Photoelectric Quantum Counters for Visible and Ultraviolet Light. Part I

By GORDON L. LOCHER[1]
The Rice Institute

(Received September 28, 1932)

Extremely sensitive instruments for measuring faint light, from 900A to 7500A, have been made by combining the essential features of photoelectric cells and Geiger-Müller tube counters, so that the photoelectrons ejected by the radiation are individually counted. With some of the tubes described, photocurrents of 0.05 electrons per second can be measured. Photoelectric surfaces of Sn, Cd, Zn, Cu, brass, Ag, Hg, Mg, I_2, and Se, were used for measuring ultraviolet light. Visible-sensitive surfaces were made by coating Cu cathodes with fused NaCN, and with amalgams of Na, K, Cs, Sr, and Na-K, and subsequently directing intense H^+ bombardment against them, in a hydrogen atmosphere. In this manner, thin films of hydrides of the respective metals were formed by reduction. The KH-on-Hg cathodes were the most sensitive to visible light, while the most sensitive one for ultraviolet light was a thin layer of I_2 on Se. Very thin films of about 30 aniline dyes and photographic sensitizers were successively coated on the zinc cathode of a counter. The dye usually shifted the photoelectric threshold toward the ultraviolet, but increased the total sensitivity of the surface. Similar effects were obtained by reversing the direction of field in the counting tube and introducing traces of certain organic liquids into the vicinity of the tungsten wire, which was then the cathode. Thus diethyl-aniline increased the sensitivity by a factor of about 25. Different gases were also tried in the counting tubes; it was found best to use a gas with a high minimum ionization potential, when possible. A counter was used for comparing the total ultraviolet luminosities of several light sources. Thus a particular quartz mercury arc, using about 120 watts, gave 6×10^6 times as much ultraviolet as did a 1000-watt incandescent lamp. Amplifying and recording apparatus is described which is suitable for counting as many as 100 electrons per second, arriving at random times. The paper also discusses criteria for determining the useful electron-counting sensitivity of a counter, the factors limiting its counting speed, an explanation of its mode of operation, and evidence for the existence of other ionic emissions, besides electrons, from counter cathodes. Some possible applications of the counters are mentioned.

I. INTRODUCTION

THE devices described here are combined photoelectric cells and Geiger-Müller tube counters. Photoelectrons liberated from the sensitive surfaces cause small individual discharges between the electrodes, which are amplified and made to operate an impulse recorder or oscillograph. The number of photoelectrons liberated, hence the number of impulses, in unit time, is a measure of the intensity of the incident light.

The main advantage of these counters over other kinds of light detectors lies in their enormous sensitivity for measuring photocurrents. This is shown by comparison of the counters with a Hoffmann electrometer and photoelectric cell. About 1000 electrons per second are required to give a detectable

[1] Later, National Research Fellow, Bartol Research Foundation of The Franklin Institute.

current in the electrometer, even when adjusted to very high sensitivity, whereas some of the counters described here will readily detect a "current" of 0.05 electrons per second, or about 1/20,000 as much. Other desirable features of the counters include simplicity of construction and use, portability while operating, and cheapness of construction. Certain limitations inherent in them will be discussed in a later section of this paper.

In counting individual photoelectrons, occasionally liberated, one seems to approach the limit of sensitivity of a photocurrent measuring device. So the problem of measuring the faintest light becomes one of preparing stable photoelectric surfaces of high quantum efficiency, that have the most suitable spectral distribution of response for the light to be measured.

The work reported here is of a preliminary nature. It includes details of construction of the counters, their general behavior while in use, methods of amplifying and recording impulses, and most especially, methods of preparing numerous photoelectric surfaces that respond to light from the far ultraviolet to the infrared.[2] The writer believes that these counters will find useful application in numerous problems requiring the detection and measurement of faint radiation, and that by their high sensitivity they will make possible the performance of others hitherto very difficult, or impossible. One may especially cite astronomical photometry, spectroscopy, and physical optics, as fields where advantageous application is expected.

B. Rajewski[3] has shown that the usual type of Geiger-Müller[4] tube counters can be modified to respond to ultraviolet light, by adding quartz windows and coating the interior of the metal tubes with cadmium or zinc. He believes one of these to be sensitive enough to detect 12 quanta of 2650A light per sq. cm per second, and further reports the detection of the "mitogenetic rays," supposed by some biologists to be emitted by rapidly dividing plant cells and certain animal tissues. Rajewski's counters were sufficiently large to give a rather high rate of spontaneous counting, in darkness. This is due to radioactivity, cosmic rays, and other spurious causes. By surrounding the counters with a heavy iron shield, the accidental rate was reduced to 20 or 30 impulses per minute.

Rapid spontaneous counting is objectionable for two reasons. In the first place, the accidental count is subject to statistical variation, and in the second, it forms a background on which the true count is superposed, thereby raising the minimum detectable light intensity. In this respect, the use of counters exactly parallels that of vacuum photoelectric cells. Statistical variation in their dark currents becomes troublesome when very feeble light is to be measured; and the superposition of the fluctuating dark current on the true photocurrent diminishes the useful sensitivity of the cell. By the *useful*

[2] The important matter of measuring the quantum efficiencies and sensitivities of particular counters, expressed as the least number of quanta that can be detected in a given time, has not yet been done.

[3] B. Rajewski, Phys. Zeits. **32,** 121 (1931).

[4] H. Geiger and W. Müller, Phys. Zeits. **29,** 839 (1928); Phys. Zeits. **30,** 489 (1929); Phys. Zeits. **30,** 523 (1929).

sensitivity of a cell or counter, one means the best sensitivity for which the results may be *reproduced*, within arbitrarily assigned limits of error, under identical experimental conditions.

The problem in hand is one of measuring light that can be concentrated by lenses and mirrors. This offers a means of reducing the accidental count inherent in large tubes, by using small ones and focusing the light on the photoelectric surfaces. However, the resistance between electrodes must be at least 10^{10} ohms,[5] so a modified form of counter construction is necessary in order to get the required insulation. The use of alkali photoelectric surfaces lowers the resistance and greatly accentuates the difficulty of maintaining good insulation.

The tube described in the next section had a minimum path between electrodes of about 25 cm, over Pyrex glass. Its resistance is estimated at 10^{18} to 10^{16} ohms. The rate of accidental counting, in darkness, depended on the electrodes. Thus the average for cathodes of copper, zinc, cadmium, tin, and mercury was about 1.5 per minute. Similar electrodes bearing alkali metals gave accidental counts ranging from about 3 per second to 6 per minute. Several iodine-coated silver and copper ones showed very high sensitivity to ultraviolet light, with rates as low as 0.7 per minute, in darkness. No shield was used for stopping penetrating radiation; the count due to stray γ-rays and cosmic rays should be 0.5 to 0.9 per minute, with counters of the size used.

II. Description of the Counters

Fig. 1 is a sectional diagram of the counting tube. Essential parts are the axial electrodes E_1 and E_2, the Pyrex tube A, and the quartz window B, which is attached with wax. E_2 is a three-fourths-cylindrical cathode, carrying the photoelectric surface on its concave side. The tube is filled with a gas at 6 to 8 cm pressure. E_2 is maintained at a high negative potential with respect to E_1, so that photoelectrons set free by the impinging light will be drawn to E_1 with sufficient velocity to start "bursts" of ionization by collision. These cause minute current-impulses that are amplified and automatically counted. By means of the ground joint C, the part-cylindrical electrode may be removed for replacement or treatment. The wire electrode is also removable. It is attached to the lead wires L_1, by hooks, and is kept under a slight tension by a small steel spring.

