Photoelectric Yields in the Extreme Ultraviolet

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The photoelectric yields for various surfaces (Ni, W, Mg, W–O and Constantan) illuminated by the extremely short wave-length radiation given out by the positive columns in He, Ne and A respectively, have been determined. The effect of the extremely short wave-length radiation was separated from that of the complete radiation by the use of a quartz disk which, when inserted, cut off all radiations, below 1500A. The yields obtained (in electrons per 100 quanta) range from 11 in the case of Constantan and He, to 0.14 in the case of Mg (surprisingly) and Ne. The yields, e.g., for well degassed Ni for He, Ne and A, were 4.4, 1.6 and 0.6 respectively; those for the other surfaces except Mg varied with the gas in the same general way. Thus the maximum in the yield for most ordinary metal surfaces probably lies on the short λ side of 584A. W–O gave greater yields than W (except in A) and in general undegassed metals gave yields several times greater than well degassed ones. The size of the yields suggests that the photoelectric emission from probe and cathode surfaces in the rare gases may be of considerable importance.

MEASUREMENTS of photoelectric yields in the ultraviolet have been few and extend only to about 2000A. The present paper describes measurements, earlier briefly reported in part,[1] of yields in the case of the resonance radiations of He, Ne, and A (at about 1061A, 740A, and 584A respectively) incident on a number of surfaces.

I. Apparatus and Method

In Fig. 1 radiations from a positive column type discharge, in a rare gas at low pressure, between a hot tungsten cathode K and an anode A fall upon the receiver H of an absolute thermopile of the type developed by Coblentz and Emerson.[2] A suitably connected grid G collects and measures the saturation photoelectric emission from H. A crystalline quartz plate Q, which can close the circular opening in the Ni cylinder D, permits separation by the method of differences of the effects of the extreme ultraviolet (EUV) radiations (which lie within the relatively narrow regions 584–505, 744–575 and 1066–788A in He, Ne and A respectively[3]), from the effects of the remainder of the arc spectra (which extend into the ultraviolet only to 2600, 2400 and 2950A respectively[4]).

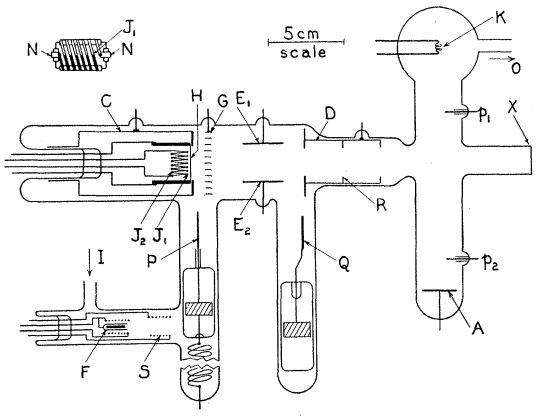

FIG. 1. Diagram of apparatus.

The receiver H is a Constantan strip $1.78\times2.20\times0.000635$ cm through which a calibrating current can be passed. About 1 mm behind H are 19 thermopile junctions J_1 and at about 1.5 cm behind H the corresponding cold junctions J_2. J_1 and J_2 are schematic in the main figure; they were made by spot-welding suitable lengths of Fe and Constantan ribbon (0.0025×0.1 cm) together to form a string which when wound on

[1] Carl Kenty, Phys. Rev. **38**, 2079L (1931).

[2] W. W. Coblentz and W. B. Emerson, Bull. Bur. Stand. **12**, 503 (1915–16).

[3] Dorgello and Abbink, Physica **6**, 150 (1926) and **7**, 1 (1927) have shown that mainly only the resonance lines are developed in the extreme ultraviolet by positive column discharges in He, Ne and A.

