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AN EXPERIMENTAL TEST OF THE IONIZATION CHAMBER METHOD OF MEASURING THE RELATIVE INTENSITIES OF X-RAY SPECTRUM LINES

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Abstract

A two-compartment ionization chamber has been constructed with the following properties: (1) The fraction of the x-ray energy absorbed in the front compartment could be directly measured, (2) The volume of gas from which the ionic saturation current was drawn was sharply defined, (3) Photoelectrons produced in the chamber could not reach the walls before expending their ionizing energy, (4) The direct beam entered and left the chamber through thin windows and encountered no other parts of the chamber. The relative ionization currents produced in methyl iodide, methyl bromide, argon, sulfur dioxide, and air by the α_1, β_1, γ_1, lines of the tungsten L series were measured and the ratios obtained after correction for fraction of the direct beam absorbed were found not to vary more than 2.5 percent in the first four gases. If the air values are corrected for loss through scattering, concordant results are obtained. Similar experiments have been made using the uranium L-series, where large corrections for loss through escape of fluorescent K-radiation must be made, including the case of krypton, where the K limit comes between the uranium $L\beta_1$ and $L\alpha_1$ lines. The results give strong support to the following hypothesis: The saturation current obtained from a given volume of any gas is proportional to the fraction of the x-ray beam transformed into β-rays within it, providing the β-rays come to the end of their ionizing range within the volume.

Introduction

In attempting to measure the relative intensity of x-ray spectrum lines by the ionization chamber method, one actually measures the ionic saturation current produced by the x-ray beam in a volume of gas bounded by the walls of the chamber. The question then arises: is this observed ionization current proportional to the intensity we wish to measure? The question becomes especially important when we wish to compare the intensities of two x-ray beams of different wave-lengths. Several investigations, designed to give an experimental answer to this question, have been carried out.[1] The method has been to measure the intensity of an x-ray beam by converting the energy into heat, and then to find the ionization produced by this beam in air. All but a negligible part of the ionization in air results from the ionizing action of photoelectrons or recoil electrons ejected by the x-rays, and by measuring the number of ions produced per second one may calculate the energy ϵ expended by a beta-ray per pair of ions formed. Although various

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[1] Kulenkampff, Ann. d. Physik **79**, 97 (1926); Kircher and Schmitz, Zeits. f. Physik **36**, 484 (1926); Rump, Zeits. f. Physik **43**, 254 (1927); Auren K. Vetenskapsakad, Nobelinst. Medd. 6, **13**, 1 (1927); Steenbeck, Ann. d. Physik **87**, 811 (1928); Crowther and Bond, Phil. Mag. **6**, 401 (1928).

researches give values of ϵ for air which differ somewhat, they all show that ϵ is independent of wave-length over the range investigated, or from about 0.5 to 1.5 A.U. This question of the variation of ϵ with λ is vital to the ionization measurement of the intensities of x-ray beams of different wave-lengths. The result that ϵ is constant may be stated in the following form: the relative intensity of two x-ray beams of different wave-length is correctly given by the relative ionic saturation currents produced in air in an ionization chamber in which all of the x-ray energy is transformed to beta-ray energy in air, and the beta-rays produced come to the end of their ionizing range before reaching the boundaries.

Another type of problem which involves similar considerations is the experimental determination of the efficiency of production of fluorescent radiation, in which the intensities of the primary and secondary x-rays, necessarily of different wave-lengths, must be measured.[2] (These considerations do not apply to the direct method of counting the relative number of double and single tracks in a Wilson chamber.) The experiments of Martin, and of Compton have an especially important bearing on the results to be reported here. It seems quite obvious from the quantum theory that the fraction w_k of a number of atoms ionized in the K shell which return to their normal state by a process involving the emission of K series characteristic radiation is independent of the wave-length of the primary beam which produced the ionization. Martin and Compton find by experiment that such is the case, on the assumption that the energy spent in producing a pair of ions is the same for the primary and fluorescent x-rays. We may then conclude from their experiments that if ϵ varies with the wave-length, then w_k, the fluorescence yield,[3] varies with the primary wave-length, and because such a variation of w_k is highly improbable, the experiments furnish evidence of the constancy of ϵ. The assumption of the constancy of ϵ is set forth very clearly in the paper of Martin, who used oxygen gas in his ionization chamber.

