EFFICIENCY, STABILITY, AND CHARACTERISTICS OF PHOTOSENSITIVE G. M. COUNTERS

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This paper presents the results of investigations of photosensitive counters used in direct reading spectrometry.

Stable photosensitive counters constructed from metal with a cathode in the form of a strip set into the counter tube are described. The method used to measure the photoelectric efficiency is based on the known spectral distribution of an ultraviolet standard and the transmission of a UCП 22 spectrograph. Counters with a platinum cathode proved to be the most stable.

The variation of the photoelectric efficiency of G. M. counters was investigated. Three types of changes are discussed.

a) Initial changes leading to a stable photoelectric threshold and a stable photoelectric efficiency. In order to abtain this about 10^6 counts are necessary.

b) Reversible changes in efficiency of short duration are observed above a certain counting rate. These depend on the counting rate and the wave length, and occur with a certain delay.

c) Changes in the photoelectric efficiency connected with the ageing of the counter. These changes involve a slow increase in the efficiency and a shift of the photoelectric threshold in the direction of the longer waves. They were absent only in counters with a platinum cathode.

A relation between the slope of the characteristics for ultraviolet radiation and the photoelectric efficiency has been found: slopes between 5—55%/100 V correspond to efficiencies between 10^{-3} and 10^{-10}.

Introduction

One of the most sensitive detectors of ultraviolet radiation is a G. M. counter fitted with a quartz window. Although such counters have been known and used since 1930 and many investigations have been devoted to them, there has been no systematic analysis of their properties. The reason for this is mainly due to the fact that the photoelectric effect in the presence of gases and vapours is very complicated and, in many details, not quite clear. The mechanism of the operation of a G. M. counter has not yet been sufficiently investigated as regards the influence of the photoelectric effect on the processes occurring during the discharge.

One of the most important aspects of photosensitive counters which till now has not been satisfactorily explained is the question of the stability of the photoelectric efficiency. Karev and Rodionov (1935) tried to describe the connection between the photoelectric efficiency Y and the counting rate N by the relation $Y = A + B\sqrt{N}$, A and B being constants. These authors make no mention of the inertia of the changes in efficiency.

By changing the length of the slit in the monochromator providing the light for the counters, Duffendack and Moris (1942) found that up to a counting rate of 18000 cpm there is a linear dependance between the counting rate and the slit length. Katz (1954) also found that at low light intensities there is no relation between the photoelectric efficiency is independent of the counting rate for light quanta. In these three experiments non-selfquenching counters were used.

Neuert (1948) has investigated counters using cathodes sputtered with silver and magnesium. He found that the photoelectric efficiency of a counter of this type when irradiated by a gamma ray source increases by a factor of the order of 10 and subsequently, in about 10 minutes after the gamma source is removed, the efficiency returns to its former value. This effect has been investigated by Neuert only for a wavelength of 2650 Å.

It is a well-known fact that counters with mica windows and glass counters begin to respond to daylight from incandescent lamps (λ greater than 3000 Å) after having counted about 10^7 pulses. This matter is discussed in detail in the papers of Aron (1953) and Schwartz (1953).

Neuert has measured large changes of the photosensitivity but he has not observed any changes for counters with brass cathodes.

The present paper deals with cases in which the changes in efficiency were rather small.

Another important problem connected with photosensitive counters is the question of the differences between the photosensitive characteristics for ultraviolet light and the characteristics for gamma radiation. Locher (1932) and Christoph (1936) pointed out that a greater photoelectric efficiency can be obtained by using a strong electric field at the cathode.

This effect is caused by the back-diffusion of photoelectrons in the counter gas, which results in a considerable decrease in the probability that these electrons are caught by the electric field around the anode. The probability that a photoelectron will not return to the cathode increases with the electric field intensity E and decreases with the gas pressure in the counter p, i. e. it is proportional to $\sqrt{E/p}$. Christoph calculated that only about 10% of the photoelectrons do not return to the cathode. According to the most recent data (Theobald 1953 a and b) in pure argon, under counter conditions of pressure and electric field intensity, only 10 – 20 % of the photoelectrons do not return to the cathode. The probability of not coming back to the cathode increases with the decreasing energy of the photoelectron. At present there are no

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other accurate data concerning back-diffusion, in particular no measurements have been made for monochromatic radiation and for the filling mixtures used in G. M. counters.

Ito (1952), using a reduced hydrogen pressure in the counter, obtained a slight increase in the photoelectric efficiency.

Wilkinson (1948) drew attention to the fact that the beginning of the plateau of the characteristics for ultraviolet is about 150 V above threshold, whereas for gamma radiation this voltage difference is only about 70 V. Wilkinson presented a theory of this effect based on considerations of statistical fluctuations in the initial avalanches, which can check the development of the discharge. The probability of stopping the development of the discharge along the wire decreases when the discharge in the counter is initiated not by a single electron as in the photoeffect, but by several electrons produced by nuclear radiation.

The author performed systematic investigations on the problems described above and on the mechanism of counter operation. The aim of this work was, among others, the design of photosensitive counters for direct reading spectrometry. The results of studies on the mechanism of G. M. counters obtained by means of photosensitive counters are given in another paper (Ostrowski and Turek 1958).

2. *Apparatus*

The measurements were made on metal photosensitive counters with quartz windows, the construction of which has been described in several papers (Jurkiewicz et al. 1953, Ostrowski 1951, Buja et al. 1957). In Fig. 1 are shown two ways of mounting the quartz window by means of "Araldit" manufactured by the Ciba firm of Switzerland.

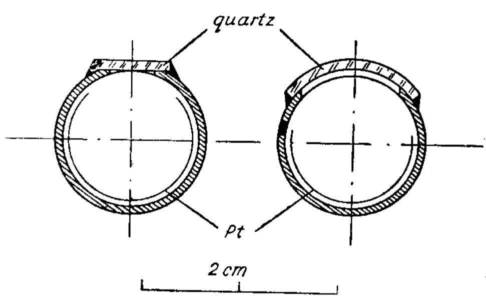

Fig. 1. Two methods of mounting quartz window to the copper tube of a G. M. counter

For the counter diameters used most frequently, outer dia. 16 mm, the maximum dimension of the windows were 10×40 mm^2. Usually windows measuring 5×20 mm^2 were used. The metal investigated had the shape of a bent springy strip. Its surface was cleaned with emery paper and washed with benzene. During soldering with a soft solder the counter was placed in a fixture in which running water was used to cool the window and the sample. About 80 counters were assembled, the majority having diameters of 16 mm. The counters were filled with an argon-alcohol mixture (120 mm Hg of argon and 12 mm Hg of ethyl alcohol). The counters used with gamma rays had a plateau length of 150 – 250 V, the slope of which was 1 – 5%/100 V. Counters with a platinum cathode had the smallest plateauslope. The counter background was 0.8 – 1 cpm/cm^2 in agreement with the value given by various authors (0.5 – 1.5 cpm/cm^2). For counters with an Au and Pt cathode, which have a greater gamma-ray efficiency, the background was 2 cpm/cm^2. Counters with platinum cathodes had an efficiency for gamma rays from radium 2.5 times greater than copper cathode counters.