[4] Infrared radiations beyond the limit of transmission of quartz (about 30,000A) will be generated mainly only by the glass walls of the tube (see below).

a three legged frame insulated by thoria tubing (the two front legs are shown in the inset) gave J_1 and J_2 in the positions indicated. The leads, serving also as supports for the device, were welded to Ni parts (shown schematically at N) clamped around sections of thoria tubing. This rugged construction permitted repeated baking out at 450°C. A Ni cylinder C insures that scattered radiation cannot reach J_1 and J_2.

H is a left bright in order to decrease relatively the sensitivity to the visible and infrared rays (the EUV radiations being only slightly reflected, see below); this is important in the case of He, below, where the EUV radiation available is small compared with the visible, infrared and heat rays. A Ni plate P, of the same area and shape as H, is movable magnetically to a position directly in front of H; it may be degassed inductively in the position shown, or rotated and moved opposite S and coated with Mg (see below). A potential of 45 volts across the Ni plates E_1E_2 removes any ions and electrons diffusing away from the discharge (a small effect detected only at the lowest pressures in He).

The tube is of Pyrex and has a quartz window at X attached by a graded seal. The metal parts except H and J_1 and J_2 were vacuum fired before assembly. Before each run the tube was exhausted for 1 hour at 450°C and then for two hours at 300°C; meanwhile parts of the vacuum system not in the furnace were torched. The metal parts, except the thermopile assembly and D, were degassed by inductive heating. The gases, of high initial purity, were further purified by continuous circulation, over chabazite[5] in liquid air in the case of He, over charcoal in the case of Ne, and through a misch metal arc in the case of A. Two liquid air traps in series (filled with glass beads) at the intake I, and one at the outlet O, insured that no Hg vapor from the circulating Hg diffusion pump entered the tube. Tests similar to those described in an earlier paper[6] assured that the purity of the gas in each case was as high as or higher than that attained formerly.[6]

II. Isolation of the Photoelectric Effect from the Effects of Metastable Atoms

From experimental results already described[6] we can conclude that, at least in Ne and A, the contribution of metastable atoms to the currents between H and G either in (1) emitting electrons from surfaces[7] or (2) in ionizing traces of impurities[6, 8] will be negligible.[9] Especially will this be true since considerably lower gas pressures are used here than in the former experiments, gaseous collision during the lifetime of the resonance atoms being necessary for the forma-

[5] Chabazite, when well degassed (here at 450°C) and placed in liquid air, is known to absorb all gases except He. The sorption process in this mineral is discussed by M. G. Evans, Proc. Roy. Soc. **A134**, 97 (1931).

[6] Carl Kenty, Phys. Rev. **43**, 181 (1933). See also Phys. Rev. **38**, 377L (1931).

[7] Simon Sonkin, Phys. Rev. **43**, 788 (1933) and numerous other writers.

[8] F. M. Penning, Zeits. f. Physik **78**, 454 (1932) and other papers. See also O. S. Duffendack and R. W. Smith, Phys. Rev. **43**, 586L (1933).

[9] In early experiments with the tube of Fig. 1 a 2.5 cm magnetically rotatable, mica-backed Mo disk replaced the plates E_1E_2. Approximate saturation electron currents from this disk when its bare side faced perpendicularly the discharge were much greater (e.g., 6-fold in Ne at 0.1 mm) than when it was parallel to the axis of the tube. This showed that at least the "$\perp$" currents were caused mainly by the photoelectric effect of the primary radiation beam. The objection (only partial in any case) of Reichrudel and Spiwak (Ann. d. Physik **17**, 65 (1933), note added in proof) is invalid since the EUV radiations in question will be only slightly reflected (cf. references 21, 22 below). These writers (see also Phys. Rev. **42**, 580 (1933)) bring a glass surface up in the rear of a small spherical probe located beyond a discharge in Ne, and observe that the apparent electron current from this probe is thereby considerably reduced. They conclude that such a current is largely caused by metastable atom emission of electrons from the probe. While metastable atom emission may be of somewhat greater importance in the case of a small probe than in the case of relatively large surfaces (comparable with the dimensions of the surroundings) as in our experiments, we believe in regard to Spiwak and Reichrudel's conclusion that careful consideration is necessary of the effect of the glass surface on the geometry of the surrounding space insofar as this influences (1) diffusing radiation (which like metastable atoms will be destroyed by the glass), (2) ionization of gaseous impurities by metastable atoms, (3) the field near the probe and (4) the diffusion of ions and electrons across the relatively short space between the discharge and the probe, which may be of different relative importance in their Ne experiments and in their control experiments in Hg.