It is not always practicable to use such light gases as air and oxygen in ionization chambers because of the small fraction of the primary beam absorbed in a chamber of convenient length, and the resultant loss of intensity. In Compton's work on w_k, methyl bromide was used, and such gases as argon, methyl iodide, and krypton have also been used in various researches involving intensity measurements. When such gases are used, the possibility arises that fluorescent x-rays excited in the gas may reach the boundaries of the space from which the ionic saturation current is being drawn without being absorbed. Martin has derived equations expressing the corrections to be applied when fluorescent radiation is produced, and used them for the calculation of w_k from measurements of the ionization relative to air of the heavier gases, as reported by other investigators. Compton has also derived such equations, and applied them to his work with methyl bromide. In certain of the experiments reported here, these corrections are given a rather severe

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[2] Harms, Ann. d. Physik **82,** 87 (1926); Balderston, Phys. Rev. **27,** 696 (1926); Martin, Proc. Roy. Soc., Lond. **A115,** 420 (1927); Compton, Phil. Mag. **8,** 961 (1929).

[3] Auger, Ann. d. Physique **6,** 183 (1926).

test, and their derivation will accordingly be reviewed. The development of the equations follows closely the method given by Compton.[2]

DERIVATION OF CORRECTIONS TO OBSERVED IONIZATION CURRENTS

Consider a cylindrical volume of gas, of length l and radius r. The beam of x-rays enters at the center of one end of the cylinder and traverses the volume along the axis of the cylinder. In the following calculations the cross-section of the beam is not limited by the area of the opening of the ionization chamber, but is supposed to be small compared to πr^2. We can speak of the power, P, of the beam of x-rays entering the chamber. The x-rays may interact with the gas in the chamber in three ways, (1) The ejection of photoelectrons, (2) The classical scattering, and (3) The Compton scattering. We shall simplify the problem at once by assuming that the Compton effect plays no significant part in the process. This assumption is justifiable in the experiments reported here, but of course would not be valid over all wave-length ranges with all gases. Another simplifying assumption which we shall make is that the diameter of the chamber is sufficiently great so that the photoelectrons come to the end of their ionizing range within the gas. In the present experiments it was not difficult to construct the ionization chamber so that this condition was fulfilled. The amount of the energy of the primary beam absorbed in the chamber per second is

$$P(1 - e^{-\mu l}) \equiv PF \tag{1}$$

where μ is the absorption coefficient of the gas for the wave-length of the primary beam. If appreciable amounts of fluorescent or scattered secondary x-rays of sufficient hardness to reach the walls are produced, the power PF is not all expended in producing ions. We shall proceed to set up expressions for the power lost through these secondary x-rays. We shall first treat of the losses through fluorescent radiation. If ν be the frequency of the primary x-ray beam, the number of quanta absorbed per second is $PF/h\nu$. The number of atoms ionized in the K shell per second will be

$$\frac{PF}{h\nu}\cdot\frac{\tau_k}{\mu} \tag{2}$$

where τ_k is the absorption coefficient of the gas corresponding to frequency ν for the ejection of photoelectrons from the K level. The L and softer fluorescent radiations are completely absorbed in the gas in all cases reported here, so that it will not be necessary to consider them. The number of atoms ionized in the K-level per second which recombine by processes involving the emission of K-series x-ray lines is

$$\frac{PF}{h\nu}\cdot\frac{\tau_k}{\mu}w_k \tag{3}$$

where w_k is the fluorescent yield for the K-series as defined by Auger.[3] Let f_i be the fractional part of the total number of quanta emitted having the frequency ν_i of the ith line of the K-series, then the power escaping from the chamber in the form of K-series radiation from the gas may be written

$$\frac{PF}{h\nu}\frac{\tau_k}{\mu}w_k\sum_i f_i h\nu_i e^{-\tau_i r} = w_k PF\frac{\tau_k}{\mu}\lambda\sum_i\frac{f_i}{\lambda_i}e^{-\tau_i r} \tag{4}$$

where τ_i is the fluorescent absorption coefficient of the gas for the ith line of its own K-series, and r is the effective path length of the radiation in the gas before reaching the walls. In an ionization chamber in which $l \gg r$, and in which the absorption of the primary beam is not so pronounced that it is almost all absorbed before penetrating a distance short compared with r into the gas, we may as a first approximation identify r of Eq. (4) with the radius of the chamber.

