

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF THE GENERAL ELECTRIC COMPANY]

## THE CATHODE RAY TUBE IN THE X-RAY SPECTROSCOPIC ANALYSIS OF COLUMBIUM AND TANTALUM

BY GORTON R. FONDA

RECEIVED AUGUST 6, 1931

PUBLISHED JANUARY 7, 1932

A method of analysis using cathode rays was recently developed and applied with success to the analysis of several series of binary alloys.<sup>1</sup> In this method the sample to be analyzed is placed in the open air above the window of a Coolidge cathode ray tube and is excited directly by the electron beam.

This method has now been applied to the analysis of tantalum and columbium mixtures. A Seemann spectroscope was used and a current of hydrogen was passed through it to decrease the absorption of the radiation of longer wave length. The Hevesy method was followed of calibrating against a comparison element. For the analysis of columbium a sodium chloride crystal was used and the K radiation studied. For tantalum the choice was made of the L radiation and in order to record its longer wave length, a crystal was used of beta alumina. This was given us by the Norton Company through the courtesy of Mr. Raymond R. Ridgeway. We are particularly indebted to him for it, since it proved to be very much better than any samples of gypsum available. The lattice spacing on the cleavage face was determined to be 11.00 Å.

The cathode ray tube was operated as before in a vertical position from a regulated DC circuit with a current of 0.2 ma. at 86.0 kv. A jet of hydrogen was played between the window of the tube and the sample. It gave such effective cooling that no change could be observed in the physical condition of the sample nor was there any noticeable evaporation. Repetitions of an exposure upon the same sample gave always the same relative intensities of its constituents.

**Factors Affecting Intensity.**—It is desirable to discuss some general features of the procedure, particularly to bring out the various factors which influence the intensity of the radiation. Exposures involving comparison were made on pieces of film cut from the same strip and their development was carried out together in the same bath.

The position of the sample was important. The window itself had a diameter of 7 mm. In the present experiments the intensity of radiation was increased by placing the edge of the sample 1 mm. from the edge of the window, and by increasing the angle between specimen and window from 10 to 20°, beyond which there was no further advantage.

The radiated spot in the specimen showed a uniform luminescence, as estimated visually, over an area having a width in the horizontal plane of 9 mm. This distribution of electron energy is a distinct advantage, for it checks the heating of the sample. It leads to no loss in efficiency when the Seemann spectroscope is used.

<sup>1</sup> G. R. Fonda and G. B. Collins, *THIS JOURNAL*, 53, 113 (1931).

In this instrument a wedge of tungsten is placed directly above the crystal, so that the distance between them constitutes the slit width. The wedge, crystal and photographic film are part of a fixed system which is rocked as a whole rather than simply the crystal alone. The intensity of the recorded line is not inversely proportional to the rocking angle, as is the case with collimating slits, but depends upon the width of the irradiated area and its intensity distribution. This was demonstrated by recording the intensity of the  $K\alpha$  doublet of molybdenum for several angles, setting the spectroscope each time so that the swing took place with a symmetrical distribution on each side of the critical angle between the crystal and the central point of the irradiated area.

Rocking angle.....	1°	2°	3°	4°	6°
Intensity.....	1.00	0.88	0.71	0.49	0.28

Another factor is the position of the tube. When the intensity from molybdenum was measured with the cathode ray tube in a horizontal position and the molybdenum plate in a vertical position, the irradiated area thereby became such that its maximum dimension lay in a vertical position. Its width was reduced to about 2.5 mm. and this proved to be so important that the intensity fell to 50%. The vertical position of the tube was therefore chosen for all other experiments.

In order to have the maximum intensity available, the slit width was maintained at 0.50 mm. This was insufficient to resolve the  $K\alpha$  or  $L\alpha$  doublets, but there seemed to be no disadvantage in basing a quantitative determination upon the peak of their combined intensity. To reduce the absorption a slow current of hydrogen was passed through the spectroscope. A measure of the improvement is shown in Table I from measurements made on the relative absorption of the  $K\alpha$  doublets of iron and titanium.

TABLE I  
RELATIVE ABSORPTION OF AIR AND HYDROGEN

Element	Wave length, $K\alpha_1$	Absorption, %		Absorption coef. of $H_2$
		In air	In $H_2$	
Fe	1.93	63	4	0.0010
Ti	2.74	94	63	.025

The wave lengths under investigation in the analytical work were all of them below the  $K\alpha$  line of iron and therefore in a range in which absorption was negligible in the presence of hydrogen.