The counters were tested at a counting rate of 200000 cpm at an overvoltage of 100 V. After such tests it was found that counters with Zn, Cd, Al and aluminium cathodes became unstable (i. e. they flashed over). Al cathode counters withstood a test with a counting rate of about 100000 cpm, whereas Zn and Cd cathode counters already were burned out at a rate of about 50000 cpm.

We can regard as stable, in the sense of this test, counters with cathodes of Ag, Au, C, Cu, Fe, Ni, Pt, brass, phosphor-bronze, copper-beryllium (2% of Be) and German new silver.

The instability of the first group of counters occurs together with a shift of the photoelectric threshold towards the longer wavelengths for a period of the order of one hour. Thus, e. g. the threshold of Al cathode counters, after counting about 3×10^5 pulses in a few minutes, shifts from 3200 Å to the visible region. After the counter is disconnected, the photoelectric threshold shifts back towards the smaller wavelengths. The instability and the changes of the photoelectric threshold should be considered as closely related to one another.

A special counter-box has been constructed to be used in the UCП 22 quartz spectrograph instead of a plate box. The displacement of the counter together with the exit slit was made by means of a micrometer screw at a distance of 18 cm, so that the accessible range of the spectrum was 2030—4500 Å. A medium-pressure mercury lamp with liquid electrodes and an "Original Hanau S 300" lamp with optical properties very similal to those of a standard ultraviolet source were used as light sources. The similar optical properties of these two lamps result from the nearly identical arc size in both. The lamp and the rate-meter used in the measurements took their power from a magnetic stabilizer.

3. The measurement of the quantum photoelectric efficiency of G. M. counters

The quantum photoelectric (or briefly, photoelectric) efficiency is defined as the ratio of the number of pulses produced in the counter by radiation of a given wavelength to the number of photons of this radiation falling on the cathode. Up till now thermopiles were used to determine the number of photons (Kreuchen 1935, Rodionov et al. 1955). This method has some disadvantages arising from the very large difference between the sensitivities of the counter and the thermopile. One is compelled to use absorbers, reducing the intensity by several orders of magnitude, which can be the source of large error.

Another method, based on calculations of the number of photons for a black body (Raich 1930, Katz 1954), has also been used. In this method one can obtain in practice only very low counting rates, and the measurements can be made, only for radiation of wavelength greater than 2600 Å.

In the present work the known spectrum of the ultraviolet standard lamp was used and the transmission of the spectrograph in the various ranges of the spectrum have been calculated. The measurements of the spectral distribution of the standard ultraviolet source were made by Rössler (1939, 1952) by means of a quartz photoelectric cell calibrated with a thermopile. In this case the difference in the sensitivities is not so important as in the case of a thermopile and a counter. The standard ultraviolet lamp is a medium-pressure mercury lamp and it is known that the deviations of the relative intensities for particular spectral lines do not exceed a factor of 2, despite the different parameters of these lamps such as length of arc and quartz tube diameter (Kern 1938, Sewing 1938, Meyer and Seitz 1947). Comparison with a standard source was of course made after reducing the intensity to the same input power (e. g. 100 W).

From the work of the above-mentioned authors it follows that when using, instead of a standard source, a lamp of similar properties one obtains intensities for particular spectral lines which do not differ by more than a factor of 2, and probably considerably less.

In the calculations of the spectrograph transmissivity one must take into consideration the radiation losses due to reflection from the quartz surfaces, the mirror surface of the aluminium collimator and also the absorption in the quartz. In order to neglect aperture losses the lamp should be placed at a sufficiently large distance from the entrance slit (in the present work this distance was 1.4 m) along the axis of the instrument. The region in which the mercury arc should be located can be determined experimentally by placing a strong lamp in the spectral

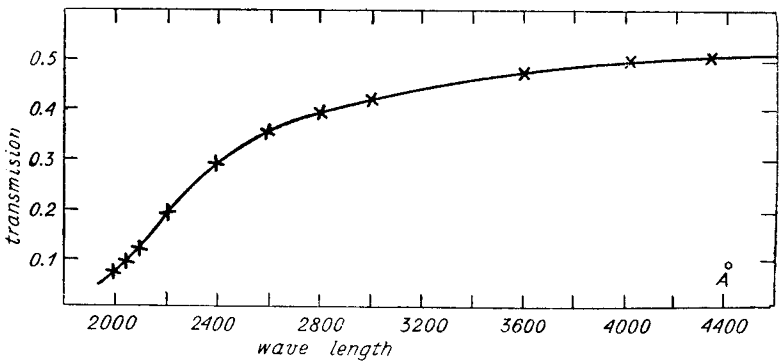

Fig. 2. Transimission of the UCП 22 spectrograph. The data for the reflection coefficient of the aluminized mirror of the collimator were taken from the Critical Tables (1950, Vol. VI) and the data on the absorption of quartz, from Koller (1936) as cited in the book of Mayer and Seitz "Ultraviolette Strahlung" (1949). The scattering (about 5%) was neglected

plane of the spectrograph and observing a light spot (rectangular with cut corners) on a screen mounted in place of the standard source. If we place the arc in this region, the radiation illuminating the slit will not illuminate any surface inside the spectrograph besides the surface of the lens and the collimator mirror. By using a wide enough slit we can avoid losses due to diffraction at the slit. The results of calculations of the spectrograph transmission are given in Fig. 2.

It is possible to de termine the transmission if we use two monochromators, so that the exit slit of the first is the entrance slit of the second. In this method we place the detector first behind the common slit and then behind the exit slit. Practically speaking, this is a very difficult procedure because of the necessity of avoiding light losses due to the aperture. The results obtained by various authors (Katz 1954) for the two-monochromator method and for the transmission calculations are in agreement as regards the order of magnitude; differences of from 7 to 60 percent were noted in the various cases.

It should be expected that the theoretical values should be greater than the actual transmission, owing to the scattering loss, which is taken as 5% for 10 layers (Angerer 1956 p. 261).

The quantum efficiency of a photosensitive counter for the standard ultraviolet lamp at a distance of 1 m from the slit, is given by:

$$Y = \frac{|N - N_{B\lambda}| \cdot h\nu}{k \cdot O_{L\lambda} \cdot S} \tag{1}$$

where N denotes the counting rate (in cpm) of photons corresponding to a given spectral line together with the background due to the continuous spectrum and natural background:

$N_{B\lambda}$ is the background due to the continuous spectrum and to the counters' own background.

k is the spectrograph transmission.