X-ray energy which has been scattered from the primary beam may also reach the walls before its energy has been expended in the production of ions, and the rate of such loss may be written

$$\frac{\sigma}{\mu}PFe^{-\tau r} \tag{5}$$

where σ is the scattering coefficient of the gas for the primary wave-length, and τ is the absorption coefficient for fluorescent processes for the primary wave-length. In the experimental arrangement to be described later, these secondary x-rays actually reached the metal walls of the chamber, and ejected photoelectrons from them, some of which went back into the gas volume and produced ionization. This effect is not taken into consideration in the equations, and the results show that it must introduce a correction to relative intensities which is less than 2 percent in the wave-lengths studied. Combining Eqs. (1), (4), and (5), we have

$$I = cPFR \tag{6}$$

where

$$R = 1 - \frac{\tau_k}{\mu}w_k\lambda\sum_i\frac{f_i}{\lambda_i}e^{-\tau_i r} - \frac{\sigma}{\mu}e^{-\tau r}. \tag{7}$$

In this expression, I is the ionic saturation current, and c is a constant for the gas which is inversely proportional to ϵ, where ϵ is the energy spent in producing a pair of ions.

If we are comparing the intensities of two lines α and β, we have

$$\frac{P_\alpha}{P_\beta} = \frac{I_\alpha F_\beta R_\beta}{I_\beta F_\alpha R_\alpha} \tag{8}$$

if ϵ is independent of λ, as discussed in the first section. For convenience, we shall write Eq. (8) in the following form

$$P_{\alpha\beta} = I_{\alpha\beta}F_{\beta\alpha}R_{\beta\alpha}. \tag{9}$$

Experimental Procedure and Apparatus

An experimental test of the adequacy of Eq. (9) for relative intensity measurements has been carried out as follows. X-ray beams of constant relative intensity and different wave-length were obtained by using lines in the L-series spectrum as diffracted by a calcite crystal from an x-ray tube run at constant voltage and current. Observations were taken on the relative ionic saturation currents resulting from these lines when absorbed in an ionization chamber filled in turn with as many different gases as could be conveniently obtained. The corrections of Eq. (9) were applied and the P ratios calculated, with a view to finding out if any variations occurred from gas to gas.

The x-ray tube was of the type previously described by Allison.[4] The equipment for generating the high voltage included a 5 kva 540 cycle generator driven by a 8.5 H.P. synchronous motor with a small d.c. exciter connected in the same shaft. This low voltage 540 cycle current was stepped up to x-ray voltages in an appropriate transformer, rectified by kenetrons, and smoothed by a condenser of 0.1 microfarad capacity. The high voltage could be read directly from a specially constructed electrostatic voltmeter, the smallest division on the scale of which corresponded to 297 volts in the region between 30 and 40 kv. Half of a division could easily be read so that at 30 kv the voltage could be kept constant to 150 volts or 0.5 percent. The calculated ripple was 0.3 percent at 5 m.a. and 30 kv.

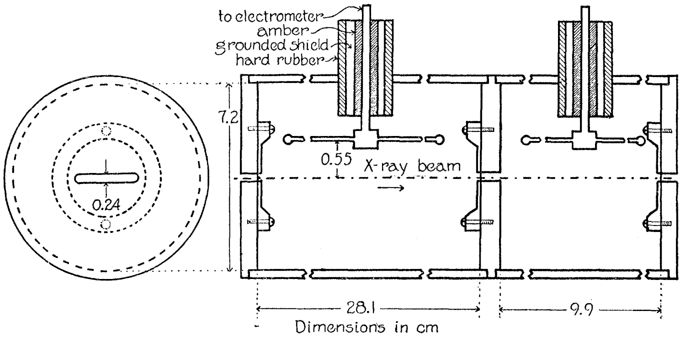

Fig. 1. Diagram of apparatus.

The x-ray beam left the tube through an aluminium window 1.65×10^{-3} cm thick. Its angular divergence was limited by two slits, 25.4 cm apart and each 0.0114 cm wide so that the angular spread of the beam was about 3 minutes of arc. A vertical stop 4 mm high was put in the path of the beam at a point 38 cm from the target of the tube. The distance from the target of the tube to the rear window of the compound ionization chamber was 88 cm. The distance in air traversed by the x-rays before entering the front compartment of the ionization chamber was 37 cm.