tion of the metastable atoms in Ne and A.[10] In He, however, the former experiments indicated that metastable atoms were of relatively greater importance. This was shown to be at least partly due to a relatively high formation of metastable atoms from resonance atoms, probably spontaneously by radiation of the strong line 20,582A (a process which does not exist in Ne and A and which will be relatively little reduced by lowering the gas pressure).

To improve matters in He, the grid G (also used in Ne and A) was designed with rectangular passages 0.3 cm square and 0.4 cm long. According to Schottky's law of diffusion[11] in tubes metastable atoms diffusing through these passages will be reduced at the walls to relatively negligible numbers; the only metastable atoms reaching H (or P) will practically be those formed within a small region extending from H (or P) about halfway toward G. From rough consideration of the diffusion problem with and without G we estimate that G will reduce (1), above, by a factor of at least 5 or 6. The reduction in pressure as well as the narrowing of the space between H (or P) and G will still further greatly reduce (2) (by reducing the *concentration* of metastable atoms which may be built up, on which (2) depends) so that we may consider the effects of metastable atoms practically eliminated even in He. As an example of the efficiency of G in reducing the effects of metastable atoms, strong irradiation[6] of the space between the plates E_1E_2 with He light reduced the currents between them (due to a discharge between K and A in He at 0.3 mm containing a minute trace of impurity) by about 10 percent but similar irradiation between H and G had no detectable effect on the currents between these electrodes.

III. Energy Measurements

A galvanometer of sensitivity 2.2×10^{-8} volt per mm, resistance 13.75 ohms and period 5 sec. was connected in series with the thermopile junctions which had a resistance of 26.9 ohms. An additional resistance of 23 ohms was shunted across the galvanometer for approximate critical damping.

Curves A and B, Fig. 2 show the response-time curves of the galvanometer, as thus connected, without and with Q, respectively, caused by a 300 m.a. discharge in Ne at 0.12 mm. Curves C and D represent similarly response curves due to the calibrating currents indicated.

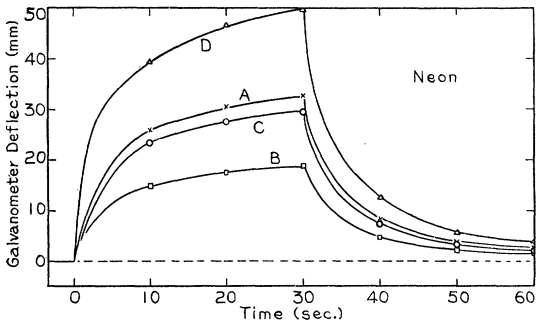

FIG. 2. Thermopile response-time curves; A: for a 300 m.a. discharge between K and A (Fig. 1) without quartz filter Q; B: for same with Q; C and D: for calibrating currents in thermopile receiver, H, of 42 and 55.1 m.a. respectively. Sources of heat are applied at $t=0$ and shut off at $t=30$ sec.

As shown by curves C and D the response of the thermopile is approximately proportional to the heat input to H (Ri^2, where $R=0.057\pm0.003$ ohm is the resistance of H) in the two cases (a result found to be true within the experimental error over a wide range) and yields a mean value of the thermopile sensitivity (based on the deflections at 30 sec.) of 3.42 microwatts (μw) per mm.[12] Curves A and B then give the heating effects of the discharge without and with Q respectively as 112 and 64μw. The return of the galvanometer toward zero after the shut off of the energy input in approximately the same way for all curves shows that heat rays from the glass warmed by the discharge were unimportant (see below). We assume therefore that the only important radiations shut out by Q are the EUV radiations. Increasing the 64μw values by 8

[10] C. G. Found and I. Langmuir, Phys. Rev. **39**, 237 (1932).