This design has been found very convenient for experimentation with photoelectric surfaces, and for studying the operating characteristics of the tube. The counter used by the writer has been assembled and dismounted some hundreds of times during the course of various tests.

The cylindrical electrodes had an average length of 11 mm, and were about 7 mm in internal diameter. Longitudinal slots about 4.5 mm wide were sawed in them to admit the light. The wire electrodes were usually of polished platinum or tungsten, from 0.038 mm to 0.11 mm in diameter.

[5] Otherwise, fluctuations in the leakage current across the insulators are amplified and recorded as impulses. This spurious count becomes more numerous as the insulator resistance diminishes. The writer found a metal-ebonite G.-M. tube, 1 cm in diameter, to be very unsatisfactory for that reason.

It has been found desirable to use especial care in centering the electrodes, and in making the anode surface smooth. If the wire does not lie nearly along the axis of the cylinder, or if there are major irregularities on the latter, the field may be so distorted as to render much of the photoelectric surface feeble or inoperative. Photoelectrons released with very low velocities in small pits in the metal probably fail to get into the field, and are not counted. It

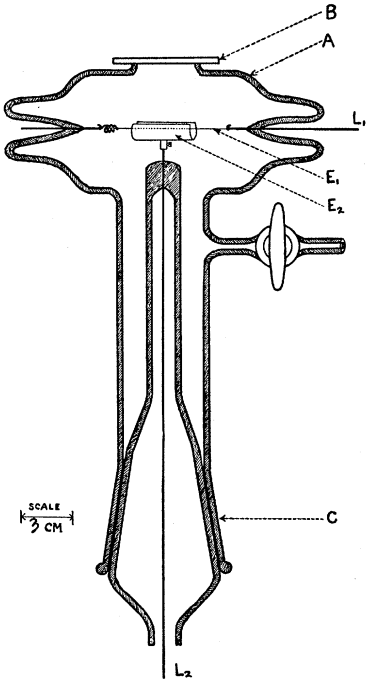

Fig. 1. Cross section of the counting tube. E_1, wire electrode; E_2, cylinder electrode, carrying the photoelectric surface; B, quartz qindow; A, glass body of tube; C, ground joint; L_1 and L_2, leads to amplifier and high-potential source, respectively.

was shown that cathodes differing appreciably from cylindrical form were completely unsatisfactory. Sharp points on the wires are even more objectionable than those on the cylinders, because of the tendency to discharging action. Hence it is good practice to polish the wire with rouge paper before introducing it into the counter. The use of oxide and other coatings on the wires will be discussed in the section dealing with the preparation of electrodes.

III. Amplifiers and Impulse Recorders

Numerous good amplifiers for use with Geiger-Müller counters have been described elsewhere.[6] But the requirements of the present work are rather

[6] For example: J. A. Van den Akker and E. C. Watson, Phys. Rev. **37**, 1631 (1931); B. Rajewski, reference 3; R. Jaeger and J. Kluge, Zeits. für Inst. **52**, 229 (1932); N. A. de Bruyne and H. C. Webster, Cambridge Phil. Soc. Proc. **27**, 113 (1931).

more stringent than for other counters, because the tube electrodes are much nearer together and less ions are produced by collision at each impulse. The impulse current must also be kept sufficiently small that no *light* will be emitted by the discharge. Even when this light is far below the limit of visual sensitivity, its photoelectric action will generally cause extended impulses, instead of sharp ones. It is little more than a fortunate accident that one can get impulses that are strong enough to amplify and record, but too weak to generate light in the counters, especially when alkali metals are present. These remarks apply as well to Geiger-Müller counters for cosmic rays, γ-rays, and x-rays. On the basis of the behavior of photoelectric counters with many different cathodes, filled with different gases, and on comparison of their behavior with that of ordinary tube counters, the writer has become of the opinion that the extension (i.e., "drawling") of impulses observed when the operating potential across the tube is slightly too high, results chiefly from this secondary photoelectric action of the light generated by the discharges themselves.

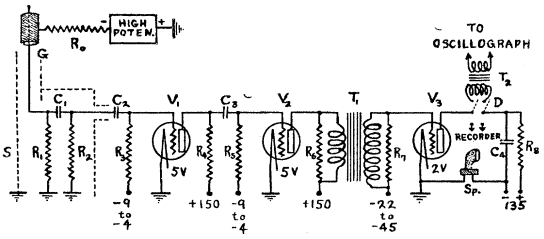

Fig. 2. Amplifying and recording circuit. The resistances, R, are in megohms; capacities, C, are in microfarads.

$R_0=1000.$ (xylene)	$R_7=2.$ to ∞	V_1, UX 240
$R_1=30.$ (xylene)	$R_8=0.1$ (variable)	V_2, UX 240
$R_2=0.5$	$C_1=0.01$* to 0.0005	V_3, W.E. 269-A (thyratron)
$R_3=10.$	$C_2=0.01$	G, counting tube
$R_4=5.$	$C_3=0.01$	Sp, loud speaker
$R_5=1.$	$C_4=1.$	S, grounded shield
$R_6=0.5$ to ∞	$T_1=1$ to 3	D, d.p.d.t. switch

Another feature of obvious importance is that the amplifier and recorder be capable of accurate and very fast counting when relatively high light intensities are being handled. Several high-gain amplifiers were tried and discarded before a rather satisfactory one was developed. The circuit diagram of this one is shown in Fig. 2. The use of a thyratron as a relay tube is a great convenience; it gives uniform impulses and eliminates the relatively slow-moving mechanical parts of a relay, yet allows enormous gain in amplification. The arrangement for stopping the thyratron discharges is patterned after that of Jaeger and Kluge:[7] the condenser C_4 is charged through the resistance R_8; when an impulse causes an arc to strike in the thyratron, C_4

* The 0.01 mfd condenser used was of rather low resistance, so that R_1C_1 did not represent the true constant for the discharge of C_1. In this case, C_2 was added in order to better isolate the grid of V_1 from the high-potential source.

[7] R. Jaeger and J. Kluge, Zeits. für Inst. **52,** 229 (1932).

discharges through the tube and recording device, after which the arc stops. R_8 is made just large enough to keep the arc from being maintained directly from the battery. Fig. 3 shows some typical impulses recorded on an overdamped string oscillograph. It will be observed that they normally last for about 0.01 second. With oscillographic recording, the thyratron recovers quickly enough to record about 100 random-spaced impulses per second. Considerable gain in the time resolving-power of the apparatus is effected by recording the impulses on an oscillograph so that the wave form of the amplifier output can be examined.