There is another variable factor of influence upon the intensity ( $I$ ) of radiation from the target and that is the voltage ( $V$ ) of the electrons in terms of the excitation voltage ( $V_0$ ). For both  $K$  and  $L$  radiation the relationship holds  $I = k(V - V_0)^2$ . For the lower voltage ranges there is general agreement that  $x$  approximates 2. In the case of aluminum targets upon which the electron beam impinges normally and from which the x-radiation is observed at an acute angle, Lorenz<sup>2</sup> has observed that at higher voltage ratios of  $V/V_0$ , the intensity increases less markedly and finally decreases when the ratio exceeds about 10. The explanation lies in the greater penetration of electrons which occurs as their voltage is increased. As a result proportionately more x-radiation is generated at such greater depths that more material is interposed to its emission and its absorption becomes greater.

Fonda and Collins have shown that, under excitation by a cathode ray tube, the exponent remained 2 up at least to voltage ratios of 4 for molybdenum and 11 for iron, with no indication of a change in slope. These measurements have now been repeated photographically with the same results. Additional measurements have been made with elements whose radiation is of still longer wave length. For the  $K\alpha$  doublet of titanium

<sup>2</sup> Lorenz, *Z. Physik*, 51, 71 (1928).

at 2.743 Å., a value for the exponent of about 1.4 was found for the range in voltage ratio of 8-16. The result remained the same whether the specimen was placed at a 45 or 10° angle and whether a crystal of gypsum or of beta alumina was used. For the K $\alpha$  doublet of calcium at 3.352 Å. about the same slope was obtained at a 10° angle over a range of 9-16. From that point up to a value of 20 the increase in intensity was very much less. This is evidently the same phenomenon which Lorenz observed with aluminum radiation of 8.319 Å. at as low a voltage ratio as 10.

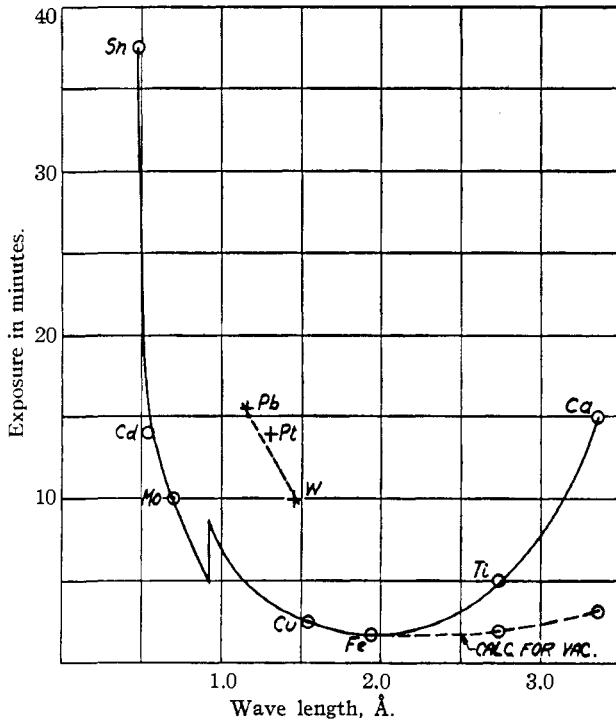


Fig. 1.—Time of exposure required for constant density of  $\alpha$  doublet: —K radiation, - - -L radiation.

The indication is therefore that the eventual decrease in intensity occurs at a voltage ratio which becomes greater as the atomic number of the element involved becomes higher. This is a reasonable consequence of the increase in penetrating power of characteristic radiation which develops as the element emitting it becomes of higher atomic number.

For the L radiation of a tungsten target, placed at a 20° angle to the aluminum window, it was found that the exponent remained definitely 2 over the range in voltage ratio of 4 to 9.

It is helpful to know the variations in time of exposure in hydrogen that are required for the various elements involved. Measurements were made with polished metallic plates and the results for both the K $\alpha$  and L $\alpha$  doublets are shown graphically in Fig. 1 in terms of the time needed to produce the same photographic density of line. The time for columbium is about the same as for molybdenum, and that for tantalum the same as for tungsten, as each of these pairs is of adjoining elements.