[11] W. Schottky, Phys. Zeits. **25**, 635 (1924).

[12] Similar sensitivities at 0.3 and 0.4 mm of Ne were 2.7 and 2.4μw per mm respectively, and in 0.12 mm of A and 0.07 mm of He, 2.7 and 6.4μw per mm respectively. In vacuum, the sensitivity was 16μw per mm and the response relatively slow. It is evident that the performance of this type of thermopile is much better with gas present than in a vacuum.

percent to allow for the reflection by Q of the remaining radiations and subtracting from $112\mu w$ we find $42.5\mu w$ for the heating effect of the EUV radiations or 38 percent of the total. Curves A and B, Fig. 2 each represent the average of several individual curves. Curves taken for argon at 0.12 mm and for a 150 m.a. discharge were closely similar to those of Fig. 2; the heating effect of the EUV radiations was $36.4\mu w$ which was 47 percent of the total.

Similar measurements were carried out in He. The EUV radiation from He was found to be very small. (1/12 and 1/25 as great as in Ne and A respectively, per unit positive column wattage) and heat rays from the glass, warmed by the discharge, were of considerable importance. This was shown by the fact that the curves corresponding to curve A, Fig. 2 did not approach saturation normally and did not return toward zero after shutting off the discharge but toward a higher semi-equilibrium value. By trial, a unique curve could be constructed to represent the effects of these heat rays which when subtracted from the actual curve gave a curve which conformed closely to the normal type and which was therefore taken to represent the true effect of the discharge radiations. A He pressure of 0.07 mm was used and a discharge of 160 m.a.[13] A large number of runs were made, each run being corrected for slow galvanometer drifts. The average of the results showed the heating effect of the EUV radiations to be $3.5\mu w$ or 16 percent of the total energy received.

IV. Photoelectric Measurements

Fig. 3, curve A, shows the current between H and G (Fig. 1) as a function of the voltage applied between these electrodes in the case of a 300 m.a. discharge in Ne at 0.12 mm (same conditions as in Fig. 2). In all cases the photoelectric measuring system was left floating with respect to the discharge. Curve B shows the similar current between P and G when the former is placed directly in front of H. Curve C is the same as B except P is coated with Mg (see below). Fig. 4 shows somewhat similar curves for argon. Curves obtained for He (conditions as in § III) were closely like those for Ne in form and need not be given; they indicated saturation currents of 1.9, 0.7 and 0.13×10^{-8} amp. for Constantan, Ni and Mg respectively. All curves were taken with Q removed; with Q in place currents were negligible in all cases.

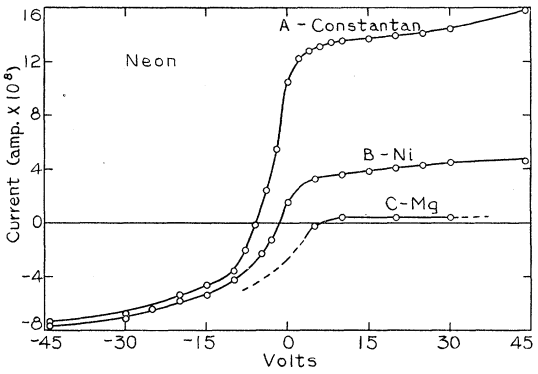

Fig. 3. Current voltage characteristics; A: of G and H (Fig. 1), B: of G and P, C: of G, and P covered with Mg. Positive voltages are for G positive to the other electrodes in every case. Discharge: 300 m.a. in Ne at 0.12 mm.