R_0 and R_1 are liquid resistors each consisting of an appropriate mixture of pure xylene and absolute alcohol, sealed in a small glass T-tube provided with platinum electrodes.[8] The resistance is adjusted by altering the proportions of the two liquid components, while filling the tube. The magnitude of

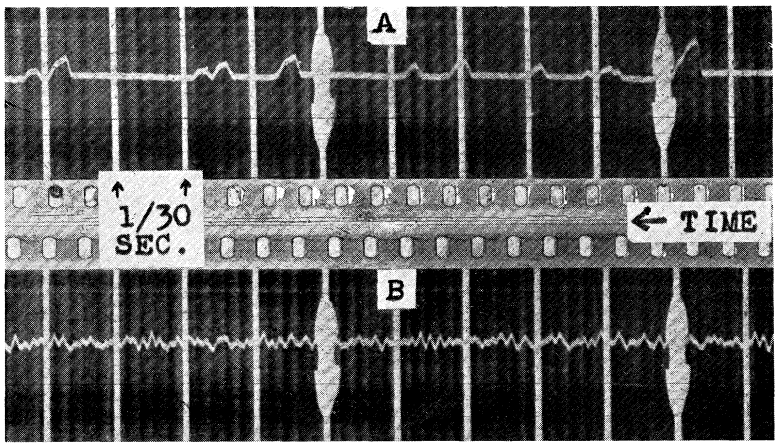

Fig. 3. Oscillograms showing rapid counting: *A*, about 30 per second; *B*, about 225 per second.

the resistance is not critical, but should be constant, for good operation. R_0 limits the current that can flow during each impulse, in order to prevent the discharges from being luminous. The resistance of the counting tube, itself, becomes relatively small while the discharge is taking place, hence it cannot be used to limit the current

A convenient recorder for low-speed impulses has been made by replacing the balance wheel of an Ingersoll watch with an electromagnetic escapement. The energy required to operate the recorder is about 0.03 watt, and its maximum counting speed for regularly spaced impulses is about 40 per second. But for impulses spaced at random, the safe counting rate is only about 10 per

[8] Similar to that of N. Campbell, Phil. Mag. **22,** 301 (1911), and **23,** 668 (1912). Other constant high-resistance units have been described by J. A. Van den Akker, reference 6., H. C. Rentschler and D. E. Henry, Rev. Sci. Inst. **3,** 91 (1932), and by H. L. White and E. A. Van Atta, Rev. Sci. Inst. **3,** 235 (1932). The writer is indebted to Dr. L. M. Mott-Smith for the loan of a shielded xylene resistor and condenser used in the preliminary part of this work.

second. The characteristics of this device seem to be similar to those of a recorder used by Van den Akker[9] for counting x-ray photoelectrons.

Wynn-Williams[10] has recently described an elegant arrangement for counting electric impulses at high rates. This might be used to a great advantage with any kind of Geiger counter, to increase the range of intensity of the phenomenon being measured. Instead of recording every impulse, each second, or fourth, or eighth, etc., is recorded, depending on the number of reducing units put in the circuit. A time resolving-power of about 1/1400 second is reported, so that the circuit should be capable of accurately counting *several hundred random impulses per second.* The limiting factor is the deionization time of the thyratron tubes used, not the inertia of any mechanical system. Corresponding to a count-reducing factor F, there is an uncertainty in the number of impulses, $\pm F/2$. But since F would rarely be made greater than 16, the error thus introduced is negligible, except for short or slow counts.

IV. The Field in the Counter

For supplying the potential across the counters, a high-voltage battery is considered preferable to a rectifier, in all respects except economy. A simple rectifier, similar to that of Van den Akker and Watson,[6] was used in most of the experimental work reported here. It consisted of a 1 mfd condenser charged by a small transformer and kenotron tube; voltage variation was obtained by altering the primary voltage of the transformer. However, a rectifier that draws its energy from a fluctuating source of power is very apt to have slow but troublesome fluctuations in its output potential. There is also some difficulty in accurately adjusting this potential, because the "soakage current" into the condenser makes the voltage drift slowly upward to its maximum value.

The voltage suitable for operating a counter depends on the shape, material, and state of the cathode surface, and on the kind and pressure of the gas in the tube. In the present work, the voltages ranged from 600 to 2000; they were usually 1000 to 1200 volts. The correct value for a given counter may be ascertained by causing faint light or γ-radiation to strike the cathode, while slowly raising the applied voltage until it crosses the threshold value. The threshold is the same for light, x-rays, and radioactive radiations.

It is important to determine and maintain the correct operating potential. The low-voltage edge of the threshold is quite sharp, but above this there is usually a *voltage plateau*, any part of which may be used. Impulses will be feeble or absent on the low-voltage side of the plateau; on the high-voltage side they become extended (mushy), and spontaneous discharges develop with increasing rapidity and finally merge into a steady discharge. The width of the plateau may be 10 to 100 volts; this depends on the gas, and on the counter cathode.

The range just described is one in which the counter *must* be operated,

[9] J. A. Van den Akker, Rev. Sci. Inst. **1,** 672 (1930).
[10] C. E. Wynn-Williams, Proc. Roy. Soc. **A136,** 312 (1932).

if its results are to have any significance. But the characteristics of operation are not constant within this range. In particular, the sensitivity of the counter usually increases as the applied potential increases toward the high-voltage side of the plateau, a gain as high as 100 percent sometimes being observed. The augmented count is believed to be a *bona fide* effect, if the potential is not too near the edge of the range. The explanation of this is not yet clear. Since the increase in field strength never exceeded 10 percent of its initial value, it is impossible to account for any large added sensitivity by merely supposing that the photoelectric work function of the surface was diminished by the increase of field, although this effect undoubtedly takes place to a certain extent in counters.[11] So if the quantum efficiency (ratio of the number of photoelectrons to the number of incident quanta) remains about the same across the voltage plateau, while the sensitivity of the counter increases, it is reasonable to suppose that the efficiency of the tube *for counting the photoelectrons liberated* is improved by the use of a more intense field. Two possible explanations of this appear. The first and more favorable one supposes that under normal conditions, a few of the photoelectrons cross the inter-electrode space without producing enough ionization by collision to give impulses, but that on accelerating them more strongly, a larger fraction will be counted. The second possibility is that higher fields may extend more deeply into the microscopic crevices in the cathode surface, thereby removing and counting photoelectrons that were liberated with almost zero velocity in them. In photoelectric counters we have a problem not met in other counters, or in vacuum photoelectric cells, namely the difficulty of collecting the very slow photoelectrons that are set free by light just shorter than the threshold wave-length; if these electrons are in a weak field, many will be turned back into the metal by collisions with gas molecules. In practice, it seems safest to use a potential slightly higher than the threshold value. The voltage plateau of the best visible-sensitive counters is so narrow that there is little choice, anyhow.

V. Preparation and Characteristics of Electrodes

Photoelectric quantum-counters have characteristics of behavior not less distinctive than those of photoelectric cells. The sensitivity, spectral distribution of response, and wave-length threshold of a counter depend not only on the material of its cathode, but on its previous history, its physical state, the presence of traces of foreign substances, and amount of previous ionic bombardment. The use of outgassed surfaces, or of surfaces in vacuum, is precluded by the principle of operation of the counters. Further, the success of those with alkali metal surfaces, or any other, is contingent upon the maintenance of very high resistance between electrodes.