The construction of the ionization chamber is of special interest in this investigation, and is shown in Fig. 1. It consisted of two compartments, one

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[4] Allison, Phys. Rev. **30**, 245 (1927), Fig. 1.

behind the other. The front compartment (28.1 cm long) was used to measure the ionic saturation currents. The rear compartment was used to measure the F-values directly, since in some of the cases they could not be computed with sufficient accuracy from the tables of absorption coefficients. The collecting electrodes in the front and rear chambers could be alternately connected to the Compton electrometer used. The rear chamber was filled with methyl bromide gas at about 74 cm pressure throughout the whole period of the experiments. Let i_0 be the ionization current in the rear chamber when the front chamber is evacuated, and i the corresponding current when the front chamber contains the gas to be tested. Then,

$$F \equiv 1 - e^{-\mu l} = (i_0 - i)/i_0 \tag{10}$$

and

$$F_{\beta\alpha} = \frac{(i_{0\beta} - i_\beta)i_{0\alpha}}{(i_{0\alpha} - i_\alpha)i_{0\beta}} \cdot \tag{11}$$

From Eq. (11) it is seen that the F-values were obtained directly from observations of ionization currents, and their values obtained in this way are independent of the accuracy of tables of absorption coefficients, or of measurements of the length of the ionization chamber, or of manometric measurements of the pressure of the gas in it.

The diameter of the chamber must be great enough so that ejected photoelectrons come to the end of their ionizing range within the gas. In the experiments reported here, the longest range photoelectrons were those ejected by the uranium $L\gamma_1$ line (0.6136A) in argon. Information on the length of path may be obtained from results of C. T. R. Wilson.[5] The length of path x is roughly given by

$$x = V^2/b$$

where V is the energy of the electron in kilovolt equivalents, and b is a constant. Wilson's results lead to the value of 4.41×10^2 for b in air at atmospheric pressure if x is in centimeters. b is proportional to the density so that in argon at atmospheric pressure b is 6.1×10^2. The quantum voltage of $UL\gamma_1$ is 20.1 kv, hence if one of the outer electrons of the argon atom is ejected (binding energy negligible), x is 0.66 cm. The diameter of the chamber was 7.2 cm, hence in the most unfavorable case the ionization was confined to a narrow bundle down the axis of the chamber.

The x-ray beam entered the front compartment through a window 0.24 cm wide and 2.54 cm high, covered with cellophane 7.6×10^{-3} cm thick in the case of the tungsten L-series experiments, and with aluminium 1.65×10^{-3} cm thick in the experiments with the uranium L series. The window through which the beam left the front chamber was similar in size to the one previously described and covered with mica 1.3×10^{-3} cm thick. The rear window of the rear compartment was covered with a thicker piece of cellophane and was used in sighting through the chamber to adjust it relative to the spectrometer.

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[5] Reported in A. H. Compton, X-rays and Electrons p. 256.

The chamber was constructed of brass, which was nickel plated inside to reduce chemical action with the gases. The collecting electrodes were steel rods 1.59 mm in diameter; the length of the rod in the front chamber was 24.8 cm, so that its ends were roughly 1.6 cm from the ends of the front compartment. Connection to these collecting electrodes was made through amber insulators set in through the walls of the chamber and protected by grounded guard rings in the usual manner. The entire walls of the chamber were charged to 277 volts. Between 177 and 277 volts the ionization currents obtainable from a constant x-ray input did not vary by more than 0.5 percent, hence it was judged that saturation had been reached.

A Compton electrometer, mounted over the axis of the spectrometer, was used. The electrometer had a sensitivity of 580 divisions per volt on a scale 96 cm distant. The current through the x-ray tube was adjusted until the strongest line ($L\alpha_1$) gave a rate of deflection of about 8–9 mm per second. The rates of deflection observed varied between this and the base-line rates which were of the order of 0.1 mm per second.

ADJUSTMENTS AND METHOD OF TAKING READINGS

The ionization chamber was mounted on the arm of a Bragg type spectrometer, in such a way that it could be rotated about a vertical axis through its center. The usual adjustments of the ionization spectrometer were made. The x-ray tube was mounted on a carriage which could be moved in a direction perpendicular to the line joining the centers of the slits, and by observing the ionization currents for a constant spectrometer setting during this translation the center of the tube window could be found. It was also desirable that the beam pass through the centers of the ionization chamber slits. This was accomplished by rotating the ionization chamber about a vertical axis through its center until the ionization curves obtained from the front and rear compartments as the chamber was swung about the axis of the spectrometer with the crystal stationary had a common center. When this had been found, the ionization chamber arm was placed at its angular position locked to the crystal table through a set of 2 to 1 gears, so that the chamber necessarily followed the reflected beam. The height of the beam was observed by turning the ionization chamber to the position corresponding to zero glancing angle, removing the crystal, and placing a fluorescent screen behind the rear window of the chamber. The height of the x-ray tube and of the slit limiting the vertical spread of the beam was adjusted until the fluorescent screen showed that the beam left the rear window of the chamber at its center in the vertical direction.