The relative saturation of the right-hand parts of these curves, at least in limited regions, suggests that the effects of (1) back diffusion[14] and (2) ionization in the space caused by the applied field (cf. the rise in curve A, Fig. 4 at 15 volts) are not great in these regions. The currents at 20 volts were chosen to represent the saturation photoelectric currents in He and Ne

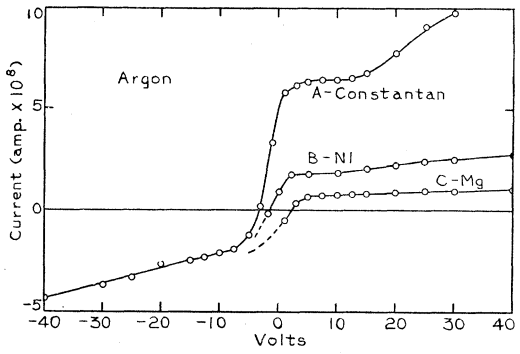

Fig. 4. Current voltage characteristics similar to those of Fig. 3 but for a 150 m.a. discharge in 0.12 mm argon.

[13] These were found to be the most favorable conditions. The discharge was greenish in color due to the singlet line 5016A. Higher discharge currents and particularly higher gas pressures tended to bring out the triplet spectrum to the exclusion of the EUV (singlet spectrum).

[14] I. Langmuir, Phys. Rev. **38**, 1656 (1931).

and at 10 volts in A. The errors in the calculated quantum yield, E, due to (1) and (2) will be in opposing directions; however, measurements of E at higher pressures (up to 1 mm) in Ne and A gave values of E substantially lower (up to 50 percent) than those obtained around 0.1 mm, which indicates that (1) is probably more important than (2) at the above applied voltages and that (1) is of relatively increasing importance at higher pressures.[14] Probably, on account of (1) therefore, the values for E calculated below will be slightly too small notwithstanding the low pressures used.

The left-hand parts of the curves do not saturate, probably because higher fields penetrate further into the spaces of G drawing off more of the electrons emitted from the walls of these spaces by scattered radiation.

Comparison of photoelectric currents from W, oxidized W (W−O) and some Mg surfaces already briefly reported[15] were made with an apparatus previously described.[16] Well degassed Ni has now been studied in the same apparatus so that the photoelectric yields obtained from the surfaces studied in the two different tubes can all be compared in terms of Ni.

V. Treatment of Photoelectric Surfaces

The Ni plate P was degassed by repeated inductive heating in vacuum to the point of evaporation, and the W disk of Fig. 1 reference 6 by similar heating to about 2000°K (as determined by an optical pyrometer).[17] The oxidized W surface was prepared by heating the W disk to a bright red heat for a few seconds in 0.020 mm O_2. The Mg surface was prepared by distilling the metal in vacuum first from a pure Mg wire inside the iron cylinder F (Fig. 1) on to the W spiral S and then, placing P in front of S, on to P. We believe this procedure gave a purer Mg surface than that attained in the earlier experiments.[15, 18]

During the preparation of a surface the gas in each case was temporarily removed from the tube into the purifying apparatus by the circulating pump, a suitably placed Hg cut-off having been raised to stop circulation. The gas could then be returned to circulation and to its former pressure by lowering the cut-off.

The photoelectric thresholds of the different surfaces were roughly measured by the method of filters[19] by using a quartz Hg arc (at X in the case of Fig. 1). The values given in Table I below are those obtained directly before taking the curves of the preceding section. Working quickly, these curves were obtained before minute traces of impurities, dislodged by the discharge, had appreciably affected the surfaces. The changes thus produced caused slowly increasing EUV photoelectric responses and decreasing thresholds in all cases except oxidized W. Cathodic sputtering of Ni and W *in situ* returned the surfaces to approximately their former state; indeed sputtering appeared to produce slightly cleaner surfaces than the heat treatment, as indicated by thresholds slightly nearer the most reliable values for the clean

Table I. *Percentage photoelectric yields.*

Surface	Approximate P. E. threshold	Percentage Yield (E) He(λ584)	Ne(λ740)	A(λ1060)
H (Constantan) undegassed	>2537	11.2	5.5	2.10
P (Ni)	2537	4.4	1.56	0.60
Mg	3300	0.6	0.14	0.25
W	2537	5	2	0.7
W-0	<1849	6	3	0.6

[15] Carl Kenty, Phys. Rev. **43**, 776A (1933).

