

[CONTRIBUTION FROM THE RESEARCH LABORATORY, GENERAL ELECTRIC COMPANY]

**THE CATHODE RAY TUBE IN X-RAY SPECTROSCOPY AND  
QUANTITATIVE ANALYSIS**

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The methods of x-ray spectroscopy have for several years proved of value in their application to chemical analysis. The lines in an x-ray series are so few as to obviate the confusion that sometimes arises in the case of the complex arc and spark spectra. Qualitative analysis by means of x-ray spectra is simple and direct. Quantitative analysis, based on measurements of line intensity, involves a knowledge of the influence of several factors upon the intensity. It has been used with well-known success in certain special cases and is capable of general application for elements of higher atomic number than fluorine.

Hitherto two methods have been in vogue that involve excitation. According to the first, the sample to be analyzed is made the target in an x-ray tube, as by rubbing it onto the surface of the anode. It was in this way, for instance, that Hevesy and Coster<sup>1</sup> detected hafnium and the subject has been pursued still more recently.<sup>2</sup>

The second method may be denominated fluorescent, as it involves exciting the x-ray spectra of a sample placed outside of the x-ray tube by allowing radiation from the latter to fall upon it. Experiments with this method have been discussed by Schreiber and by Hevesy, Böhm and Foessler.<sup>3</sup> The latter article is noteworthy for its tables of "comparison elements" which may suitably be added to the sample as a calibrating medium for the analysis of any particular element.

It is the purpose of the present paper to describe a third method according to which the x-ray spectrum of a sample is excited directly by allowing the electrons from a cathode ray tube to impinge upon it as target. The possibility of doing this has been known and a paper has in fact been published showing that it is possible to get sufficient energy from such a tube to allow of recording photographically a spectrum line.<sup>4</sup> Another purpose is to present information on the use of an ionization chamber and a vacuum tube amplifier as a means of registering the spectral lines and recording their intensity. In all quantitative work hitherto which has come to our attention, the lines of the spectra have been recorded photographically and their intensities measured with a microphotometer. We have used this

<sup>1</sup> Hevesy and Coster, *Nature*, **111**, 79 (1923).

<sup>2</sup> Glocker and Schreiber, *Ann. Phys.*, **85**, 1089 (1928); Schreiber, *Z. Physik*, **58**, 615 (1929); Eddy and Laby, *Proc. Roy. Soc. (London)*, **A124**, 249 (1929); **127**, 20 (1930).

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

<sup>4</sup> Eisenhut and Kaupp, *ibid.*, **54**, 427 (1929).

method also, but our description will deal more particularly with the ionization one because of its novelty.

The intensity of a line in an x-ray spectrum is not directly a measurement of the concentration of the element emitting that line, as compared with other elements, even when corresponding lines of the same spectrum are considered. Its relative intensity varies from the following causes. (1) The heating of the sample during excitation may lead to a change in relative concentration due to a greater volatility of one of the constituents.

(2) The reflecting power,  $R$ , of the crystal used as a grating varies with the wave length of the individual lines as expressed by the formula for sodium chloride<sup>5</sup>

$$R = 6.757 \frac{1 + \cos^2 2\theta}{\sin 2\theta} \lambda^{0.25}$$

where  $\theta$  is the critical angle of reflection for a line of wave length  $\lambda$ .

(3) The intensity,  $I$ , depends also upon the excitation voltage,  $V_0$ , of the series to which the line belongs, according to the relationship  $I = \text{const.} (V - V_0)^k$ , where  $V$  is the voltage applied to the impinging electrons and  $k$  is an exponent whose value is 2, at least within a certain range of the exciting voltage.<sup>6</sup>

(4) Absorption by whatever media lie between the source of the x-rays and the ionization chamber or photographic film.

(5) Excitation of one element by another takes place if there is present in appreciable extent a second element of neighboring atomic number, one of whose lines is of shorter wave length than the absorption band of the first element. In this case the line of the first element is intensified and that of the second element is of course weakened as a result of its absorption.