$O_{L\lambda}$ is the illumination in erg/cm^2 sec of the radiation corresponding to the particular ultraviolet standard spectral line at a distance of 1 m.

S is the area of the entrance slit (in the present experiments $0.2 \times \times 0.0050$ cm^2).

Thus $O_{L\lambda} \cdot S/h\nu$ is the number of photons entering the entrance slit in one second.

For wavelengths below 2300 Å no mercury lines were measured and we are obliged to use the continuous spectrum, the formula for which is similar to (1), namely:

$$Y = \frac{|N_{B\lambda} - N_B| \cdot h\nu}{k \cdot O_{B\lambda} \cdot S} \tag{2}$$

where N_B is the counters' own background,

$O_{B\lambda}$ is equal to $o_{B\lambda} \cdot z \cdot d_2/\sin \alpha$,

where $o_{B\lambda}$ denotes the illumination in erg/cm^{2}sec by radiation of wavelength λ from the continuous spectrum of the standard source, at distance of 1 m,

z is the dispersion in Å/mm,

d_2 is the exit slit width in mm (0.2 mm),

α is the angle between the axis and ta spectral plane.

Since plane of the entrance slit is nearly perpendicular to the direction of the light (but not parallel to the spectral surface), it subtends a wavelength interval of $z \cdot d_2/\sin \alpha$ and $k \cdot O_{B\lambda} \cdot S$ is the power corresponding to the spectral interval subtended by the exit slit.

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If we use another mercury lamp at a distance of metres from the slit, we must multiply formulae (1) and (2) by $M_n \cdot a^2/M$, where M_n is the power of the standard lamp (250 W), M — the power of the mercury lamp which was enployed.

From formulae (1) and (2) and from the results of Rössler the author prepared tables (for the line spectrum) and a graph (for the continuous spectrum) which permitted direct readings of the photoelectric efficiency for a given wavelength from the rate-meter readings. Over a period of several years the apparatus gave readings that were reproducible within the limits of 30%.

The error was probably due to the mercury lamp with liquid electrodes, since the distribution of the mercury in the lamp was presumably random.

The photoelectric efficiency obtained from the continuous spectrum was compared with that from the line spectrum. The both efficiency obtained from the platinum cathode counter was in good agreement. (The difference being smaller than 50%). Since the discrepancies between the results of various authors are rather great (several orders of magnitude) such an error should be regarded as sufficiently small.

Recently, the results obtained with a mercury lamp S 300 (Original Hanau) were compared with those obtained earlier, and the results were found to be in agreement. As already noted, the properties of the S 300 lamp are very similar to those of a standard ultraviolet lamp.

It should be remarked that the published comparisons of mercury lamps were made only for the spectral lines. The agreement between the efficiencies obtained for both the continuous and the line spectra in the 2300 – 3000 Å range allows one to suppose that below 2300 Å one can also use the continuous spectrum to determine the photoelectric efficiency. Nevertheless, the deviation from the real values in the vicinity of 2050 Å may be greater than that in the 2300 – 3000 Å range. The cut-off in the measurements in the proximity of 2050 Å is due to the end of the continuous spectrum of mercury.

4. *Results of the photoelectric efficiency measurements*

Fig. 3 shows the most typical variations of the photoelectric efficiency with wavelength for various metals.

Counters with copper cathodes:

The efficiency of the copper cathode counter shown in Fig. 3 was obtained after cleaning the cathode with emery paper. For the uncleaned cathodes the efficiency is about 30% of the value given in the figure.

The reproducibility of the efficiency for various counter samples prepared under identical conditions is expressed by a factor of 2 for wavelengths below 2300 Å. The use of various tubes and copper cathode elements of different origin did not result in any essential differences. The photoelectric threshold, taken as the maximum wavelength of the mercury line spectrum for which the counting rate is at least 100 cpm

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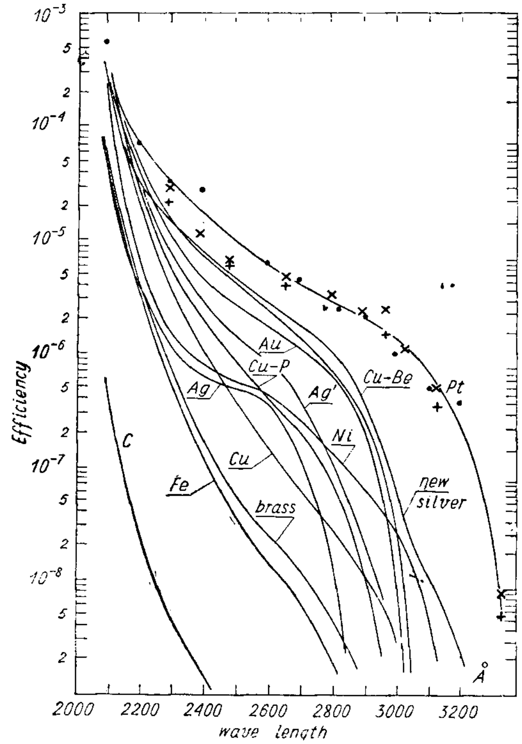

Fig. 3. Results of the efficiency measurements of counters with different cathodes. A typical example was chosen for each sample. In the case of platinum the results for the same counter from May 1955 are denoted by the „+" sign; from May 1956, by the „×" sign. The measurements from May 1956 for the continuous spectrum of a mercury lamp are denoted by „•"

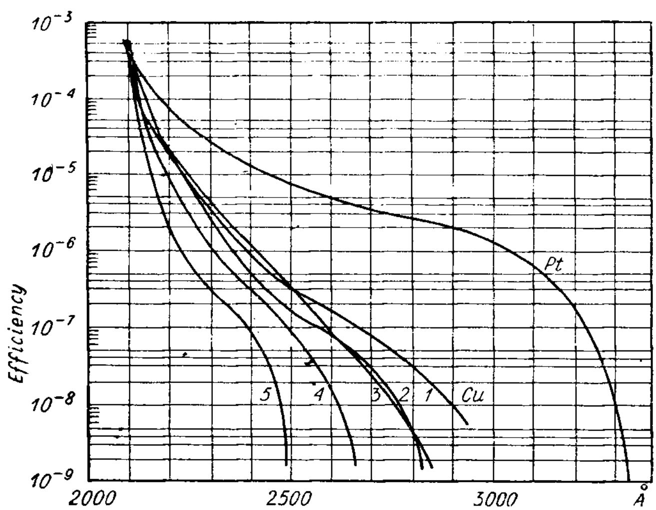

Fig. 4. Comparison of the efficiencies of different counter samples with copper cathodes

in a given geometry was found to be within the limits of 2399 – 2965 Å for copper cathode counters. The lack of a sufficient number of mercury lines did not allow this threshold to be determined more accurately.