[16] The W disk D (Fig. 1 of reference 6) was used first well degassed and later oxidized; it was later replaced by a Ni disk of the same size. Similar discharge currents and gas pressures (0.5 mm) were used in all cases. Curves were obtained similar to those of Fig. 2 (reference 6) but better saturated owing to the lower pressure. The ordinates of the "⊥" curves at 15 volts were taken to represent the saturation photoelectric currents (see footnote 13 of reference 6). A quartz window was sealed on to the tube so that the photoelectric thresholds of the surfaces could be obtained.

[17] At this temperature oxygen rapidly evaporates from W. See I. Langmuir and D. S. Villars, J. Am. Chem. Soc. **53**, 486 (1931).

[18] The threshold of Mg here obtained (Table I) agrees with that recently found by Déjardin and Schwégler, Comptes Rendus **196**, 1585 (1933), but is lower than that of Cashman and Huxford, Phys. Rev. **43**, 811 (1933).

[19] R. C. Williamson, Phys. Rev. **21**, 107 (1923) and others; see Hughes and DuBridge, *Photoelectric Phenomena*, p. 48.

metals[20] and by slightly lower EUV photoelectric responses. Since these changes were small we believe our yields (Table I) are fairly representative of the clean metals.

VI. Calculation of Photoelectric Yields

The first row of Table I shows the number (E) of electrons emitted from H per 100 *absorbed* quanta, calculated from the data of §§ III and IV by using the approximate wave-lengths of the resonance lines concerned.[3] The second and third rows show the similar yields for Ni and Mg respectively based on the ratios of the ordinates of the curves in § IV as discussed above and the assumption that the absorption coefficients of all the surfaces are approximately the same for a given EUV radiation. This assumption is probably sufficiently true for the present purposes since from the works of Gleason[21] and of O'Bryan[22] the reflection coefficients for *normal incidence* for the surfaces and radiations in question are probably <0.1 in all cases. To a higher degree of accuracy the values in the table represent (within a given column) the relative yields per unit *incident* energy.

Rows 4 and 5 show similarly the yields from W and W−O based on the ratios of the currents from these surfaces to the current from Ni (§ IV).

It was observed with other apparatus that approximate saturation EUV photoelectric currents, in the case of Ne, from Ni, Fe, Constantan and graphite were all of the same order of magnitude and that undegassed Ni, Fe and Constantan gave two to three times as much current as the well degassed surfaces.[23]

Measurements of E for Ne and A could be repeated within 5 percent and those for He within 10 percent. Uncertainties in the method of correcting for heat rays may increase the error in He to 20 or 30 percent. Any appreciable infrared radiation beyond the limit of transmission of quartz, developed *in the discharge*, would cause the calculated values of E to be too small (cf. the effect of back diffusion, § IV).

VII. Discussion and Conclusion

It has long been recognized that the photoelectric yield from an ordinary metal surface probably reaches a maximum somewhere in the extreme ultraviolet.[24] The curves of Fig. 5 which

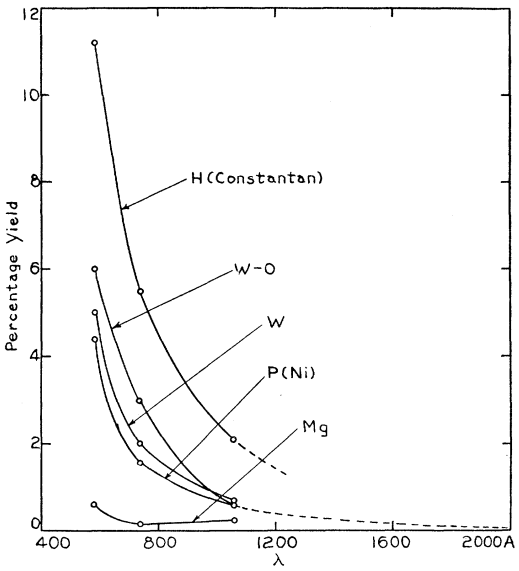

Fig. 5. Photoelectric yields as a function of wave-length. (Plotted from Table I.)