(6) In the case of fluorescent radiation, the more remote an element is in wave length from that of the exciting radiation, the weaker will be its intensity.<sup>7</sup>

(7) The relation between intensity and blackening of the film enters, if the recording of intensity be done photographically. This depends upon the extent of absorption and accordingly upon the wave length.<sup>8</sup>

The simplest case for analytical treatment by x-rays is that of a binary alloy whose metals are of adjacent atomic number. Mutual excitation is absent and the other causes of variation in intensity enumerated above may be made so small under proper choice of conditions that corrections for them can safely be applied despite some uncertainty in their exact magnitude. In other cases the Hevesy method can be used by adding a

<sup>5</sup> Wagner and Kulenkampff, *Ann. Physik*, **68**, 369 (1922).

<sup>6</sup> Lorentz, *Z. Physik*, **51**, 71 (1928).

<sup>7</sup> Compton, *Phil. Mag.*, **8**, 961 (1929).

<sup>8</sup> Dorgelo, *Physik. Z.*, **26**, 756 (1925); Glocker, *Z. Physik*, **43**, 827 (1927).

comparison element. This involves a preliminary calibration of synthetic mixtures of the element to be analyzed.

In the case of routine analyses of similar mixtures in which the ratio of two constituents varies, the addition of a comparison element is not necessary, a simple calibration to show the relation between intensity and composition being sufficient.

In the use of the cathode ray tube or the fluorescent method, there is the advantage that the sample may simply be exposed to radiation from an exciting tube. This saves the time of introducing it to a tube and also makes it possible better to cool the sample.

### Cathode Ray Tube and High Voltage Equipment

The cathode ray tube used was of the type developed by Coolidge<sup>9</sup> but considerably smaller than that described by him. Its aluminum window of special design had a minimum thickness of 0.013 mm. and a diameter of 6 mm., and was soldered to the opening in the anode arm. Due to its small diameter, a support was unnecessary. It was designed and constructed by Mr. George Hotaling of this Laboratory and we are indebted to him for supplying us with it.

It was evacuated continuously with a mercury condensation pump to assure maintenance of a satisfactory vacuum. It is hoped that eventually these tubes can be sealed off at a good vacuum during manufacture. The window was water cooled.

The tube was operated in a vertical position, with the window uppermost and the sample placed above it at an angle of 10° to the surface of the window, an angle that was found to give the maximum intensity of x-rays in a horizontal direction. The energy of the cathode rays was sufficient to heat the sample considerably. To reduce this and at the same time to prevent oxidation of the sample, a jet of hydrogen was played over it. When the sample was a metal plate, its temperature in a current of hydrogen did not rise above about 60° under bombardment at 85 kv. and 0.2 ma., the operating conditions during an analysis. When cadmium iodide, whose boiling point is 710°, was used as the sample and bombarded at 88 kv. in air without cooling, it sublimed in heavy clouds at 0.4 ma., slightly at 0.3 ma. and imperceptibly at 0.25 ma. It is readily possible, of course, to use much more rigid cooling wherever desired, such as cooling water or ice or liquid air placed upon the sample.

The tube was operated by a high voltage d. c. outfit to avoid heating of the window under a. c. operation by electrons of too low velocity to contribute to excitation of x-ray spectra. The circuit used is shown diagrammatically in Fig. 1: 60-cycle regulated a. c. at 110 v. was supplied from a control transformer. A 1:1 transformer, whose secondary was insulated for 100 kv., supplied an x-ray high voltage transformer, with middle points of windings connected, resting on porcelain insulators 40 cm. high. The output from

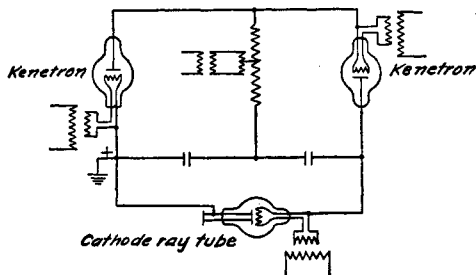


Fig. 1.—Diagram of high voltage set.

<sup>9</sup> Coolidge, *J. Franklin Inst.*, 202, 693 (1926).

this was shared between two kenetrons supplying a bank of fourteen condensers, each of 2.5 mf. capacity and capable of standing about 7000 v.<sup>10</sup> The voltage delivered to the cathode ray tube is double that coming from the x-ray transformer as the current is alternately rectified by each kenetron and delivered to one-half of the bank of condensers. The function of the latter is to deliver a current of nearly uniform voltage—the capacity of each half being such that it may deliver energy to the tube without appreciable voltage drop during the half cycle when the rectified current is being delivered to the other half of the condensers.