Fig. 4 illustrates the differences in efficiency for various counter designs. Counter No 5, was tightly sealed by "Araldit", and then heated at a temperature of 150°C for five hours in an atmosphere of air.

Counters with brass and iron cathodes.

Brass and iron cathode counters have a photoelectric efficiency distribution similar to that of the copper cathode counters, but the efficiencies are only about 20% of that measured for the copper cathodes.

The reproducibility of the measurements was somewhat better than in the case of copper counters.

Counters with cathodes from the alloy Cu + 2% Be -alloy.

The interest in this alloy is connected with the fact that it is used as a material for electrodes in photomultipliers. The photoelectric efficiency of these counters was in some cases higher than that of copper cathode counters, even by a factor of 100 (for 2800 Å), but unfortunataly the reproducibility was not satisfactory especially above 2400 Å (e. g. by a factor of 10 or even more). The reason for this lack of reproducibility is probably connected with processes analogous to those which are encountered in the activation of photomultipliers with Cu + Be -electrodes. This activation involves oxygen treatment at a high temperature.

Counters with platinum cathodes.

Counters with platinum cathodes and platinum iridium (2% Ir) cathodes have several very important properties in comparison with the other counters. These counters had a higher sensitivity in the measurements described here at least in the spectral range below 3200 Å. The reproducibility of the efficiencies in this case was rather good. Also the reproducibility of the threshold was the best for all types of counters investigated. Since the threshold is about 3500 Å it can be determined rather accurately by investigating the radiation from an incandescent lamp, the slit of the spectrograph and the counter being set wider. The slope of the characteristics of these counters for gamma rays is, as a rule, lower than 1%/100 V. In the first period after filling, changes in the Geiger threshold were observed to be greater than those in other counters. No satisfactory interpretation of this phenomenon was found.

Counters with German silver cathodes (Cu + Ni + Zn).

The photoelectric efficiency of these counters is only a few times smaller than that of platinum counters. This case shows the possibility of finding cheap alloys having good photoelectric efficiencies. The reproducibility of the efficiency was similar to that of the platinum cathode counters.

Counters with cathodes made of silver, gold (22 carat), nickel and phosphor-bronze.

In certain wavelength intervals counters of these materials show an efficiency slightly greater than that of copper counters. The greatest efficiency was found for a gold cathode counter. Silver (Ag) and nickel coatings were obtained by electrolytical plating. The symbol Ag' in Fig. 3 refers to a cathode made from a strip of chemically pure silver.

For other metals as aluminium, zinc, cadmium, lead, and tantalum no interesting results were obtained, i. e. their photoelectric efficiencies were in general much lower than those of the copper cathode counters, especially below 2400 Å.

Counters with cathodes of aluminium, zinc and cadmium were unstable.

Carbon cathode counters.

Carbon cathodes were obtained by evaporating India ink onto a copper strip. In the wavelength region above 2030 Å the efficiency of this counter did not exceed 2% of a copper cathode counter. It was observed that in this case the sensitivity was associated with the copper itself and not with the carbon, i. e. a small part (2%) of the radiation is reflected by the area coated with India ink towards the uncoated copper, thus giving rise to the effect mentioned above.

India ink coating of the interior of counters has been successfully used in our laboratory to improve the stability of duraluminium beta-ray counters and of large aluminium cosmic ray counters.

5. *Comparison of the efficiency measurements with the results of other experiments*

The quantum photoelectric efficiency of photosensitive G. M. counters was determined in only a few cases. The measurements of Kreuchen (1935 a and b) and Rodionov et al. (1955) seem to be the most accurate. Kreuchen obtained the best results for zinc. This material, however, is not suitable for G. M. counters because of the instability of zinc cathode counters, especially at high counting rates. Almost the same photoelectric efficiency as that obtained by Kreuchen can be obtained for platinum cathode counters and with satisfactory stability.

Rodionov et al. investigated counters with platinum cathodes coated by sputtering. These counters were filled with an argon-methyl mixture. The photoelectric efficiency of these counters below 2600 Å is comparable to the efficiency of the platinum counters described in the present paper, but for longer wavelengths it is lower (e. g. by 2 orders of magnitude at 3100 Å). The reproducibility of the threshold and of the efficiency given in the paper of Rodionov is smaller than that observed by the author (for about 35 cases). This might possibly be connected with the "maturing" effect described in 6*a*.

It is worthwhile to call attention to the paper of Katz (1954), who, in the interval 2600 – 3200 Å, obtained for non-self quenching counters with sputtered platinum

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cathodes efficiences 30—50 times greater than those observed by the author. The counters designed by Katz have a plateau of only about 50 V. Similarly, Labeyrie (1951) obtained an efficiency of the order of 10^{-3} in the sensitivity maximum at 2500 Å, for his counters with sputtered platinite (a Fe—Ni alloy with small additions of other metals). These counters were stable and had a good plateau. The efficiencies obtained by Katz and Labeyrie seem to be rather too high.

The photoelectric efficiency of the metal, and especially the work function in vacuum after heating, have no simple connection with the corresponding quanties for counters containing gaseous mixtures. Gases soluble in metals have a strong influence on the photoelectric efficiency and on the work function.

Platinum is a typical example; its photoelectric threshold in vacuum (2350 Å) does not seem to encourage its use in photosensitive counters, while from the experiments described above, it follows that it is a suitable material for photo cathodes. This is probably connected with hydrogen ions being in solution with the cathode material. Another example is provided by the results of Eremin (1956) who obtained for polished magnesium and aluminium a threshold at 7300 Å, where the counters showed a good photoelectric efficiency stability for several years, when a low counting rate was maintained. A change in the photoelectric threshold produced by the adsorption of gases, is probably the reason for the different behaviour of some metals under conditions of high vacuum and under conditions met inside a counter.

6. Three types of changes in photoelectric efficiency

In the group of stable counters three fundamental types of efficiency changes may be distinguished:

a) "Maturing" of of the counter.

b) reversible changes of short duration connected with the process of counting.

c) changes connected with the ageing of the counters during its operation.

We shall now consider each of these changes in the photoelectric efficiency.

a) "Maturing" of the counter.

In order to stabilize the spectral distribution of the efficiency and the photoelectric threshold of a new counter, or one which has not been used for a certain period, e. g., a month or more, it is necessary to count a certain number of pulses. For counters with the internal diameter of 13 mm this stabilizing number of pulses is about $(5 - 10 \times 10^5$ at an overvoltage of about 100 V. If the counter was "matured" previously, then the required number of pulses is much smaller e. g. by one order of magnitude. Fig. 5 illustrates the results obtained for a platinum cathode counter. A definition of the photoelectric threshold entails basic difficulties, since the description of the changes in the threshold are necessarily of approximate character. A certain indeterminacy of the photoelectric threshold occurring in vacuum is connected with the thermal motion. If the adsorbed substance has a definite potential barrier, then the indeterminacy of the photoelectric threshold will be further increased when the tunnel effect is taken into account. The „maturing" of the counter in the sense mentioned above is accompanied by a number of other changes (which can, at least partially, be reduced to photoelectric changes), such as the change in the slope of the characteristic, the increase in the plateau-length, the decrease in the length of the segment of the characteristic between the threshold and the beginning of the plateau.