Two different targets were used, tungsten and uranium, and in each case the $L\alpha_1$, $L\beta_1$ and $L\gamma_1$ lines were selected for the test, these being the strongest lines in the three groups of greatest wave-length separation. Before beginning the experiments on tungsten, for instance, the spectrum in the vicinity of these lines was investigated and the angular settings found on the scale of the spectrometer corresponding to the tips of the peaks, and to convenient adjacent points on the base-line of the general radiation. The front chamber was then filled with the gas to be tested and the pressure noted on the manometer. The voltage on the x-ray tube was set to the value adopted for the spectrum in question (30 kv for tungsten, 41.2 for uranium), and the electron current was brought to a value which in preliminary trials had been shown to give adequate ionization currents, as previously mentioned. The collecting electrode of the front compartment was connected to the electrometer, and the ionic saturation currents observed for the base-line near $L\gamma_1$. The spectrometer was then set at an angle 15 seconds of arc less than that which had previously been determined as the peak for $L\gamma_1$, and moved in 15 second steps over the top of the peak. The maximum ionization current observed

TABLE I. *A. Comparison of* $L\alpha_1$ *and* $L\beta_1$ *lines of tungsten.*
$\lambda L\alpha_1 = 1.473\text{A}$
$\lambda L\beta_1 = 1.279\text{A}$

Gas	Pressure	No. of trials	$I_{\alpha\beta}$	$F_{\beta\alpha}$	$R_{\beta\alpha}$	$I_{\alpha\beta}F_{\beta\alpha}$	$I_{\alpha\beta}F_{\beta\alpha}R_{\beta\alpha}$
CH_3I	20.49cm	7	1.614	0.997	1.00	1.609	1.609
CH_3Br	75.00	3	1.623	0.995	1.00	1.615	1.615
Argon	69.43	3	1.715	0.953	1.00	1.632	1.632
SO_2	72.99	4	1.759	0.914	1.00	1.607	1.607
Air	74.30	7	2.421	0.702	.98	1.70	1.66

B. Comparison of $L\alpha_1$ *and* $L\gamma_1$ *lines of tungsten.*
$\lambda L\alpha_1 = 1.473\text{A}$
$\lambda L\gamma_1 = 1.095\text{A}$

Gas	Pressure	No. of trials	$I_{\alpha\gamma}$	$F_{\gamma\alpha}$	$R_{\gamma\alpha}$	$I_{\alpha\gamma}F_{\gamma\alpha}$	$I_{\alpha\gamma}F_{\gamma\alpha}R_{\gamma\alpha}$
CH_3I	20.49cm	7	6.97	0.991	1.00	6.91	6.91
CH_3Br	75.00	3	7.20	0.950	1.00	6.84	6.84
Argon	69.43	3	8.07	0.833	1.00	6.72	6.72
SO_2	72.99	4	8.64	0.791	1.00	6.83	6.83
Air	74.30	7	16.34	0.450	.950	7.35	7.0

TABLE II. *A. Comparison of* $L\alpha_1$ *and* $L\beta_1$ *lines of uranium.*
$\lambda L\alpha_1 = 0.9087\text{A}$
$\lambda L\beta_1 = 0.7185\text{A}$

Gas	Pressure	No. of trials	$I_{\alpha\beta}$	$F_{\beta\alpha}$	$R_{\beta\alpha}$	$I_{\alpha\beta}F_{\beta\alpha}$	$I_{\beta\alpha}F_{\beta\alpha}R_{\beta\alpha}$
CH_3I	20.07 cm	4	3.19	.820	1.00	2.61	2.61
Argon	74.74	3	4.05	.631	.99	2.56	2.53
Krypton	10.10	4	1.65	2.55	.621	4.22	2.62
CH_3Br	14.26	6	2.89	.801	1.15	2.32	2.66

B. Comparison of $L\alpha_1$ *and* $L\gamma_1$ *of uranium.*
$\lambda L\alpha_1 = 0.9087\text{A}$
$\lambda L\gamma_1 = 0.6136\text{A}$