The filament of the kenetron on the grounded side was lighted by a transformer of low voltage insulation; the filaments of the other and of the cathode ray tube were necessarily operated by transformers whose secondaries were insulated 100 kv. above ground.

To assure uniformity of voltage distribution along the condensers, the terminals of each were connected to a resistance of 23 megohms. This was constructed in the following manner. A long glass tube 2 cm. in diameter was filled with a solution of 1 part of grain alcohol to 2.5 parts of xylol, and wire terminals sealed into it every 12 cm. were connected to the condenser terminals. The high voltage set was calibrated with 6.25-cm. brass spheres.<sup>11</sup>

**Experiments with Ionization Chamber.**—The spectrometer was made of brass in the laboratory machine shop. Reflection was from the 100 plane of a sodium chloride crystal which could be rotated by an arm about the center of a circular table, 12.5 cm. in diameter, graduated in degrees. Another arm extended 20 cm. beyond the table and carried a box containing the ionization chamber and the amplifying units. A vernier attachment allowed the crystal to be set at four minute intervals. The crystal was chosen from several specimens of halite, after many had been rejected because of surface irregularities which were either manifest to the eye or else sufficient to give distorted intensity curves.

A slit, kept at a width of 11 mm., was placed at the opening of the ionization chamber, at a distance of 12 cm. from the center of rotation. The collimating slits, whose opening was varied from 0.3 to 0.9 mm., were placed 4 and 12 cm. from the axis of the spectrometer. The front slit was 3.5 cm. from the axis of the cathode ray tube.

The brass ionization chamber was made of two concentric cylinders of 1-mm. material, 20 cm. long. The inner one served as one electrode and had a section of a cylinder soldered to the bottom. All connections to it were insulated with hard rubber. The other electrode was a 3-mm. rod with amber insulation, directly connected to the control grid. Aluminum foil, 0.015-mm. thick, was cemented across the opening.

The chamber was filled with methyl bromide. In the absence of leaks, its performance was consistent for weeks at a time. The chamber was large enough to allow of complete absorption of radiation on the long wave length side of the bromine absorption edge.

The amplifying system is shown diagrammatically in Fig. 2. The basis of it is the new four-element vacuum tube, FP-54, characterized by a very high input resistance. The operation<sup>12</sup> of it and of the amplifying system is based upon the facts that x-rays entering the ionization chamber produce an ionization current proportional to their in-

<sup>10</sup> A brief outline of this system is given in Glocker, "Materialprüfung mit Röntgenstrahlen," p. 28, 1927, and a discussion of the condenser requirements can be found in Hull, *Gen. Elec. Review*, 19, 173 (1916).

<sup>11</sup> Peek, "Dielectric Phenomena in High Voltage Engineering," 1915, p. 89.

<sup>12</sup> Metcalf and Thompson, *Phys. Rev.*, 36, 1489 (1930); Nottingham, *J. Franklin Inst.*, 209, 287 (1930), gives a helpful discussion of similar amplifying systems, although based on three-element tubes.

tensity and that this ionization current determines the potential of the control grid of the tube. This grid potential affects the plate current and the variations in it are read on a sensitive galvanometer, with the normal initial plate current balanced out by means of an adjustable voltage. Since the characteristic curve of the tube may be considered straight within the range used, the galvanometer deflection may be taken directly as a measure of the relative intensities of the x-rays entering the chamber.

Considerable difficulty was experienced in obtaining a suitable grid resistance. Mixtures of xylol and alcohol, copper oxide fused into glass and India ink lines on paper were found to be unsatisfactory. When they were made large enough to give the required sensitivity, they polarized readily. A pencil line on hard rubber was fairly satisfactory, giving galvanometer deflections which were reasonably steady. The best resistance, however, and the one which we used in the tests described here, was one made by Dr. Lewi Tonks of this Laboratory and which he kindly loaned to us. It was made by the distillation of tungsten from a wire upon a glass fiber in an evacuated tube.

The sensitivity of the set may be calculated from a knowledge of the galvanometer sensitivity  $S = 5.5 (10)^{-10}$  amp., the mutual conductance of the tube  $G_m = 21 \mu\text{a.}/V$ , the grid resistance  $R = 3 (10)^{10}$  ohms, the grid voltage  $V_g$ , the grid current  $I_g$ , and the plate current  $I_p$ .

$$G_m = I_p/V_g = S/V_g$$

Since  $V_g = I_g R$ ,  $I_g = S/G_m R = 8.7 (10)^{-18}$  amp. This expression for the sensitivity gives the smallest measurable grid current.