Cathodes sensitive to ultraviolet light only

Experiments were first done with cathodes of zinc, cadmium, tin, copper, brass, silver, mercury, and magnesium. Under normal conditions, the sensi-

[11] On the basis of effects found by Lawrence and Linford, Ives, Schurmann, and Nottingham (see Hughes and DuBridge, *Photoelectric Phenomena*, p. 110).

tivities and dark-rates of these counters were very constant with time; the photoelectric thresholds, which were about the same that the metals show in ordinary photoelectric cells, were in the ultraviolet, except in the case of magnesium. Silver, mercury, magnesium, and tin electrodes were more sensitive within their ranges of response than were the others. Also, the average rate of spontaneous counting in darkness, or *dark-rate*, for the entire group was about 1.5 per minute, while cathodes of magnesium and very pure silver had dark-rates consistently less than 1 per minute. This fact, and the discovery that the dark-rate of copper could be reduced to a similarly low value by covering the entire electrode with a molecularly-thick coat of iodine, leads to the conclusion that the higher rates of uncoated copper, cadmium, tin, etc., are largely due to the emission of α-particles by the metals themselves.

Following the interesting work of Olpin,[12] concerning the effect of dyes on the photoelectric properties of alkali metals, many tests were made with counters having cadmium and zinc cathodes coated with extremely thin films of aniline dyes and photographic sensitizers.[13] The relation of the sensitivity to the film thickness makes it appear that the photoelectrons were mainly liberated from the metal and drawn through the film. The *sensitivity* of zinc electrodes was markedly increased by the addition of certain thicknesses of dyes, but the photoelectric threshold was always displaced toward the ultraviolet. This displacement is the reverse of that found by Olpin, in alkali photoelectric cells. Furthermore, the thickness and texture of the coating on the cathode seems to have more to do with the increase of sensitivity than did the color or composition of the dye. An explanation tentatively suggested is that the dye merely served as an insulating layer, which allowed the potential to be raised above the normal operating value, with a resulting increase in the sensitivity. Reasons for the rise of sensitivity with voltage have already been discussed. On this theory, one would account for the shift of photoelectric threshold by assuming that the slowest photoelectrons failed to penetrate the film. A similar effect was remarked in the case of thin oxide films on magnesium and copper: the sensitivity increased, but the threshold moved toward the ultraviolet. Fig. 4 shows the response of a slightly oxidized magnesium cathode to light from a carbon arc. Cadmium was found less sensitive to the effects of dyes than was zinc. Much additional work will be required to determine with certainty what the action of dyes on counter electrodes may be. In view of Olpin's results, it would be especially interesting to try dyed alkali metal cathodes.

The total sensitivity of a thin cathode in an air-filled counter was found to decay almost exponentially with time, falling to half its original value in 12 hours. The air was at 6 cm pressure. This decay is due to the formation of a film of oxide of increasing thickness. There was also a decrease in the dark-rate during the same period (28 hr.), but it was by a smaller percentage. How-

[12] A. R. Olpin, Phys. Rev. **36**, 251 (1930).

[13] Including: aesculin, alizarine, aniline black, anthracene, China-blue, Congo-red, cyanin, eosine, fluorescein, litmus, methylaniline violet, orthochromblau, picric acid, pinacyanol, pinaverdol, pinachromviolett, salicylic acid, uranin, and others.

ever, the sensitivity and dark-rate of a clean tin cathode, in nitrogen, were not perceptibly altered by standing $5\frac{1}{2}$ months.

If either electrode is coated with an insulating film of oil, grease or lacquer, the applied voltage can be raised far above the normal maximum, without starting a discharge. But once a discharge is started by the action of light or other radiation, it continues until the potential is removed. The break will then "heal" in an interval that varies from a small fraction of a second, in the case of a light oil, to nearly a minute, for a viscous grease. Under some conditions, the disruptions may begin and stop spontaneously; they then take place rythmically with a frequency that rises with the applied voltage, often to several hundred per second. This action superficially re-

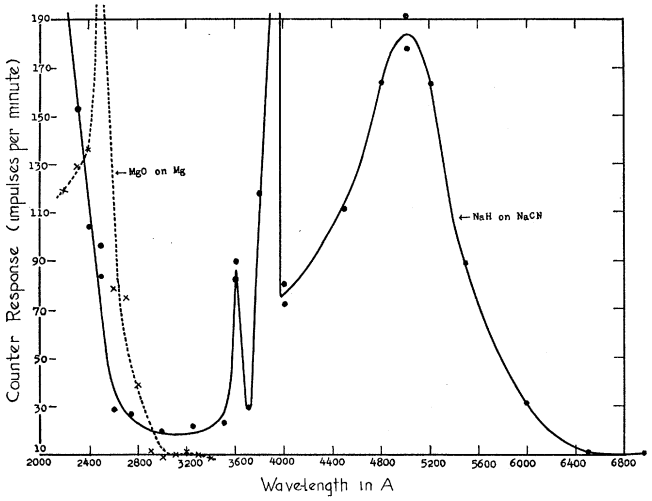

Fig. 4. Response of two counter electrodes to light from a carbon arc.

sembles that of an electrolytic interrupter. Fast rythmic discharges may sometimes take place only when light falls on the cathode. Under such conditions they might be mistaken for normal response; but their regularity shows that this is not the case.

A curious displacement of the photoelectric threshold of a tin electrode was accidentally brought about by strongly bombarding the surface with ionic nitrogen, in a nitrogen atmosphere. The counter showed greatly increased sensitivity and responded to light well into the visible region, for several minutes after treatment of the surface; it then returned to its initial state. This effect could be repeated an indefinitely large number of times. It is likely that the shift is due to the partial dislodgment of a compact gaseous layer from the electrode, in spite of the high pressure of the surrounding gas (7 cm). Another possibility is that a photosensitive but unstable compound is formed. Unfortunately, no other gases have yet been tried for the effect with tin, nor has nitrogen bombardment been tried on cathodes of other metals. The thresholds of silver and copper did not show any appreciable shift after strong and extended bombardment with ionic hydrogen, in a

hydrogen atmosphere. The large *permanent* shift of the threshold toward the red, effected by bombardment of some salts with hydrogen, is the subject of part of the next section.

Alkali metal cathodes

The advantages of alkali metal cathodes, arising from their high sensitivity and response to long wave-lengths, more than compensates for the difficulties met in preparing them. Even if it were possible to move the photoelectric thresholds of other metals into the visible region by means of dyes, it seems certain that the quantum efficiencies of such surfaces would be much inferior to those of alkali metals. The chief obstacle encountered is in finding a good way to introduce the latter into the tube as a deposit on the cathode. If sent in by distillation, the metal tends to spread over the interior surface of the glass. This results in diminished resistance that is fatal to the successful operation of the counter. A possible alternative is to coat the photoelectric material on the demountable cathode, while *outside* the counter, and then seal it into the counting tube. Naturally the air and moisture must be kept away from the surface during all processes, and this is not easy to do. However, two modifications of this second method have been devised and carried out by the writer, with very gratifying results.