Gas	Pressure	No. of trials	$I_{\alpha\gamma}$	$F_{\gamma\alpha}$	$R_{\gamma\alpha}$	$I_{\alpha\gamma}F_{\gamma\alpha}$	$I_{\alpha\gamma}F_{\gamma\alpha}R_{\gamma\alpha}$
CH_3I	20.07	4	12.8	0.668	1.00	8.56	8.56
Argon	74.74	3	18.6	.463	.98	8.60	8.43
Krypton	10.10	4	6.22	2.04	.675	12.7	7.56
CH_3Br	14.26	7	10.7	.634	1.22	6.78	8.27

was taken as the uncorrected value of the line intensity. This was repeated for the $L\beta_1$, and $L\alpha_1$ lines. By subtracting the base-line readings, a set of I-values was obtained. The electrometer was then connected to the rear compartment, and the same set of readings taken, giving a set of i-values. A set of i_0-values was then obtained by a third repetition of the readings with the front compartment evacuated. From the i and i_0-values, the F-values were calculated from Eq. (11), and thus the IF-values obtained.

RESULTS

The results are shown in Tables I and II. Some remarks on the various processes taking place in the ionization chamber follow.

Tungsten lines in CH_3I.

The wave-lengths of the lines are all between those of the K and L absorption limits of iodine, so that the L-series of iodine (2.5 to 3.2A) was the hardest fluorescent radiation emitted. The scattering is negligible in comparison with the fluorescent absorption. The soft fluorescent rays were all absorbed before reaching the walls of the chamber, hence R is unity, and the P ratios, which in general are IFR, (Eq. (9)), in this case are simply IF.

Tungsten lines in CH_3Br.

The wave-lengths of the lines lie between the K and L-limits of bromine and the situation is similar to the previous case of CH_3I.

Tungsten lines in argon.

The quantum voltage of the lines is sufficient to excite the K-series of argon. Two facts, however, contribute to keep R very near unity. w_k is small, about 0.07, and the argon K-series (about 4A) is highly absorbed on its way to the walls of the chamber.

Tungsten lines in SO_2

The case is somewhat similar to argon in that the sulfur K-series wave-lengths may be excited but as in argon, do not escape to the walls. The scattering coefficient is negligible in comparison with the total absorption coefficient at these wave-lengths.

Tungsten lines in air.

No fluorescent wave-lengths of sufficient hardness to reach the walls are excited. The loss through scattering is appreciable, making R less than 1. See Table III.

In the results with the tungsten spectrum, it is seen that the corrected intensity ratios ($I_{\alpha\beta}F_{\beta\alpha}R_{\beta\alpha}$) are constant to about 1.5 percent, and the $I_{\alpha\gamma}F_{\gamma\alpha}R_{\gamma\alpha}$ ratios constant to within 2.5 percent, in the first four gases. In air slightly higher values are obtained, perhaps due to the uncertainty of the scattering correction. The experimental errors, calculated from the least squares formula as applied to the deviations of the I ratios obtained in various trials, run about 1 percent in the $\alpha\beta$ comparison, and 1.5 percent in the $\alpha\gamma$ ratio, where the weakness of the γ_1 line with respect to the background reduces the accuracy. In air the experimental errors are roughly twice the above, since F becomes an important factor, which cannot be determined more accurately than I. The tungsten lines covered the wave-length range from 1.095 to 1.473A; the measurements could be extended downward to 0.6136A by using the uranium L-series.

Uranium lines in CH_3I.

The conditions here correspond to the tungsten lines in CH_3I. The fluorescent radiation produced is not sufficiently penetrating to reach the walls and scattering is negligible.

Uranium lines in argon.

The K-series of argon can be emitted, but the previous comments on argon still are valid for fluorescence. The scattering becomes appreciable here, hence R is less than 1. See Table III.

Uranium lines in krypton.

Here we have an interesting case where large deviations from the P ratios given by CH_3I and argon would be expected if the theory were inadequate. The K absorption limit of krypton (0.864A), lies between the $L\beta_1$ and $L\alpha_1$ lines of uranium. The gas is practically transparent to $L\alpha_1$ and opaque to $L\beta_1$. This unusual condition makes the F factor large, and greater than 1, whereas in all the other cases it is less than 1. The product IF, listed in column 7 of the tables, may be considered as the ionization current ratio which would be observed if the entire primary beam were absorbed in a chamber of this diameter. In Table II it is seen that in the case of krypton the IF value is farther from the P-value obtained from argon and CH_3I than is the I-value alone. This discrepancy is clearly due to the excitation of fluorescent radiation by the $L\beta_1$ and $L\gamma_1$ lines of uranium, and the escape of this radiation from the regions from which the saturation current is drawn. The calculated R factor, however, is just the correct one to bring the P ratio in line with the other gases, and gives us great confidence in our analysis of the processes occurring in the ionization chamber.