As the high voltage outfit was not enclosed, adequate screening was our greatest difficulty. As the first step, to make the connection from chamber to grid as short, and at the same time as well insulated, as possible, all of the amplifying set, including the vacuum tube and resistances Nos. 5-9, was mounted with the chamber on the movable spectrometer arm in a completely enclosed wooden box lined with tin foil and covered with 2-mm. aluminum sheet and with the side toward the crystal faced with lead 3 mm. thick. The box contained calcium chloride as drying agent. The entire spectrometer was enclosed in a galvanized iron box, open at the top. The upper part of the cathode ray tube, including the window and sample, was enclosed in a lead box open at the bottom and with a small opening opposite the sample.

The flexible connection from the amplifying set to the batteries and galvanometer was enclosed in the metal casing of BX cable. The batteries, insulated on pieces of bakelite, were also enclosed with galvanized iron, and the galvanometer with a tin box. All of the metal protective enclosures were grounded and all connections soldered. Steady conditions in the amplifying system were obtained by allowing it to run for half an hour.

An approximate estimate of the sensitivity of the spectrometer was obtained from an experiment with a copper target. With the tube operating at 85 kv. and 0.2 ma., and with 0.4 mm. slits, the peak of the  $K\alpha$  doublet gave a net deflection of 90 cm. with an accuracy of 0.5 cm. on a scale 2.6 m. distant, corresponding to an ionization current of  $3 (10)^{-13}$  amp.

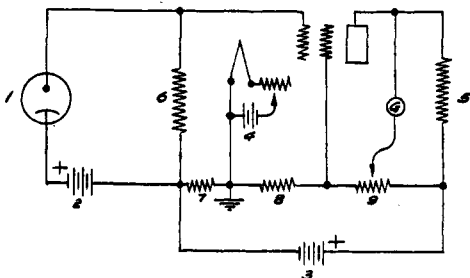


Fig. 2.—Diagram of amplifying set.

1, Ionization chamber; 2, 180-v. B battery units; 3, 12-v. storage battery; 4, 6-v. storage battery; 5, 50,000-ohm. resistance; 6,  $3(10)^{10}$ -ohm. grid resistance; 7-9, 500-ohm. resistances.

Measurements were based on the first order of the K radiation, using the intensity coming from the unresolved  $K\alpha$  doublet. The slit in front of the ionization chamber was kept at an opening of 11 mm., to have assurance that all of the reflected energy would enter the chamber. Actually the chamber could be turned through an angle of  $2^\circ$  for a particular setting of the crystal before a decrease in intensity was noticed. In practice the angle of the chamber was kept at twice the angle of the crystal, being reset for every 30' change in the latter. The curves for intensity against crystal angle were plotted on coordinate paper and the area of the doublet, lying above the continuous radiation, was measured by counting squares, as this method gave greater accuracy than a planimeter.

The loss in velocity of the electrons in passing through the aluminum window was determined by measuring the continuous radiation of tungsten on the short wave length side. The curve expressing the results is given in

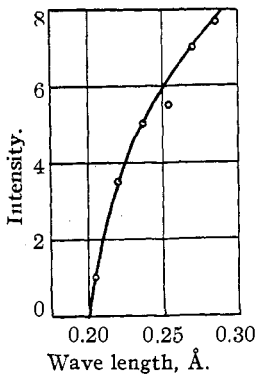


Fig. 3.—Continuous radiation curve for tungsten at 74.7 kv.

Fig. 3. The abscissas are plotted not as angular setting of the crystal, but rather as wave length, in terms of  $\lambda = 5.628 \sin \theta$ . Zero radiation occurs sharply at 0.200 Å., from which the exciting voltage can be calculated as  $V_0 = 12.34/\lambda = 61.7$  kv. As the window produces some straggling, this represents the optimum velocity. The potential applied to the tube was 74.7 kv. Terrill's<sup>13</sup> formula for the loss in velocity in aluminum foil is  $v^2 - V^2 = 1.1(10)^{12}x$ . If this is applied to our case, for a thickness  $x$  of 0.0013 cm. and a primary velocity  $v$  of 74.7 kv., the final velocity  $V$  should be 64.5 kv. For a final velocity of 61.7 kv., that obtained by us, the thickness should be 0.0016 cm. The latter value probably expresses better our effective loss in

velocity, as the thickness of gas contributes to it and also irregularities on the surface of the window, which was made purposely non-uniform.