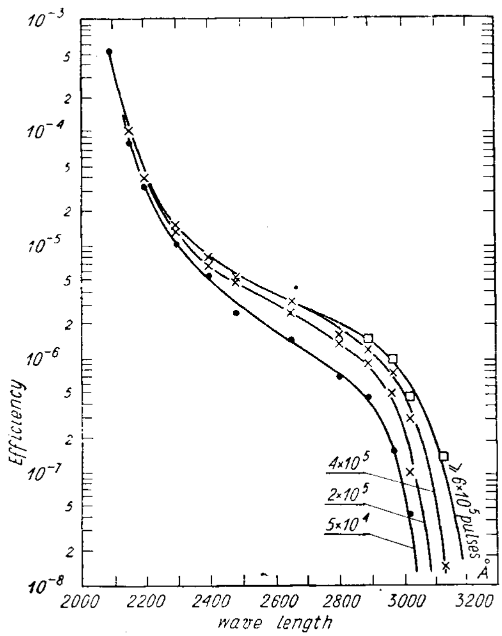

Fig. 5. Initial changes in the efficiency of a platinum cathode counter. After 6×10^5 counts at an overvoltage of 100 V no further changes were observed

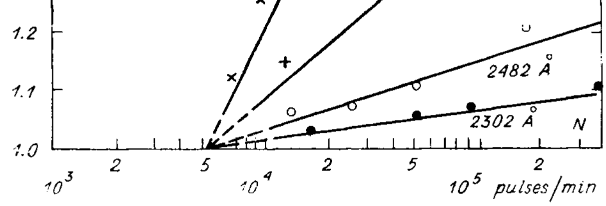

Fig. 6. Plot of efficiency *vs* counting rate (in a state of equilibrium). The counter illustrated had a copper-berilium cathode (2% Be), internal diameter of 13 mm, overvoltage of 100 V. Measurement error about 3%

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b) Reversible changes of short duration connected with the process of counting.

If we measure the photoelectric efficiency of a counter at a low counting rate for a definite wavelength and if by bringing the gamma ray source closer to the counter, we increase the counting rate, e. g. to 50000 cpm for a few minutes, we observe, after removing the gamma-ray source, an increase in the photoelectric efficiency, e. g. by several percent. Changes greater than 5% have actually been measured.

Investigations have disclosed some regularity in this effect. This is illustrated in Fig. 6. It was found that measurable changes of the photoelectric efficiency can be obtained only if a certain critical counting rate N_0 is exceeded. Let us denote the photoelectric efficiency of a counter below this critical value by Y_0, and the efficiency at a given counting rate N by $Y_r(N)$. This efficiency automatically remains constant if the counting rate remains constant. The time sufficient for this is about 1 min. The efficiency measurement was made very rapidly (several seconds) at a low counting rate. In Fig. 6 is plotted the ratio Y_r/Y_0 *vs* the counting rate N, for different wavelengths. We see that the counting rate at which the above-mentioned increase in efficiency begins is independent of the wavelength of the radiation for which we are measuring the efficiency. Also, no relation was found between N_0 and the cathode material. No difference was observed for the two different filling mixtures (argon-alcohol, and argon-methylal) used in the work, although these last measurements obviously could not be very accurate. It was established that N_0 is at least approximately proportional to the counter diameter and inversely proportional to the overvoltage.

The following formula has been taken as an empirical working formula giving sufficient agreement with the observed data

$$Y_r(N) = Y_0 \left[1 + A \log \frac{N}{N_0} \right] \tag{3}$$

The index r refers to the efficiency at "equilibrium". This formula is presumably not the only one which can describe the phenomenon. The introduction of the constant A is convenient, since it characterizes quantitatively the increase of the efficiency with the counting rate.

Fig. 7 gives the slopes of Y_r/Y_0 *vs* N curves for the values of the constants A in formula (3) for various wavelengths and materials used as counter cathodes.

After removal of the radioactive source the photoelectric efficiency decreases. This decrease can be measured e. g. every 10 seconds for a period of one second, if we use the 0.5 sec time constant of the rate meter, by momentarily uncovering the window of the counter. It was found that $Y - Y_0$ decreases exponentially with time. The time after which the efficiency Y drops to the arithmetic mean of the values Y and Y_0 is independent of the wavelength, the cathode material, and the counting rate. For argon-alcohol mixtures it is 1.5 ± 0.2 min and for argon-methylal mixtures, 2.5 min.

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For aluminium cathode counters, another time equal to (7 ± 2) min has been found, in addition to the value 1.5 min mentioned before. In this last case the measurements were performed for 4350 Å and 3650 Å, i. e. for wavelengths for which the photoelectric efficiency is initially too small to be measured ($< 10^{-12}$). In the case of unstable counters, such as those with aluminium cathodes, we can consider the whole phenomenon as a case with a variable Y_0 and a half-life of 7 min.

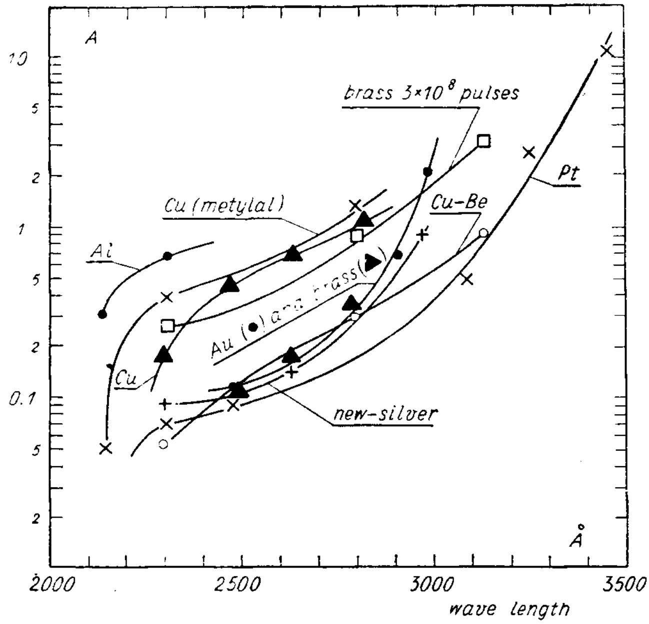

Fig. 7. Variation of the constant A as defined by Eq. 3 with wavelength. As may be seen, the values of A for the platinum cathode are the most advantageous. The least favourable are the values for an aluminium cathode. It should be noted that a small addition of Be to the copper is advantageous

As already mentioned the decrease of the efficiency $Y - Y_0$ can be considered as exponential. Since the whole increase of the induced photoelectric efficiency does not last longer than 1.5 min there are experimental difficulties in investigating the nature of this increase. Let us consider as an example the data in Table 1, which gives the time in secs. required to reach the value $Y_r + Y_0/2$, starting from Y_0. N_r is the counting rate after attaining equilibrium. The counter used in this test had a platinum cathode.