The first process *consists in the formation of a hydride of the desired metal on the cathode, by reducing a salt with atomic hydrogen.* For example, a copper cathode, coated with a thick layer of fused sodium cyanide, was introduced into the counter; the tube was then exhausted and filled with dry hydrogen at a pressure of 7 centimeters of mercury. Next, a discharge of 15 to 100 microamperes was passed through the gas for 30 minutes, so that the cyanide was under strong bombardment with hydrogen ions. A reaction such as

$$NaCn+2H^{+}\rightarrow NaH+HCN, \text{ or } 2\ NaCn+2H^{+}\rightarrow NaH+2C+N_2$$

is believed to have taken place on the surface; the sensitivity of the counter was greatly increased, and its photoelectric threshold was permanently shifted from the ultraviolet to about 6400A. Choice of the cyanide for this purpose, in preference to another salt, was made on the basis of its low heat of formation; it seemed likely that such a salt could be most easily reduced. Fig. 4 shows the approximate distribution of the response of this counter to the light from a carbon arc. The curve was made with a quartz monochromator, and is uncorrected for the stray light that gets through the instrument. One may observe that the peak at 5000A does not coincide with any shown by sodium metal in an ordinary photoelectric cell. The question may justly be raised as to whether the response is really from sodium metal. The answer seems affirmative, for the high sensitivity and response to red light appear only after the ionic bombardment, and immediately vanish with the admission of any air into the tube. It is also well known that the spectral distribution of response of thin films depends greatly on the nature of the underlying surface, and on the previous ionic bombardment.[14] The dark-rate of

[14] See: A. L. Hughes and L. A. DuBridge, *Photoelectric Phenomena* (McGraw-Hill Book Co., Inc., 1932).

this counter subsided from 86 impulses per minute, just after preparation, to 2.95 per minute, a few hours later. (The results shown in Fig. 4 were obtained about a day after forming the surface.) The peaks at 3600A and 3900A are due to groups of lines in the spectrum of the arc used. Three other similar surfaces were prepared from sodium cyanide; the kind of surface on which the salt was used was found to be immaterial.

It should be mentioned that during the discharge used for sensitizing the cathode, an irregular film was always deposited on the wire anode. These films can, and must, be removed by electrically heating the wire to a bright glow for a few seconds.

Several attempts were made to produce potassium hydride surfaces from the cyanide by a process like that just described. These met with little success and were abandoned when it was found that excellent surfaces could be prepared from amalgams of the alkali metals.

The second process consists in the *formation of alkali hydrides by bombardment of amalgams with atomic hydrogen.* Two surfaces of this type were prepared with sodium, three with potassium, one with sodium-potassium, and one with caesium. The sodium counters made by this process were several times as sensitive as those previously prepared from the cyanide; but their sensitivity was far exceeded by the potassium ones. The latter were, in fact, the most sensitive counters for visible light that the writer has been able to prepare.

The technique for forming them was much like that with the cyanide. The demountable cathode, of heavy copper, was lightly coated with clean mercury and dipped into the amalgam, which was preserved under xylene.[15] While still coated with a protecting film of xylene, the electrode was sealed into the counting tube, from which the air was immediately swept out with dry hydrogen. Long pumping removed the xylene, after which fresh hydrogen was introduced to the proper pressure. A discharge was then passed between the electrodes, and the coating was evaporated from the wire, as before. The copper acted as an absorbent for excess mercury, which presently disappeared into the cathode. At the same time, the physical appearance of the surface changed: sodium and potassium ones became dull gray, while caesium took on a light golden luster. It is not known whether or not this was accompanied by the expected concentration of the alkali metal on the surface. The question hinges on determining whether the light metal sinks into the copper along with the mercury, or is filtered out at the surface. The final step was to evaporate the film that was incidentally deposited on the wire during the discharge. The counter was then ready for use.[16]

[15] Amalgams were prepared by electrolysis of salt solutions, using mercury cathodes. They were then washed with water and xylene. See: J. W. Mellor, *A Comprehensive Treatise on Inorganic and Theoretical Chemistry*, 4, 1010 (Longmans and Co., London).

[16] While preparing this paper, it has occurred to the writer that the use of mercury is superfluous. The technique suggested is to immerse the counter cathode in clean alkali metal, melted under an inert but volatile liquid, and make the transfer to the counter while a film of the liquid remains as a protective coating.

The photoelectric thresholds of the amalgam counters were found by means of filters to be roughly the same as for the alkali metals in photoelectric cells. Thus for sodium, the threshold was around 6000A, for potassium, 6500A, and for caesium, >7500A.[17] Sodium-potassium mainly showed the response properties of sodium, which predominated in the mixture used. Amalgams of potassium and sodium became granular at fairly high concentrations of the light metals, while the mixed amalgam remained fluid at similar concentrations. The latter was thus easier to apply to the electrode than that of the single metal.

Minimum rates of accidental counting for the several cathodes were as follows: sodium, 4.7 per minute; caesium, 5.8 per minute;[18] potassium, 2.3 *per second*. It is not known what part of the potassium count is due to β-particles from its radioactivity. This might, of course, be approximately calculated by measuring the amount of metal, thickness of film, and coefficient of absorption of the particles by the film. The writer believes that the major part of the count is due to other spurious causes, such as the evaporation of charged molecules, or a chemical change involving the emission of electrons or light. In support of this view, it may be mentioned that various other electrodes that were presumedly devoid of radioactive material showed high rates of accidental counting for short periods after their introduction into the counter, or after strong ionic bombardment. The duration of this high count could sometimes be controlled by the length or manner of treatment of the surface, and usually subsided within a period that varied from a few seconds to several hours after treatment.

Several cathodes coated with ammonium amalgam were also tried in the counter. But the ammonium always decomposed before it could be used, in spite of the fact that the time between its preparation and exposure as a photoelectric surface was less than two minutes.

A strontium amalgam counter was also prepared by a process like that used with the alkali metals. Its response was good for $\lambda < 4600$A, and could be detected at $\lambda \sim 7000$A. The sensitivity to light from an incandescent lamp was estimated to be about one-sixth that of the sodium counters. The sensitivity was neither improved, nor was the spectral distribution altered, by directing a stream of hydrogen ions against the cathode. Several barium amalgam surfaces were also tried, but were not successful. The concentration of barium metal was initially small, so it was probably destroyed by combination before it could be tried in the counter.

Non-metallic cathodes

Thin films of numerous non-metallic substances have been tried on counter electrodes, in addition to the dyes previously mentioned. Both liquids and solids were used; the latter were usually more easily handled and more constant in behavior. A few of the surfaces that seemed especially in-

[17] Found with filters. See: A. L. Hughes and L. A. DuBridge, reference 14, p. 457–9.

[18] The electrodes of the Cs counter were not well centered, so the sensitivity and dark-rate are not comparable with those of other counters.

teresting will be mentioned here. Generally speaking, if the film is exceedingly thin, the photoelectric behavior is that of the underlying surface; if it is thick, the characteristics are those of the material of the film itself; intermediate thicknesses lead to a variety of effects.

Iodine was deposited from solution on cathodes of copper, silver, and selenium. (The size of crystals and thickness of the deposit can be reduced at will by heating the electrode in a flame.) The photoelectric threshold of a molecularly thick deposit was between 2300 and 3000A, in air or hydrogen, which were the only gases used. It was observed that the deposition of a thick film on a particular copper electrode reduced the dark-rate from about 1.5 to 0.9 per minute; also, that the behavior of the counter was the same after bombardment of the iodine with atomic hydrogen, provided that the anode wire was subsequently cleaned by heating. The distinctive feature of the iodine counters was their extremely good sensitivity. For example, the response to light from a flame was about twice as high from iodine-coated copper as from clean copper, in spite of the fact that the latter responds to longer wave-lengths. After strong heating in contact with iodine, a copper electrode became coated with a thin film of light-green material, presumedly an iodide. The dark-rate of the counter then increased to 90 per minute, and remained practically constant even after extended bombardment with atomic hydrogen!