are plotted from the data of Table I, suggest that the maxima for the surfaces studied lie to the short λ side of 584, and that they may reach relatively high values. It is of interest that Richardson[25] was led from experiments to infer yields approaching 100 percent in the soft x-ray region.* The curve for Ni is extrapolated toward longer λ to give an idea (necessarily only approxi-

[20] Hughes and DuBridge, *Photoelectric Phenomena*, p. 76.

[21] P. R. Gleason, Proc. Nat. Acad. Sci. **15**, 551 (1929); Proc. Am. Acad. Arts and Sci. **64**, 91 (1930).

[22] H. M. O'Bryan, Phys. Rev. **38**, 32 (1933).

[23] K. Sommermeyer, Ann. d. Physik **13**, 315 (1932) gives evidence for a large secondary emission of electrons (perhaps caused mainly by photoelectric action of the resonance lines) from the glass walls of a rare gas discharge tube, which is much greater for undegassed than for well degassed walls. G. Bandopadhyaya, Proc. Roy. Soc. **A120**, 96 (1928), and others find similarly that soft x-rays eject more electrons from gas contaminated metal surfaces than from well degassed ones.

[24] See for example, Campbell and Ritchie *Photoelectric Cells* pp. 26, 27. According to the theory of Tamm and Schubin two maxima would be expected; see the review by L. B. Linford, Rev. Mod. Phys. **5**, 34 (1933).

[25] O. W. Richardson, Proc. Roy. Soc. **A119**, 531 (1928).

* Recent work of J. Bell, Proc. Roy. Soc. **A141**, 641 (1933) indicates that for 1000 volt x-rays the yield probably again has become relatively small.

mate since available data are very meager, of relative yields in nearer ultraviolet regions.

The relatively steep ascent of the curves of Figs. 3 and 4 through the region of zero voltage indicates that the bulk of the electrons are emitted, in most cases, with only a few volts energy although the energies available from the incident quanta are much greater (11.6–21 volts less the work functions involved); similar observations were made by Oliphant[26] for the case of electrons emitted from a Mo surface by fast He metastable atoms. By lengthening the cells of G, Fig. 1, and coating their walls with Mg we hope to reduce the electron emission therefrom to negligible values and obtain more exact information concerning the energy distribution of electrons emitted from different surfaces (P) by extreme ultraviolet light.

It is perhaps surprising to find W−O (for example) yielding so much greater (20-fold in Ne) currents than Mg (which in most circumstances would be expected to yield the larger currents).[27] Possibly use can be made of this property of Mg in isolating the photoelectric component of the electron emission from probe and cathode surfaces.[28] From the size of the yields in Table I (they compare with the highest obtainable from sensitive films in the case of visible light[29]), we might expect this component to be higher in many cases than has usually been supposed.[6, 30]

It is a pleasure to thank Mr. E. W. Pike and Mr. J. A. St. Louis for a number of helpful suggestions and Mr. J. D. Forney for valuable aid in constructing the thermopile.

[26] M. L. E. Oliphant, Proc. Roy. Soc. **A124**, 228 (1929).

[27] K. K. Darrow, *Electrical Phenomena in Gases*, p. 362.

[28] For bibliography see K. K. Darrow, reference 25, pp. 362–365 and elsewhere. E. W. Pike, Phys. Zeits. **33**, 457 (1933).

[29] See for example Hughes and DuBridge, reference 19, pp. 170, 171.

[30] J. Taylor, Proc. Roy. Soc. **A117**, 508 (1928) and other papers.