It seemed important to determine how the intensity of the  $K\alpha$  doublet varies with the voltage, not only to show the changes in the energy available for analytical purposes, but also to get a closer value for the correction factor determining the relation between line intensity,  $I$ , and the difference between the applied voltage,  $V$ , and the exciting voltage,  $V_0$ . This relation was expressed by Webster and Clark<sup>14</sup> for the K series of rhodium as  $I = \text{const.} (V - V_0)^{3/2}$ . Kettmann<sup>15</sup> and Stumpfen<sup>16</sup> found that near the exciting voltage the exponent was 2 for the K series of chromium, copper,

<sup>13</sup> Terrill, *Phys. Rev.*, **22**, 101 (1923).

<sup>14</sup> Webster and Clark, *ibid.*, **9**, 571 (1917).

<sup>15</sup> Kettmann, *Z. Physik*, **18**, 359 (1923).

<sup>16</sup> Stumpfen, *ibid.*, **36**, 1 (1926).

molybdenum and silver, but decreased for higher voltages. Lorentz<sup>6</sup> studied carefully the K series of aluminum and found that the exponent was 2 up to double the exciting voltage, decreasing thereafter up to about nine-fold the exciting voltage; from that point on the intensity itself decreased.

We have made intensity measurements at 0.2 ma. on molybdenum up to four-fold the exciting voltage and on iron up to eleven-fold. In both cases the exponent remained 2 throughout the range, and there was no evidence of reaching an optimum value. The data are given in Table I. In calculating the exponent it was of course necessary to use values of the voltage which are characteristic of the optimum electron velocity at the target. This was done by means of the Terrill equation, using  $x = 0.0016$ , and is expressed in the table as "electron velocity,  $V$ ."

The results are shown in the curves of Fig. 4. To show the extent to which they justify an exponent of 2, the intensity is plotted in Fig. 5 on log paper against  $V - V_0$ , using values for  $V_0$  of 19.9 for molybdenum and 7.1

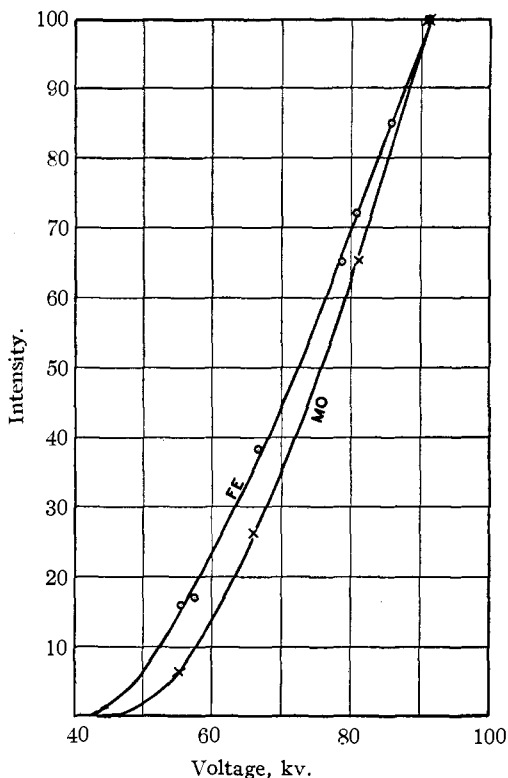


Fig. 4.—Variation of intensity with voltage for  $K\alpha$  doublet of iron and molybdenum.

TABLE I  
EFFECT OF VOLTAGE UPON INTENSITY OF  $K\alpha$  DOUBLET

Applied voltage, Kv.	Electron velocity, $V$	Intensity $K\alpha$ Doublet	
		Mo	Fe
90.8	80.4	100.0	100.0
85.7	74.6	..	85.0
80.8	69.0	65.4	71.9
78.7	66.6	..	65.0
66.6	51.7	..	38.0
65.8	50.8	26.4	..
57.5	39.3	..	17.0
55.2	35.9	6.4	15.8

for iron. The exponent is calculated from the slope of the curves to be 2.03 for molybdenum and 1.97 for iron, with no evidence of decreasing to lower values.