Selenium, deposited as a thick coat on copper, by evaporation, also had a threshold between 2300 and 3000A; its dark-rate was 57 per minute. The threshold was shifted to about 4100A by hydrogen bombardment, but returned to its former value when air was admitted to the tube, about 15 minutes later. The operating potential was also made more critical by the discharge. The reason for the change of threshold is not known, but it seems reasonable to suppose that the hydrogen bombardment produced a surface film of a compound whose photoelectric threshold was nearer the red.

The counter having the highest sensitivity to ultraviolet light of any yet prepared, had a non-metallic cathode. It was made by coating copper with a thick film of selenium, depositing on this a very thin film of iodine, subjecting the composite surface to strong bombardment with atomic hydrogen, and removing the film from the anode wire by heating. The photoelectric threshold was again between 2300 and 3000A, and the dark-rate was about 1 per second. Light from a small constant flame, which increased the count from a good tin cathode by 29 impulses per minute, increased that from the Se-I one by 460 per minute. So the sensitivity of the Se-I was about 15 times that of tin, to the source of light used! A possibility that should not be overlooked in the case of this and similar electrodes, is that *the emission of photoelectrons may merely be an electrical by-product of a photochemical change.* One seems obliged to look for the explanation of the high rates of spontaneous counting, sometimes got from electrodes in the relative absence of light, or of radioactive material, by finding out whether physical or chemical changes are taking place that are accompanied by the ejection of charged particles or the emission of photoelectrically active light.

No substance that was coated on the cathode of the counter, and that could be retained there without disturbing the necessary electrical characteristics of the device, failed to show photoelectric response. Thus barium chloride, deposited from solution, responded in the ultraviolet, but also showed very weak response to wave-lengths as long as 7200A. After bombardment, the sensitivity to the red was somewhat improved. Similar behavior was shown by a film of red cuprous oxide on copper; it showed strong response to the ultraviolet and very weak response to $\lambda \sim 7200$A. The absence of this red-response was found a convenient means of testing the "photoelectric cleanness" of the copper surface.

The wire anodes

The anode wires should be very smooth. For successful operation of any counter, a high symmetrical field must be maintained between electrodes, and this is more disturbed by microscopic irregularities on the anodes than by much larger ones on the cathodes. In other kinds of tube counters, some investigators[3,4] have used oxide-coated tungsten wires, while others[9,19] used bare ones. The oxide serves as a partial insulator which allows the operating potential across the tube to be raised above its normal value. The writer has found that the oxide film is, in general, more troublesome than desirable, because of its tendency to become disrupted in spots; even one such break is fatal to the success of the counter. Moreover, in visible-sensitive counters, and some others, it is necessary to remove other kinds of films from the wires by heating them to incandescence (usually in hydrogen), and this excludes the use of the oxide. Platinum and tungsten wires were found most convenient; they may be heated to high temperatures, and will withstand the corrosive action of bombardment with alkali-metal ions. The size of the wire determines the operating potential,[20] but any small diameter seems to serve equally well.

VI. Tests and Measurements Made

Inverse square law

Reliable measurements of light intensity cannot be made with any device, unless the rates of its response to a given source obey the inverse square law of variation with distance. To test this, a small alcohol lamp that burned at a constant rate was set at 250 and 500 cm from a tin-cathode counter; resulting increases in the rate were respectively 68.4 and 17.4 impulses per minute. The deviation of these results from the inverse square relation, (1.8 percent), is within the limits of statistical error and fluctuation of the lamp Pending tests with a better source, we may conclude that the inverse square law is applicable, at least to a good approximation. Incidentally, the maximum permissible counting rate for any counter and recorder may be taken as that at which the departure from the inverse square relation, due to

[19] H. Kniekamp, Phys. Zeits. **30**, 237 (1929), and L. F. Curtiss, Bur. Stds. Jour. Res. **4**, 601 (1930).

[20] D. Cooksey and M. C. Henderson, Bull. Amer. Phys. Soc., June 9, 1932, give an empirical formula relating field, applied voltage, and radii of the electrodes.

coincidence of successive impulses, becomes as large as the greatest permissible error. This rate is the reciprocal of the time resolving-power and can easily be found by experiment.

Ultraviolet light from different sources

Application of the photoelectric counter to intensity measurements is illustrated in Table I, which gives the relative total response of a tin-cathode counter to ultraviolet light from four sources of widely different intensities. The wave-lengths actuating the device lie approximately between 1950 and 3500A. The dark-rate, 1.7 per minute, was deducted from the rates recorded Values in the last column were reduced to a comparable basis by use of the inverse square law, and are proportional to the ultraviolet luminosities of the several sources. The extreme feebleness of the ultraviolet from all but the quartz mercury lamp is made evident by these data.

TABLE I. *Ultraviolet light intensity from various sources.*

Source	Distance (meters)	Cathode area exposed	Counting rate (No. per minute)	Computed rates for source at 1 meter and electrode area of 1 cm², per min.
Mercury arc[a]	47.0	0.000855 cm²	48.0	120,000,000.
Bunsen flame[b]	4.0	0.63 "	73.9	188.
Alcohol lamp[c]	4.0	0.63 "	18.7	47.5
Electric lamp[d]	4.0	0.63 "	7.5	19.

[a] Cooper-Hewitt quartz lamp; 4 amp., 30 volts, d.c.
[b] Meeker burner; 0.024 cu. ft. methane per minute, mixed with air.
[c] Burned 9.3 g of denatured ethyl alcohol per hour.
[d] 1000-watt projection lamp; 8.8 amp., 115 volts, d.c.

The ultraviolet from the slow oxidation of a small piece of white phosphorus was easily detected; but no "mitogenetic rays" were found from any root-tips or bacteria cultures, nor was any radiation that was capable of operating the counter detected from the slow oxidation of iron or aluminum, or from mechanically distorted crystals or other materials.

Different gases

Air, hydrogen, oxygen, nitrogen, and methane were used successfully in a counter with a tin cathode. For a given pressure, the operating potential was found to be higher for gases with high ionization potentials, than for others. Operation was most successful with the gas of highest ionization potential used, namely nitrogen; the voltage plateau was widest, so that the potential was least critical of adjustment. In this connection, one recalls the very satisfactory use of helium in other tube counters, by Bearden and Haines,[21] who also found the gamma-ray sensitivity of these to be somewhat greater than that of similar air-filled counters. Their observations seem significantly related to the fact that helium has the highest (minimum) ionization potential of any ordinary gas.

[21] J. A. Bearden and C. L. Haines, Bull. Amer. Phys. Soc., April 12, 1932.