The decrease in time of exposure observed up to 2 Å. is due both to the continuous decrease in excitation voltage and to the increasing photographic activity of the film. Beyond iron the absorption even in hydrogen becomes appreciable, and the time of exposure increases.

The dotted curve gives the results as calculated for vacuum. The slight increase for longer wave lengths is undoubtedly due to the diminished effect of high voltages in increasing the intensity of the characteristic radiation from elements of such low atomic number.

The time required to give a moderately strong density for the copper  $K\alpha$  doublet at 86.0 kv. and 0.2 ma. was two and one-half minutes. This is to be compared with the time of one minute cited by Hevesy, Böhm and Faessler<sup>3</sup> for exciting the copper  $K\alpha_1$ ,  $\alpha_2$  lines by secondary radiation at 50 kv. and 20 ma.

A peculiar phenomenon was encountered when the intensity of radiation from a polished plate was compared with that from powder of the same metal. In the cases of the  $K\alpha$  doublet from molybdenum at 0.708 Å., from copper at 1.537 Å. and from iron at 1.932 Å., no difference whatever resulted, despite the wide range of wave length involved. With  $L$  radiation, however, the intensity of the  $\alpha$  doublet from the powder was found to be only 66% that from the plate for the cases of lead at 1.172 Å., and of tungsten at 1.518 Å. The behavior of tungsten trioxide was more nearly normal, for with a target made of it the intensity was 85% that from the polished metal plate.

**Calibration for Columbium.**—It was aimed to have present in a mixture sufficient of a comparison element so that a characteristic line in its spectrum might have the same density as one of the elements under analysis. The molybdenum  $K\alpha$  doublet was chosen as the basis of comparison. As molybdenum is of adjacent atomic number to columbium, there were no complicating features. The combined effect of several characteristic factors was to increase the relative intensity of the columbium by about 2%.

The columbium oxide used was a Fansteel product and was found spectroscopically to be free of tantalum to less than 2%. This was mixed with metallic molybdenum powder. For equality of density of both lines the relation was found to hold that 1 g. of molybdenum is equivalent to 0.949 g. of columbium. With molybdenum oxide as the source of the comparison element, about the same factor resulted. The crystal of alumina gave the same relationship of intensities in both the first and second order as the crystal of sodium chloride, but the latter was used in all quantitative work. The relationship remained the same on adding an amount of  $FeO$  equal to that of the  $Cb_2O_5$  and also an amount of  $WO_3$  equal to four times the weight of the  $Cb_2O_5$ . Zirconium, which in appreciable amounts would have had an effect, was rarely encountered, and then in amounts no larger than 1%.

Comparison was also made with columbium carbide. The factor obtained was 0.936, virtually the same as with the oxide. This result is in accord with those experiments in which the intensity of  $K$  radiation was found to be the same, independent of the physical condition of the metal.

**Calibration for Tantalum.**—The  $Ta_2O_5$  used for calibration was a

<sup>3</sup> Hevesy, Böhm and Faessler, *Z. Physik*, **63**, 74 (1930).

Fansteel product and was found to be free of columbium to less than 0.1%.

The crystal of beta alumina required for the relatively long wave length involved had the curious characteristic of recording a shadow on the short wave length side of the line, a phenomenon undoubtedly due to excessive penetration of the crystal by x-radiation with corresponding reflection from layers of atoms at abnormal depths. This prevented the use of tungsten as a comparison element. The second order  $K\alpha$  doublet of molybdenum was sufficiently remote to be free of this difficulty. The density of the general radiation serving as a background to the two lines was found to be constant, within the limits of measurement, over the range covered by them. Equal density of line resulted from a mixture containing 1 g. of molybdenum to 0.656 g. of tantalum.

The  $K\alpha_1$  line of molybdenum at 0.708 Å. is so remote from the absorption edge at 1.252 Å. of the tantalum  $L_1$  radiation that excitation should be negligible. This was demonstrated by finding that the relative densities of the two lines remained unaffected (1) on adding an amount of  $Cb_2O_5$  equal to 1.12 the weight of  $Ta_2O_5$ ; and (2) on diluting the mixture with alumina equal in weight to 60% of the  $Ta_2O_5$  content.