Table 1

$\lambda \backslash N_r$	3×10^4 cpm	5×10^4 cpm	10^5 cpm
2399	15	10	—
2965	20	16	14
3120	40	24	18

As may be seen, the smaller the wavelength of the radiation used in the experiment and the higher the counting rate, the faster do we approach equilibrium.

The greatest changes in the photoelectric efficiency can be determined in the following way. If N' is the initial counting rate at which the photoelectric efficiency for some monochromatic illumination is Y_0, the following relation expressing the proportionality of the efficiency and the counting rate holds:

$$Y/Y_0 = N/N' \tag{4}$$

where Y is the actual efficiency at the counting rate N (line b, Fig. 8).

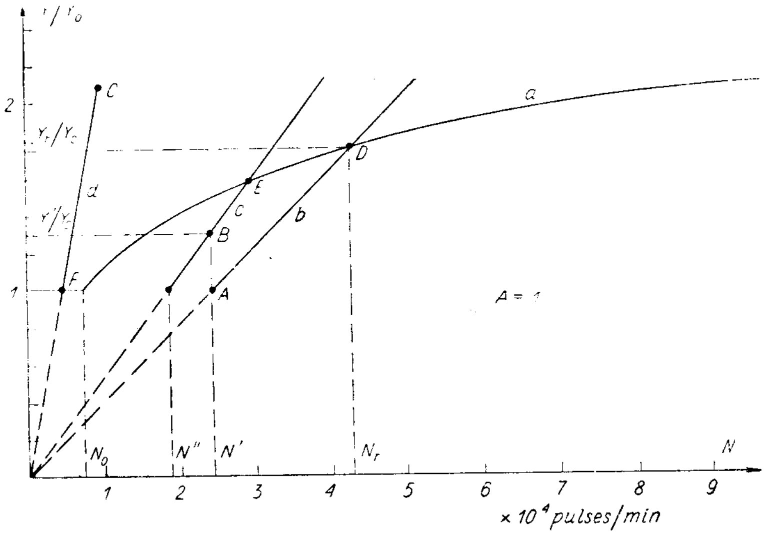

Fig. 8. Changes in photoelectric efficiency: a — equilibrium curve (Eq. 3), b, c, d — line, along which the change in efficiency takes place in the case of monochromatic illumination; A, B, C — sample initial points; D, E, F — final points of equilibrium.

The intersection of line b with the equilibrium curve (equation 3, curve a), is the final equilibrium point (N_r, Y_r). Eliminating Y_r/Y_0 from equations 3 and 4 by the method of successive approximations, we obtain N_r as a function of N'/N_0.

If, in general, the photoelectric efficiency Y' corresponds to the initial counting rate N' i. e. if we proceed from an arbitrary point B on Fig. 8, then from the equation

$$Y'/Y_0 = N'/N'' \tag{5}$$

we can obtain a value N'', which corresponds to the efficiency Y_0 (line c, Fig. 8). Starting from the counting rate N'' with the efficiency Y_0, we pass through point B with the coordinates N', Y'/Y_0. This counting rate N'' can be called the reduced counting rate.

Fig. 9 shows the results of the N_r calculations. The abscissa axis gives the deviations of the N_r — values from the reduced counting rate N'' in %. The ordinates are the values of the ratio N''/N_0, i. e. $N' \cdot Y_0/N_0 \cdot Y'$.

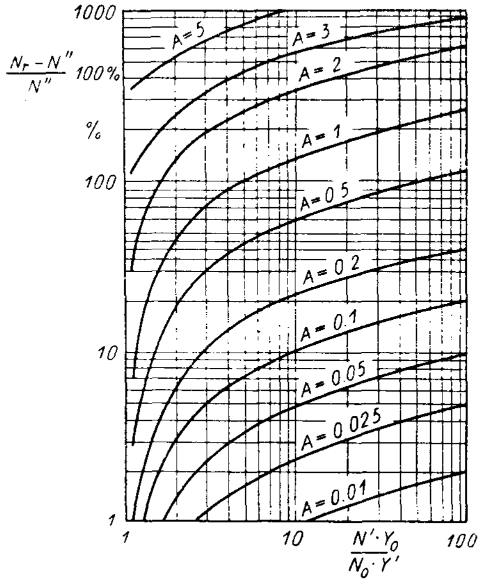

Fig. 9. Changes in counting rate $\frac{N_r - N''}{N''}$ as a function of $\frac{N' \cdot Y_0}{N_0 \cdot Y'}$, where N' is the initial counting rate at efficiency Y' and N'' ist the "reduced" counting rate

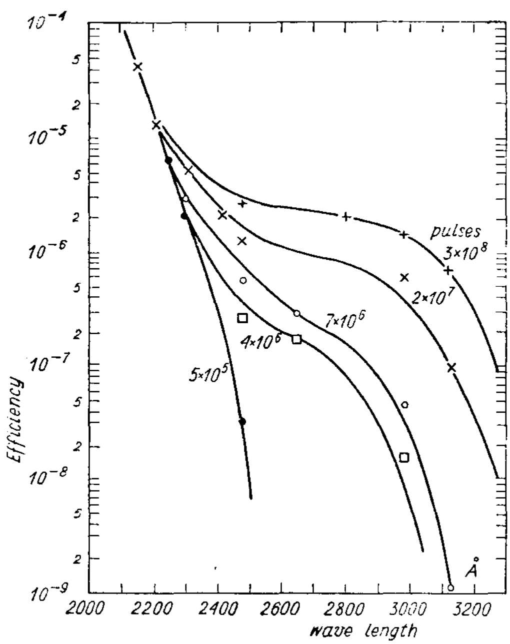

Fig. 10. Changes in the photoelectric efficiency of a brass cathode counter as a function of the wavelength and age of the counter. The counter counted 100000 cpm at an overvoltage of 100 V

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From this plot we can determine the maximum error expected in using counters for spectral analysis, if the abscissae are greater than 1. The corrections for the dead time must be made separately. For the abscissa $N' \cdot Y_0/N_0 \cdot Y' \leqslant 1$ (line d, Fig. 8) we obtain directly $N_r = N''$, and therefore

$$N_r = \frac{N'Y_0}{Y'} \quad \text{or} \quad \frac{N_r - N'}{N'} = \frac{Y_0 - Y'}{Y'} = \frac{Y_0}{Y'} - 1 \tag{6}$$

The decrease in the efficiency in the region above the curve expressed by equation 3 gives a different counting rate than the decrease along the line $N = 0$. The half-times for the decay of $Y - Y$ are very difficult to measure more accurately. These values are somewhat greater than those in Table 1, but distinctly less than 1.5 min. It is to be expected that if the decrease in the efficiency takes place at small values of N (in comparison with N_0) we obtain times close to 1.5 min.