The question has been raised: Why does the discharge of a Geiger-Müller counter *stop*, once it has been set going by an ion? The explanation proposed here is this: Before the discharge begins, there is a large field between the counter electrodes; this is sufficient to give the initial ion enough velocity to ionize the gas, hence to start a general discharge in the tube. During the course of the discharge, the voltage across the tube falls below the critical value for the gas used, and no new ions are generated. The discharge then declines and the residual ions are swept out of the field with sufficient quickness that none remain when the full potential has become reestablished across the tube. The fall of voltage during the discharge is Ri, where R is the external resistance, and i is the maximum current that flows through the tube. A possible inference from the work with different gases is that the use of a gas with a high ionization potential is desirable because it assists in quenching the discharges.

Cellophane window

The short wave-length limit of response of photoelectric counters is determined by the material of their windows; the cut-off of the counters used in most of the work described here was about 1950A. In order to get transparency to shorter wave-lengths, the quartz was replaced with a sheet of cellophane, 0.02 mm thick, supported on a thin metal plate that was drilled to half its area with 0.68 mm holes. The limit for this window should be about 900A, but the air between it and the source probably raised the limit to about 1450A.[22] In work requiring the measurement of light as short as 900A, the source might be mounted in a vacuum chamber of which the thin counter window formed one side.

VII. Modified Counters for Other Uses

The success of the photoelectric counters has led to their use for other purposes. Three slightly modified types will be briefly described here. The first is a convenient counter for α-particles, especially intended for measuring the strengths of sources; the second is a counter for detecting and measuring faint x-rays and γ-rays; the third is a reversed-field counter which may be useful for measuring intensities of spectral lines.

Alpha-particle counter

This adaptation was made by replacing the quartz window with one of very thin mica, 1.05 mm in diameter. The mica reduced the range of the α-particles from polonium by 1.73 cm, in air, so that its thickness must have been approximately 0.007 mm. In order to have a low spontaneous count and to avoid response to visible light, an iodine-coated copper cathode was used; its dark-rate, 0.7 per minute, was negligibly small.

Fig. 5, A, and B, illustrates the use of the counter with a polonium source about 0.0086 cm^2 in area; C was made with a source 2 cm^2 in area. The polonium was electrolytically deposited on platinum foil; different parts of the deposit were found to be of similar activity. Distances shown on the

[22] A. L. Hughes and L. A. DuBridge, *Photoelectric Phenomena*, p. 458.

curves are subject to a lateral displacement of about 0.5 mm, due to the uncertainty of the initial position of the micrometer frame that carried the source.

Other tests with the α-ray counter led to favorable results. The first showed that the voltage plateau was wider than those of most photoelectric counters, so that small fluctuations of the potential applied to the tube did not alter the count from a constant source. A second test showed that variation of the gas pressure in the counting tube had no detectable effect on the

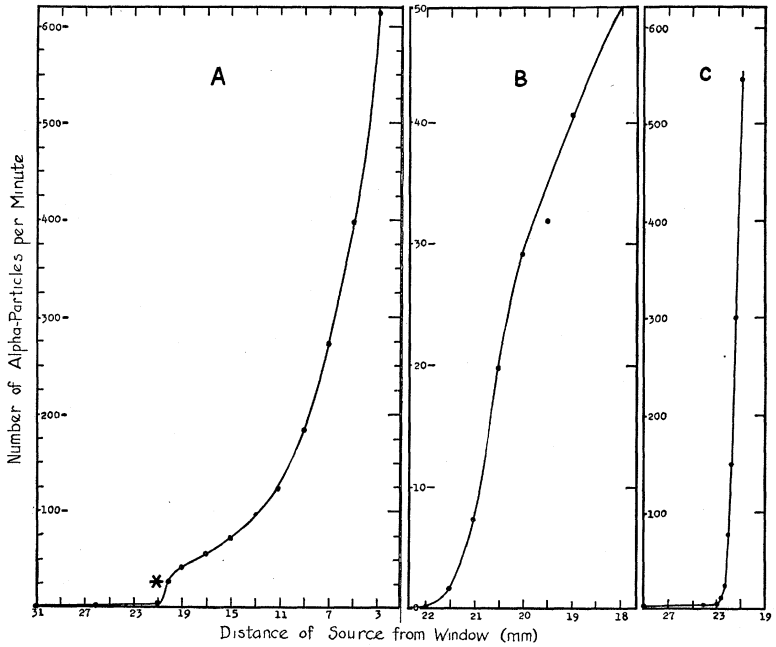

Fig. 5. Curves illustrating use of the α-particle counter with a polonium source: A, count from a plane source of small area; B, starred portion of A, on a larger scale; C, count from a plane source of large area.

range of the α-particles, as determined with the counter. It seems that if the particle gets through the window, it is almost certain to produce enough ions to start an impulse. A third test indicated the order of accuracy to be expected with short observations. Table II contains the data of this test.

TABLE II. *Experiments with alpha-rays.*

Time in minutes	Total number of α-particles	Number per minute	Percent deviation from the mean rate
10	1431	143.1	−0.56
10	1441	144.1	+0.14
10	1450	145.0	+1.10
10	1403	140.3	−2.50
10	1475	147.5	+2.50
10	1436	143.6	−0.21
		Mean: 143.9	

The statistical error of the average count (1.77 percent) is larger than the mean of the absolute values of the observed deviations from the mean rate (1.17 percent).

X-ray and gamma-ray counters

Photoelectric counters may be used for detecting and measuring faint x-rays and γ-rays, without modification of form. A series of experiments, described in a previous note,[23] were done with a tin-cathode counter used in that capacity. The sensitivity of the apparatus was calculated for each arrangement, in terms of the minimum amount of radium, in equilibrium with its decay products, that could be detected by its γ-ray emission.

Shielding against stray radiation is facilitated by the smallness of the electrodes; the small external dimensions of the detector also allow it to be brought close to the source. It is, of course, very desirable to use a cathode with a low dark-rate, such as that used in the α-particle counter. Selection of the material and aperture of the window depends on the purpose for which the counter is to be employed.

Wire-cathode counters

The wire electrode may be used as the photoelectric element of the counter by reversing the direction of the electric field. Some interesting results were obtained with a cathode of tungsten wire, in the presence of vapors of certain organic liquids. These were coated on the cylinder electrode, or thinly on the wire itself. Ethyl chloride, ethyl alcohol, ether, methyl alcohol, and especially nitrobenzene, increased the sensitivity for ultraviolet light by a factor of 1.5 to 3. The effect seems to be due to the presence of *vapor* of the substance in the vicinity of the wire, or on its surface. Sensitizing agents did not appreciably increase the sensitivity of the counter for γ-rays, so their action appears to be a reduction of the photoelectric work function of the surface.

Diethyl-aniline vapor caused an unusually great increase, estimated to be 25 times the original sensitivity! This occurred when the liquid was coated on either electrode, only a trace being required for the purpose. This counter maintained its high sensitivity and low dark-rate for 10 hours; at that time it was dismantled. After treatment, the photoelectric threshold was roughly 3000A, but the matter of a shift due to introduction of the vapor was not examined. It was found that this sensitizer also extended the range of air pressures at which the tube could be operated successfully. The characteristics were about the same at 14 cm as at 0.5 cm, with suitable voltage adjustment.