Uranium lines in CH_3Br.

Here again we have a case of unusual interest, in that although all the uranium lines considered lie on the short wave-length side of the bromine K absorption, $UL\alpha_1$ lies within 1 percent of the limit. The wave-lengths are, $UL\alpha_1$, 0.90874A; Br K-limit, 0.91809A. The photoelectrons ejected from the K-levels of bromine by the $UL\alpha_1$ line have a velocity of only 140 volts, whereas the photoelectrons ejected in all the other cases reported here have velocities of a different order of magnitude, ranging from those ejected by the $UL\beta_1$ line from the K level of krypton (2890 volts) to those ejected from the outer layers of the argon atom by $UL\gamma_1$ (20,100 volts). It was at first thought that this experiment would detect a variation of ϵ, if it existed, since ϵ at 140 volts may conceivably be different from ϵ at the higher range specified above. Further consideration, however, showed that a variation of ϵ would have no measurable effect, since the larger part of the ionization is produced by electrons ejected by internal transitions of the second kind. Thus from 100 atoms of bromine ionized in the K shell by the x-ray beam, there appear 100 photoelectrons, each of only 140 volts energy, but from roughly 44 of these 100 atoms there will appear an Auger electron of approximately $(\nu_K - 2\nu_L)$ or 10,200 volts energy, the ionization from which will entirely mask any due to the photoelectrons. Again we find that our correction formulae are adequate to derive from the observed I ratios, P ratios which agree with those obtained in other gases.

The probable error in the experimental determination of the I-values in the uranium spectrum was calculated from the usual formula.[6] This gave probable errors of about 1 percent in both the $\alpha\beta$ and $\alpha\gamma$ comparisons. In the F-value determinations, the probable error for $F_{\beta\alpha}$ was about 2 percent; for $F_{\gamma\alpha}$ about 4 percent. The experimental errors in the IF-values, and therefore in the P ratios then should be on the order of 3 percent for the $\alpha\beta$ comparison and 5 percent for the $\alpha\gamma$ ratio. The observed deviations in Table II for the $\alpha\beta$ ratio are within 5 percent, and within 3.5 percent for the $\alpha\beta$ ratio. It may therefore be stated that the deviations in the P ratios are such as may be accounted for by the probable errors in the experimental determinations of the I and F factors.

Some apparently anomalous results were obtained by investigating the uranium lines in the chamber when filled with CH_3Br at 74 cm pressure. Under these conditions the $I_{\alpha\beta}$ and $I_{\alpha\gamma}$ were 2.27 and 6.51, respectively. $I_{\alpha\beta}F_{\beta\alpha}$ was found to be 2.26 and $I_{\alpha\gamma}F_{\gamma\alpha}$; 6.41. The R-values, calculated from the radius of 3.4 cm used in all other cases gave $R_{\beta\alpha} = 1.11$; $R_{\gamma\alpha} = 1.17$, hence P ratios of 2.51 and 7.50 were obtained. These definitely disagree with those of Table II. The explanation of this undoubtedly lies in the fact that r in Eq. (7) is really a function of wave-length and pressure for a given gas. Thus in CH_3Br at 74 cm pressure, 50 percent of $ULα_1$ is absorbed in the first 1.9 cm of path length in the chamber. The effective path length r which fluorescent radiation must travel to reach the walls is clearly less than the radius of the chamber, and different from the appropriate r value for $UL\gamma_1$ rays which penetrate 4.1 cm before being half absorbed. The proper value of r for

TABLE III. *Quantities used in computation of R values.* (*Eq.* (7)).

			τ_i/ρ				f_i			σ/ρ		
Gas	Target	τ_k/μ	$K\alpha_{1,2}$	$K\beta_1$	r/cm	w_k	$K\alpha_2$	$K\alpha_1$	$K\beta_1$	$L\gamma_1$	$L\beta_1$	$L\alpha_1$
Air	Tungsten	—	—	—	3.4	—	—	—	—	0.31	0.34	0.38
Argon	Uranium	—	—	—	3.4	—	—	—	—	0.44	0.51	0.64
CH_3Br	Uranium	0.85	21	15	3.4	0.565	0.298	0.582	0.116	—	—	—
Krypton	Uranium	0.85	30	21	3.4	0.587	0.298	0.582	0.116	—	—	—

Remarks on sources for data:
The value of τ_k/μ was obtained from Richtmyer and Warburton, Phys. Rev. **22,** 539 (1923).
The values of τ_i/ρ were computed from tables in A. H. Compton's "X-rays and Electrons."
w_k was obtained from A. H. Compton Phil. Mag. **8,** 961 (1929).
f_i values were computed from data on the relative intensity of K-series x-ray lines by H.-T. Meyer, Wissenschaftliche Veröffentlichungen aus dem Siemens-Konzern **7,** 108 (1929).
Scattering coefficients were computed for argon and air for the authors by E. O. Wollan of this laboratory from data reported in his paper (Phys. Rev. **37,** 862 (1931)).