The constant A increases with wavelength (Fig. 7). Platinum cathode counters have the most advantageous, i. e. the smallest, dependence of A on the wavelength. These counters have the lowest values of the A at the highest efficiency. It should be emphasized that the last point of the measurements for platinum cathode counters is only about 40 Å from the photoelectric threshold (3500 Å). The threshold in that case can be relatively easily determined by means of light from an incandescent lamp illuminating the spectrograph slit.

A platinum cathode counter responds to daylight with a continuous increase of the counting rate up to the limit of its possibility (about 10^6 cpm). This effect is not an instability in the usual sence, because its response to gamma radiation or monochromatic radiation not too close to the threshold is quite normal. The response to continuous radiation in the vicinity of the threshold is in agreement with the relations given above (large values of A).

c) Changes in the efficiency and the constant A with the ageing of the counter.

The dependance of the efficiency of a brass counter upon the life-time, expressed in terms of the total number of counted pulses is presented in Fig. 10.

For metals other than platinum the efficiency changes are very similar. The following characteristics have been observed:

1. Changes in the photoelectric efficiency are not observable within the limits of the experimental error (about 20%) for wavelengths smaller than 2200 Å.

2. The photoelectric efficiency changes strongly during the first 2×10^7 counts and the photoelectric threshold shifts to a region where the glass and the mica are partly transparent (3000 Å). This is the reason for the sensitivity of window counters to "light".

3. The maximum photoelectric efficiency for radiation below 3100 Å obtained in all cases investigated (Cu, Ag and brass) is approximately the same and is several times smaller than that found for platinum counters. The region below 3100 Å could not be systematically investigated because of the lack of a sufficient number of spec-

tral lines of mercury and because of difficulties in the experiment for this region. It was established only that the photoelectric threshold drifts towards the visible region as the counter ages and that the photoelectric efficiency attained for this spectral region is small (of the order of 10^{-9}).

4. The constant A defined by Eq (3), which in a measure of the increase in efficiency with the logarithm of the counting rate, increases strongly with the age of the counter, e. g. by a factor of 10. No such changes were observed for counters with platinum cathodes.

7. *Comparison of the results of the investigation of efficiency stability with the results of other workers.*

The similarity between the Rodionov formula given in the introduction and formula (3) seems to be coincidental, since at the counting rates used by these authors there should not be any change in the photoelectric efficiency (Duffendack and Moris 1942, Katz 1954).

The results of Neuert (1948) indicate large changes in efficiency. One may determine from Neuert's data the half-life of the quantity $Y-Y_0$. This time is about 2 minutes. The value determined in this manner is in agreement with the value given in the present work (2.5 min for methylal). It seems that the counters with sputtered cathodes used by Neuert have a greater factor A than the counters used in the work of the author with massive cathodes or obtained by electrolytic methods (Ni, Ag). It would therefore be of value to compare sensitivity and stability of these two types of counters. The results of the work of Lauterjung (1947) on the regularity of the excitation and decay of efficiency concerns, we suppose, unstable counters, where these phenomena are still very complicated. The decay time for the difference of the order of 10 minutes is in agreement with the results of the present work for aluminium.

One would expect to increase N_0 and decrease the factor A by using a fast quenching pulse (Picard and Rogoziński 1954).

8. *Counter characteristic for ultraviolet radiation*

The systematic investigations of the characteristics of photosensitive counters gave some new results on the existence of a relation between the photoelectric sensitivity and the slope of the characteristic.

a) Beginning of the plateau.

Fig. 11 gives the characteristic of a photosensitive counter of 13 mm internal diameter with a platinum cathode. As may be seen, for gamma rays it is sufficient to raise the operating voltage of the counter by about 20 V above the threshold of the equipment (with sensitivity of 0.2 V) in order to attain the beginning of the plateau. For ultraviolet radiation the corresponding increase in voltage is about 50—70 V. An unmatured counter requires for gamma rays 2—3 times greater overvoltage in comparison with a "matured" counter. This probably accounts for the difference between the results of Wilkinson and those of the author (see Introduction).

b) Slope of the characteristic.

The slope of the characteristic for a collimated gamma beam directed perpendicular to the counter axis is dependent on the point of incidence in the counter. In the case that the beam passes through the central part of the counter the slope of the characteristic is constant and is the smallest. This slope can differ from the slope of

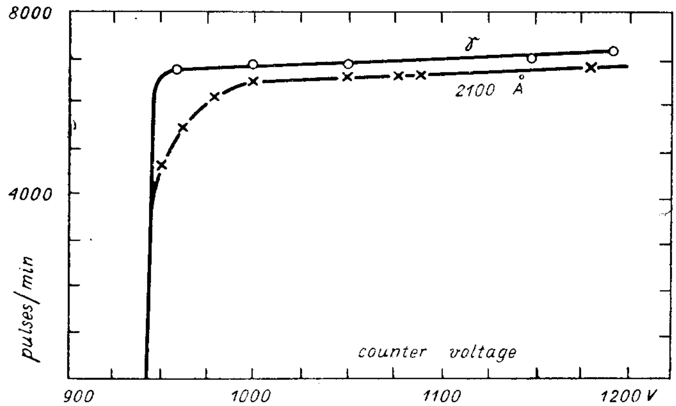

Fig. 11. Characteristic of a platinum cathode counter for gamma rays and ultraviolet radiation. The basic difference occurs at the beginning of the characteristic

the same counter irradiated by an uncollimated gamma beam by several percent, especially in the case of counters of small active length.

The slope of the characteristic measured with a collimated gamma beam is a measure of the number of spurious pulses, which depend on the voltage. The geometrical factor is eliminated in this way of irradiation.

The measurement of the slope of the characteristic of G. M. counters for ultraviolet radiation entails some difficulties connected with changes in the photoelectric efficiency during operation.