Tantalum is generally accompanied in its ores by iron. In the presence of sufficient iron the tantalum  $L\alpha$  line at 1.518 Å. is reduced in intensity as the result of absorption of its radiation by iron, the absorption edge of whose K radiation is at 1.740 Å. The calibration of  $Ta_2O_5$  with molybdenum in the presence of FeO is given in Table II and is shown graphically in Fig. 2. There is given also the relationship for equality of the  $K\alpha$  doublet of iron and the second order  $K\alpha$  doublet of molybdenum, to be used as a guide in estimating the amount of iron present.

TABLE II  
RELATIONSHIP FOR EQUAL DENSITY OF LINE IN  $Ta_2O_5$ -FeO MIXTURES

$Ta_2O_5$ , %	FeO, %	G. of Ta equivalent to 1 g. of Mo	G. of Fe equivalent to 1 g. of Mo
48.7	51.3	..	0.235
48.9	51.1	0.790	..
62.1	37.9	.705	.246
77.0	23.0	.674	.270
100.0	0	.656	..

This relationship can hold only for fairly high concentrations of  $Ta_2O_5$  and FeO, as was demonstrated by diluting the mixture containing 62.1%  $Ta_2O_5$  and 37.9% FeO with an amount of alumina equal to five times the weight of the  $Ta_2O_5$ , so that the percentages were reduced to 20.7%  $Ta_2O_5$  and 12.6% FeO. A test upon it showed that equal density of line resulted for the proportion of 1 g. of molybdenum to 0.649 g. of  $Ta_2O_5$ , about the same value found in the absence of iron.

A similar calibration was carried out between molybdenum and tungsten, the element adjoining tantalum. Equal density of line resulted for the mixture containing 1 g. of molybdenum to 0.655 g. of tungsten. For the same atomic percentage this is equivalent to 0.647 g. of tantalum, about the same as found directly. This is a desirable confirmation of the calibration for tantalum, for no complete analysis of the  $Ta_2O_5$  had been made. Very pure tungsten oxide is obtainable and the close agreement would indicate that the  $Ta_2O_5$  also is of a high purity.

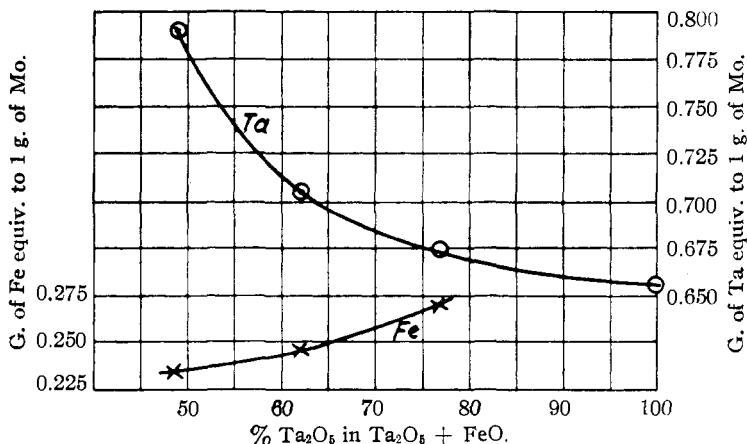


Fig. 2.—Effect of iron upon calibration for tantalum.

It has already been noted that the intensity of the  $L\alpha$  doublet of tungsten is lower for metal powder than for oxide powder. This indicates that the intensity from a metal depends upon the element with which it is combined in a compound. A calibration carried out with the carbide showed that its L radiation is less than that observed from the oxide. The extent of the reduction is the same for tungsten as for tantalum. Table III shows the relationship in terms of molybdenum as the comparison element. It is noteworthy that the intensity of radiation from tantalum becomes less as the density of packing of the metallic atoms becomes greater and also as the angle of the sample is decreased. The intensity of the  $K\alpha$  doublet of molybdenum remained the same at both angles.