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[6] For instance, Birge, Phys. Rev. Suppl. **1,** 1 (1929) p. 5–6.

a given wave-length in this case would be obtained by a rather complicated integration, and has not been attempted, but the deviations are in the right direction to be explained by the effect suggested. This illustrates a pitfall which should be avoided in intensity measurements.

Table III shows the values of the quantities entering Eq. (7) which were used in the calculation of the R-values, and gives the sources from which data were obtained. As a by-product of these experiments, it was possible to calculate the absorption coefficients of the gases used. It must be emphasized again that the validity of the conclusions drawn from these experiments does not depend on the accuracy with which these absorption coefficients are given. (Table IV.) The various gases were obtained from commercial sources and no attempt at purification was made. Although these gases have been widely used in ionization chambers, no data on their absorption coefficients, except for heterogeneous beams, are available.[7]

TABLE IV. *Absorption coefficients of various substances used in intensity measurements.*

λ	μ/ρ							μ	
	CH_3I	Krypton	CH_3Br	Argon	Air	SO_2	Al	Mica	Cellophane
1.473A			51	84	8.3	40	44	123	12
1.279	149		40	55	5.6	28	29		5.5
1.095	106		26	37	3.4	18	20		4.9
.9087	64	24	115	26			10	26	
.7185	34	79	62	13			5.4	13	
.6136	22	59	40	8.9			3.4		

DISCUSSION

From the results given in Tables I and II, we conclude that ionic saturation currents, corrected by the formulae given in this paper, are a reliable measure of the relative intensities of x-ray spectrum lines, even when these lines lie near critical absorption limits of the gas, and excite fluorescent radiation. Measurements of the relative intensities of the L-series lines of uranium at 52.8 kv[8] and of tungsten at 20 kv[9] have been reported. When the results reported here are corrected for the length of path in air and aluminium between the x-ray tube and the ionization chamber, and brought to the voltages used by Allison and Jönsson respectively, agreements within 10 percent are found.[10] The work of Hicks[11] has shown that if agreements to better than

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[7] International Critical Tables, Vol. VI p. 16.

[8] Allison, Phys. Rev. **32**, 1 (1928).

[9] Jönsson, Zeits. f. Physik **36**, 426 (1926).

[10] The present results on tungsten, corrected for absorption in air and in the windows, and expressed at 20 kv instead of the 30 kv at which they were measured, give the $\alpha_1:\beta_1:\gamma_1$ ratios as 100:43.7:9.1; Jönsson found 100:40.8:7.2. The present uranium results, corrected for absorption and brought to 52.8 kv give the $\alpha_1:\beta_1:\gamma_1$ ratio as 100:36.7:10.9; Allison found 100:40.5:9.7.

[11] Hicks, Phys. Rev. **36**, 1273 (1930). Hicks found the relative intensities in the tantalum L spectrum for lines of large wave-length separation to differ markedly from the results obtained

10 percent are to be expected, the coefficient of reflection of the calcite crystal used must be measured for the various wave-lengths. We do not, therefore, wish to stress our results as the relative intensities of the lines until the crystal used has been calibrated.

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by Jönsson in the adjacent element tungsten. Hicks also reports a qualitative trial on tungsten and states that his apparatus gave results similar to his tantalum measurements and disagreeing with those of Jönsson. The measurements reported in this paper support those of Jönsson and correspondence with Dr. Hicks has disclosed a source of error in his measurements which affected the results on lines of large wave-length separation. This error arose from the construction of his ionization chamber, which permitted the absorption of the lines in a layer of gas directly behind the window of the chamber without the ions produced being measured by the electrometer. This same source of error undoubtedly entered in the earlier experiments of Allison and Armstrong also (Phys. Rev. **26**, 714 (1925). This correction is discussed more fully by Dr. Hicks on page 572 of this issue.