Water vapor increased the photoelectric sensitivity of the wire nearly as much as diethyl-aniline did. But the water had to be introduced in a much larger quantity, so that it presently spread over the interior of the tube, decreasing the resistance and greatly increasing the rate of spurious counting

These incomplete experiments with reversed fields were among the first tried with photoelectric counters, so that good technique and auxiliary ap-

[23] G. L. Locher, Phys. Rev. **40**, 884 (1932).

paratus were not yet developed. But the results suffice to show that very high sensitivity may be reached with counters having sensitized wire cathodes. Obvious extensions of the work would include the use of thoriated tungsten and oxide-coated wires, and quantitative tests of the sensitizing effects of many other substances, both with these counters and normal photoelectric ones. Organic liquids have not yet been tried on the cathodes of the latter.

Since the wire-cathode counters have active surfaces that are very narrow, they might easily be applied to the measurement of faint spectral lines.

VIII. Discussion

Sensitivity for counting electrons

We may establish certain criteria for determining the useful electron-counting sensitivity of a photoelectric counter, without knowing the magnitude of the quantum efficiency of its photoelectric surface. The total useful sensitivity is taken as the intensity of light that causes the smallest increment in the counting rate that can be detected with certainty. An increment is regarded as "detected with certainty" when it exceeds the statistical error of the count by a pre-determined amount. It is further stipulated that the results be capable of reproduction, within pre-assigned limits of error, under identical experimental conditions.

The useful sensitivity evidently improves with extension of the time of the observation, for the relative statistical error of the count diminishes as the number of electrons recorded increases. It will also be best for a counter with a small dark-rate, for reasons set forth in section I of this paper.

Considerations of the limiting sensitivity are only important when the count is small, either due to shortness of the interval over which the observation is made, or to extreme feebleness of the radiation measured. But since the most important applications of photoelectric counters are apt to be for measurement of faint radiation, it is desirable to consider the factors that limit their sensitivity for counting electrons, in addition to the limitation imposed by the quantum efficiency of the photoelectric surface.

As an illustrative example, consider a typical counter for which the dark-rate is 1.50 ± 0.106 per minute, as determined by a one-hour observation. When exposed to a particular faint source of light for an hour, suppose the total count is 120. Of these impulses, 90 ± 6.36 are due to accidental causes, while 30 ± 3.67 result from the light. Under such conditions, it is evidently possible to detect less than one-half photoelectron per minute, with certainty. But if the same apparatus is run for only 5 minutes, and if the total count is 10, the corresponding distribution would be 7.5 ± 1.84 due to accidental causes, and 2.5 ± 1.06 due to the light. And if we take the minus sign with the latter rate, the increment due to the light is smaller than the statistical fluctuation of the dark-rate, so the light could not be detected with certainty, in 5 minutes. Similarly, if the counter had a dark-rate of 60 ± 0.67 per minute (instead of 1.50 ± 0.106), an increase of 30 ± 3.67 impulses per hour could not be detected by means of a 1-hour observation.

The foregoing discussion applies as well to counters for measuring other feeble ionic emissions, as to photoelectric ones. Moreover, S. Smith[24] has pointed out that very similar conditions obtain in the measurement of very faint light with a photoelectric cell and electrometer, when the dark-current of the cell, (>30 electrons per second) is comparable with the additional current due to the light.

In cases where the light to be measured can be concentrated on the counter cathode, the total useful sensitivity increases as the size of the cathode diminishes. But if the light cannot be conveniently concentrated, an important question arises: Does the useful sensitivity increase with the size of the cathode, and if so, within what limits? To answer this, one must recall that both the accidental count and the number of desirable photoelectrons increase with the area of the electrode, and that there is an upper limit to the speed of counting, imposed by the time required by the counter and recording apparatus to recover from each previous impulse (i.e., by the time resolving-power). The matter can probably be best settled by experiment.

Limitations of photoelectric counters

The following are believed to be the four chief limitations of photoelectric counters, which affect their use for quantitative measurement. The relative significance of each obviously depends on the specific application of the counter.

(a) The maximum intensity of light that can be measured is restricted by the speed at which the photoelectrons can be counted. Pending further developments of impulse recorders, the safe counting speed can hardly exceed 300 or 400 electrons per second; yet photocurrents of such low orders (5×10^{-17} ampere) are measurable only with great difficulty in other types of instrument. Higher intensities can, of course, be measured with the counters by using smaller cathodes, or by diminishing the area exposed, until the rate comes within the permissible limit.

(b) A very constant source of high potential is required. Otherwise, the sensitivity is apt to vary as the potential moves across the voltage plateau. The permissible variation depends on the requirements of the work, and on the width and slope of the plateau of the counter used.

(c) Accurate measurements of very small intensities require extended observations. This characteristic is shared in common with all other devices for measuring phenomena that are subject to statistical fluctuations.

(d) The spectral distribution of response may change as the counter is used. The existence and magnitude of this effect depend on the kind of gas used, the kind of cathode surface, and the intensity of ionic bombardment of the cathode. Gas-filled photoelectric cells sometimes show similar changes.[25]

It is believed that photoelectric counters will not only provide powerful means of measuring faint radiation, but also of studying a variety of photoelectric phenomena, such as the photoelectric properties of non-metals,

[24] S. Smith, manuscript not yet published.

[25] N. R. Campbell and D. Ritchie, *Photoelectric Cells* (Sir Isaac Pitman and Sons, 1929).

gases, and compounds, the feeble electron emission of substances illuminated with light of very long wave-lengths, and the effects of sensitizers on photo-electric surfaces. They should also make possible investigations of ionic and light emissions accompanying physical and chemical changes and biological processes.[26]

The author wishes to thank Dr. Sinclair Smith for his valuable assistance in the early development of the counters, and for making available the facilities of the Mt. Wilson Observatory Laboratories, where the preliminary work was done. Later development was carried out at the Rice Institute, through the kindness of Professor H. A. Wilson, whose council is gratefully acknowledged. Dr. W. F. G. Swann has very kindly read the manuscript of this paper, and has made helpful suggestions concerning its contents.

[26] One form of the apparatus described in this paper was exhibited at the A.A.A.S. meeting, Dec. 28–31, 1931.

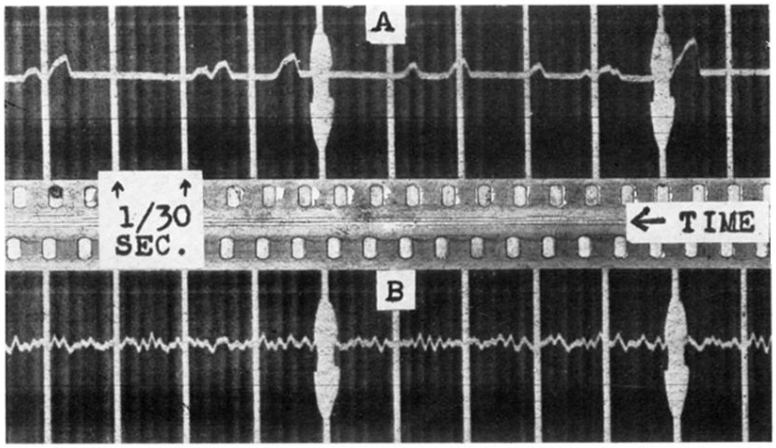

Fig. 3. Oscillograms showing rapid counting: *A*, about 30 per second; *B*, about 225 per second.