In order to eliminate the above-mentioned changes the counting rates were measured at two points of the characteristic alternately every 20 seconds. The measurements were made by means of rate meter with a time constant of 5 sec. A relatively low counting rate was used — about 4000 cpm. It was found that the slope of the characteristic distinctly depends on the wavelength. By comparison of the slopes of the characteristics and the photoelectric efficiency of the counter the plot in Fig. 12 was prepared. It turns out, as seen in Fig. 12, that there exists a relation between the photoelectric efficiency and the slope of the characteristic of the counter for ultraviolet radiation. The slope for a collimated gamma beam passing through the centre of the counter was, of course, taken from the slope measured for ultraviolet radiation. The deviation of the experimental points from the curve does not exceed a factor of 5. The difficult

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conditions of the measurement do not allow one, however, to expect better agreement. An error of 2%/100 V in the determination of the slope of the characteristic is equivalent to a factor of 2 in the photoelectric efficiency. For slopes of several ten percent (100 V an error up to 5%/100 V could be made. The error in determining the efficiency should not exceed a factor of 2.

It follows from Fig. 12 that the greater the photoelectric efficiency the smaller the slope of the counter characteristic. A careful measurement of the slope for ultraviolet could even replace a measurement of the photoelectric efficiency. This method would allow a greater choice of radiation sources and a greater choice of the range of the radiation intensities used.

The slope of the characteristics for ultraviolet radiations, in the opinion of the author, is connected with the phenomenon of the backward diffusion of photoelec-

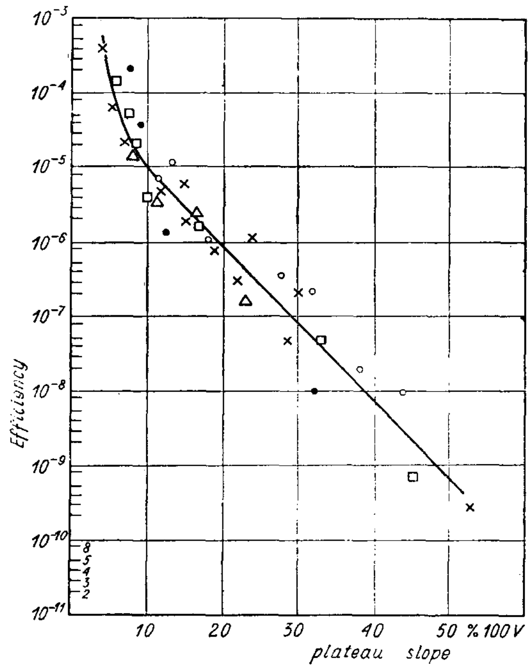

Fig. 12. Relation between the photoelectric efficiency and the slope of the characteristic for ultraviolet radiation ● and O represent counters with brass cathodes, other sings denote counters with a Cu + Be cathodes

trons. This idea, in somewhat other form, was expressed by Locher (1932) and Christoph (1936) (see Introduction). (The concept of slope of the characteristic was not yet known to these authors).

Backward diffusion, in turn, is connected with the distribution of the velocity of the photoelectrons. The results shown in Fig. 12 represent, therefore, indirectly the relation between the photoelectric efficiency and the velocity distribution in the vici-

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nity of the counter cathode. To explain this relation further detailed experimental data are necessary also in conditions of vacuum. Since the question of the relation between the photoelectric efficiency and the velocity distribution of photoelectrons is not discussed in the literature, this question should be regarded as an open one.

9. Interpretation of the phenomenon of changes in efficiency

The three types of changes in efficiency discussed above: "maturing", changes of short duration, and changes connected with the ageing of the counter are presumably due to the effect of the adsorbed molecules, mainly to their electric field.

This effect may be of two types: 1) backward diffusion of photoelectrons in the adsorbed layer, and 2) tunnel effect and the phenomenon of quantum mechanical reflection of electrons in the electric field created by the adsorbed layer.

Small changes in the shape of the potential barrier can evoke large changes in the probability of photoelectron emission, especially if the electron energy is smaller than the height of the potential barrier. In the vicinity of the photoelectric threshold the tunnel effect allows the determination of the probability of emission which is a known function of $(E-U)$, where E is the energy of the photoelectron, and U the height of the potential barrier. If the energy of the photoelectrons is greater than the height of the potential barrier there takes place a quantum-mechanical reflection of the electron wave, which expresses itself in a coefficient of reflection. This coefficient is a known function of E/U. The continuous distribution of the photoelectron energy results in a certain fraction of the photoelectrons being transmitted through the barrier in a tunnel effect.

A detailed calculation made by the author of the various heights and widths of the barrier gives changes in efficiency which are in agreement as to the order of magnitude with that observed.

Independently of the influence of the potential barrier cases are known in which an adsorbed substance of large dipole moment changes the work function of the metal in relation to vacuum. The change in the work function concerns phenomena at a depth of 10^{-8} cm and, in the absence of a potential barrier, has relatively small effect on the photoelectric efficiency far from the threshold. The structure of the deeper layers (at a depth of several tens of Å) has the greatest effect on the efficiency. In the presence of the barrier, this influence is greater since there is still the above-mentioned probability of passing through the adsorned layer. For stable counters, it seems that the change in the work function does not occur over short periods of time.

A strong dependence of the constant A on the wavelength which well accounts for the phenomena connected with the presence of a potential barrier suggests that the influence of backward diffusion in the adsorbed layer is slight in relation to the other effects; at least, such is the case for brief changes in the photoelectric efficiency resulting from the counter operation.

The following picture may explain Eq. (3) given above. The threshold counting rate N_0 can be interpreted as a minimum one, or as a kind of "extrapolated" counting

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rate necessary for the disassociation products to cover part of the cathode free from the adsorbed molecules of the quenching gas. Since these products, in the main, do not have a dipole moment, they do not give rise to a potential barrier. At a higher counting rate important changes take place, e. g. explusion of the adsorbed molecules of the quenching gas. The potential barrier then disappears in the regions in which this takes place. Other phenomena increasing the probability of photoelectric emission are also possible.

If the action of the new dissociation products were independent of the same products already adsorbed, then the relation

$$Y_r/Y_0 = 1 + B\,|N - N_0|$$

should hold. However this assumption is incorrect. The new dissociation products can displace the older ones. Thus the curve will be steep.

10. Conclusion

As a consequence of this work one may list some conditions which must be fulfilled in order for photosensitive counters to be used in spectrometry.

1. The counters should be "matured".
2. Their operating voltage should exceed the threshold by at least 70 V.
3. The choice of the cathode should be made not only with regard to the photoelectric efficiency, but also with regard to the changes in efficiency of short duration resulting from the ageing of the counter. There appears here a general characteristic of photosensitive counters, namely, a higher efficiency is accompanied, at least for a given material, by a better stability of the efficiency over both longer and shorter periods of time, and by a smaller slope of the characteristic. The behaviour of the counters with platinum cathodes is particularly favourable.
4. The sensitivity and stability of the counters increase with the decrease in the wavelength of the light. The counter (with the platinum cathode) works particularly well below 2500 Å, and sufficiently well below 3000 Å. This behaviour is somewhat opposite to that of photomultipliers.

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