TABLE III  
DEPENDENCE OF CALIBRATION UPON NATURE OF COMPOUND

Metal	Angle of sample	G. of metal equivalent to 1 g. of Mo		
		Element	Carbide	Oxide
Tungsten	20°	1.17	0.946	0.655
Tantalum	20°	..	.938	.655
Tantalum	45°	..	.73	.50

These observations are so unusual that further experiments were made to test their validity, choosing for study the difference between the intensity

of the  $L\alpha$  doublet from tungsten as metal and as oxide. This difference was found to persist (1) when the source of the oxide was oxidized metal; (2) when dry mixtures were rubbed on filter paper without the use of paste; (3) when the oxide was tested in a jet of air instead of hydrogen; (4) when the metal was mixed with 16% boric acid by weight (71% by volume) to reduce its density; (5) when  $MoO_3$  or  $Ta_2O_5$  was used as the source of the comparison element, instead of metallic molybdenum; (6) when the voltage was reduced from an electron velocity of 80.4 kv. to one of 39.5 kv. In all of these cases the relative intensities of the  $\alpha_1$  and  $\beta_1$  lines remained unaltered. It would seem then that the differences observed for tungsten and tantalum in the intensity of their L radiation as dependent upon the character of the compound represent an inherent feature of their radiation and are not due to accidental causes. The matter is being pursued further.

### Results

This spectroscopic method has been used in the analysis of ores and oxides, both in their original state as well as in products obtained during their purification and separation. In practice analyses have been made on amounts of  $Ta_2O_5$  from 0.8 to 89% and on  $Cb_2O_5$  from 0.1 to 26%. The time of exposure depends upon the amount of the element present. For the proportions mentioned it has varied from twenty minutes to three hours.

The error in analysis is probably about 2%. This is an absolute error so that the greater value attaches to the determination of small amounts. In three cases the mixtures of oxides examined were free from foreign material. Their analysis is therefore of interest because the sum of the  $Ta_2O_5$  and  $Cb_2O_5$  found indicates directly the accuracy attainable. Separate determinations were of course made for each. The results are given in Table IV. In the case of one mixture, an opportunity was presented to compare the results of the spectroscopic examination with those obtained by a chemical analysis carried out through the courtesy of Professor H. C. Fogg of the University of New Hampshire, using the Marignac method<sup>4</sup> with modifications introduced by himself. Through him and Professor Daggett of the same institution, an analysis was made of mixture No. 3. The results are in surprisingly good agreement.

TABLE IV  
ANALYSIS OF PURE OXIDE MIXTURES

Method of anal.	Sample	$Ta_2O_5$ , %	$Cb_2O_5$ , %	Total, %
Spectroscopic	No. 1	80.7	21.2	101.9
Spectroscopic	No. 1	80.7	21.0	101.7
Spectroscopic	No. 2	75.0	24.0	99.0
Spectroscopic	No. 3	77.0	19.5	96.5
Chemical	No. 3	76.5	19.3	95.8

<sup>4</sup> Marignac, *Ann. Chim. Phys.*, **8**, 60 (1866).

Mixture No. 1 was the result of a chemical separation from an ore of the combined oxides of tantalum and columbium. It was carried out through the kindness of J. H. Christopher of this Laboratory. The yield amounted to 62.5% so that the analysis of the oxides corresponds to a content in the ore of 50.5%  $Ta_2O_5$  and 13.2%  $Cb_2O_5$ . Direct analysis of the ore yielded the values of 50.3%  $Ta_2O_5$  and 12.2%  $Cb_2O_5$ . Such good agreement is of importance. It demonstrates that the intensity of the tantalum and columbium lines, as registered in oxides, is not disturbed when the metals are present in a tantalite as acid salts. This is in agreement with the conclusion of Hevesy and Böhm,<sup>5</sup> who failed likewise to find any difference in calibration as dependent on the occurrence of tantalum in the oxide or in the ore.

Before closing the author would like to express his appreciation of stimulating conversations with Dr. W. P. Jesse.

#### Summary

1. Further experiments have been made with the Coolidge cathode ray tube as a means of exciting x-radiation.
2. The variation of intensity of spectral lines has been studied as related to operating conditions and to the element examined.
3. Calibration and analyses have been carried out for tantalum and columbium in tantalites and mixtures of oxides and carbides. Molybdenum was used as a comparison element.
4. For the limited number of elements examined, differences in intensity of the  $L\alpha$  doublet were found to exist depending upon the nature of the chemical compound and upon the angle of the specimen. No similar differences were found in the intensity of the  $K\alpha$  doublet.

SCHENECTADY, NEW YORK

---

<sup>5</sup> Hevesy and Böhm, *Z. anorg. Chem.*, **164**, 69 (1927).