflection obtainable—usually somewhere between positions four and five. Finally, $R = S/D_m$.

TABLE I
SUMMATIONS OF DEFLECTIONS, MAXIMUM DEFLECTIONS, RATIOS

| S | D_m | R | S | D_m | R | S | D_m | R | S | D_m | R |
|------------|-------------|------|------------|-------------|------|------------|------------|-------------|-----|-------|------|
| 432 | 128 | 3.38 | 439 | 138 | 3.18 | 442 | 136 | 3.25 | 452 | 136 | 3.33 |
| 446 | 143 | 3.12 | 466 | 149 | 3.13 | 457 | 143 | 3.19 | 469 | 147 | 3.18 |
| 469 | 145 | 3.23 | 490 | 146 | 3.36 | 466 | 147 | 3.17 | 468 | 144 | 3.25 |
| 482 | 151 | 3.19 | 484 | 149 | 3.24 | 475 | 148 | 3.21 | 468 | 144 | 3.25 |
| 480 | 150 | 3.20 | 473 | 145 | 3.26 | 492 | 147 | 3.35 | 470 | 153 | 3.07 |
| 509 | 155 | 3.28 | 464 | 146 | 3.18 | 483 | 147 | 3.29 | 458 | 140 | 3.27 |
| 491 | 152 | 3.23 | 464 | 139 | 3.34 | 458 | 137 | 3.22 | 467 | 140 | 3.34 |
| 487 | 148 | 3.29 | 500 | 153 | 3.27 | 466 | 142 | 3.28 | 465 | | 3.24 |
| <u>475</u> | <u>3.24</u> | | <u>473</u> | <u>3.25</u> | | <u>486</u> | <u>152</u> | <u>3.20</u> | | | |
| | | | | | | 470 | | 3.24 | | | |

Variations of S along an edge run from 4 to 16%, and of R from 5 to 8%. The average of eight values of R , however, varies only half of one per cent., provided nothing is displaced but the bars. In practice, therefore, R can be found occasionally by measuring S and D_m and its average value multiplied into more frequent readings of D_m . The resulting products will, on the average, give values of S as reliable as those measured laboriously by integration. Incidentally, the time available for photochemical exposure is greatly increased.

Table II gives total energies, in ergs per second, behind the exit slit of this apparatus arranged as described above. Lines 4 $m\mu$ apart were well resolved; better monochromatism would have resulted with loss of energy, upon narrowing the slits. The figures do not give true spectral energy distributions. They are useful for predicting the time⁵ necessary to complete a projected photochemical experiment in this or a similar apparatus.

TABLE II

| APPROXIMATELY MONOCHROMATIC ENERGIES FROM ZINC CADMIUM AND ALUMINUM BARS | | | | | | |
|--|--------|--------|--------|--------|--------|--------|
| Mean λ , $m\mu$ | Zn 208 | 253 | Cd 217 | 226 | 257 | 271 |
| Intensities, ergs/sec..... | 16,000 | 30,000 | 34,000 | 79,000 | 22,000 | 27,000 |
| Mean λ , $m\mu$ | Al 186 | 193 | 199 | 210 | 226 | 237 |
| Intensities, ergs/sec..... | 341 | 449 | 622 | 4,400 | 11,000 | 8,600 |

⁵ Forbes, *J. Phys. Chem.*, **32**, 500 (1928).

Summary

Illumination automatically constant over long periods is obtained from a spark struck between adjacent edges of two square bars moving in horizontal planes at right angles to each other. Conduction and radiation of heat are so rapid that erosion is at a minimum. A simplified method of following total energy at the exit slit of a monochromator is suggested and proved to be accurate. The monochromatic energies obtainable, under specified conditions, from zinc, cadmium and aluminum sparks, are listed at several wave lengths.

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THE SOLUBILITY OF CALCIUM HYDROXIDE IN AQUEOUS SALT SOLUTIONS¹

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There have been numerous investigations of the solubility of a sparingly soluble electrolyte in a solution of another electrolyte and attempts to formulate more or less rigorous expressions for the behavior of such solutions. While most of the previous workers along this line have used as the saturating substance a uni-univalent electrolyte of very low solubility, we have investigated the solubility relations, in a series of salt solutions, of a univalent substance of considerably greater solubility, namely, calcium hydroxide, which is readily obtainable in the form of large, well-defined crystals of a high degree of purity. The fact that it is a strong base lends it further interest since it may exhibit phenomena peculiar to substances which dissociate to produce hydroxyl ion.

The salts used were selected with the purpose of obtaining series, such as the chlorides of the alkali metals, which might be expected to show some definite relationships or systematic differences, such as the effect of different valence types. To this end the solubility of crystalline calcium hydroxide was determined at 25° in solutions of each of the following salts, at a series of concentrations extending well toward saturation of the salt: sodium chloride, potassium chloride, lithium chloride, cesium chloride, strontium chloride, barium chloride, sodium bromide, potassium bromide, sodium iodide, sodium nitrate, sodium nitrite, sodium chlorate, sodium perchlorate and sodium acetate. An attempt was made to use calcium chloride but the formation of hydrated double salts vitiated the results.

In all of these cases the solubility of calcium hydroxide increases with the salt concentration to a maximum, which ranges from about 1.35 to

¹ From the dissertation presented by Clinton Grove to the Graduate School of Yale University, June, 1928, in candidacy for the degree of Doctor of Philosophy.