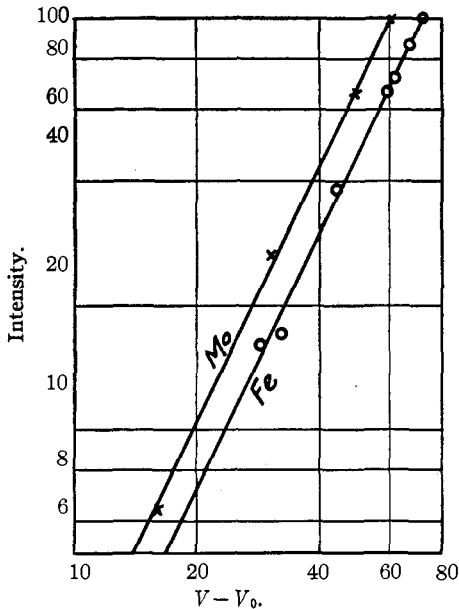


Fig. 5.—Variation of intensity of  $K\alpha$  doublet with  $V - V_0$ .

About one hour was required for such an examination of a binary alloy. In some of the cases a further check was made by repeating the run on a different day, generally on a fresh surface of the sample. This is denoted in the tables by a separate entry.

In all cases the alloys had a polished surface and for the most part were in flat pieces which had been rolled down from stock. The composition was determined by chemical analysis which was kindly carried out for us by Dr. Dorothy H. Brophy of this Laboratory.

No high degree of accuracy

This distinction from the results of others whose experiments were with x-ray tubes may be due to the presence of a certain range of velocity in the beam coming from the cathode ray tube. At a low voltage it would accordingly excite a smaller intensity of radiation than would the electrons of uniform velocity in an x-ray tube. As the voltage increases, the difference would lessen.

The variation in intensity with current is shown in Fig. 6 for the case of the  $K\alpha$  peak of molybdenum.

In the analytical work the cathode ray tube was operated at 85 kv. and 0.2 ma. The measurements were checked by repeating a run, either in whole or in part.

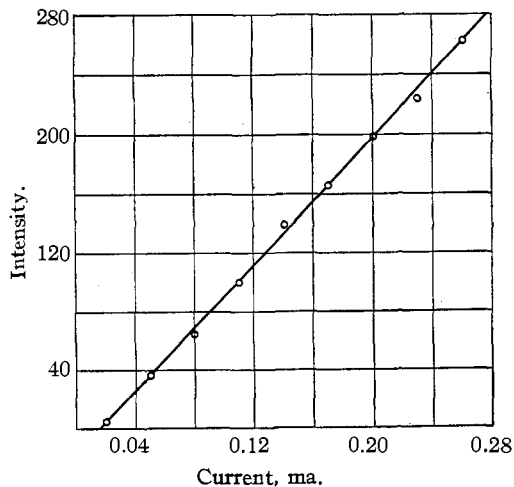


Fig. 6.—Variation of intensity with current for peak of  $K\alpha$  doublet of molybdenum.



is claimed for the results found, for the aim was rather to explore the possibilities before spending too much effort in refining features of the apparatus. One of its weak features was the crystal. As already mentioned, several were discarded during preliminary work. The final one used in these ex-

TABLE II  
RELATION BETWEEN COMPOSITION AND INTENSITY OF  $K\alpha$  RADIATION FOR ALLOYS OF ADJACENT ATOMIC NUMBER; SLITS SET AT 0.30 MM.

Alloy	Composition, atomic, % Cu	Intensity, % Cu
Copper-zinc	64.5	64.6
Copper-zinc	64.5	64.4
Copper-nickel	4.8	6.1
Copper-nickel	29.1	33.1
Copper-nickel	64.7	65.6
Copper-nickel	94.1	93.7

periments was not above reproach. Indeed in going over the curves after the work had been completed, it was noticed that in some of them there was still present a slight distortion at the base of the  $K\alpha$  doublet and that the results from these showed rather poor agreement under repetition. By chance, however, the setting of the crystal had been slightly altered at one time and the results obtained thereafter appeared more reasonable and are the ones reported below.

The results on two binary alloys whose constituents are adjacent in atomic number are given in Table II. These represent the simplest cases, as mutual excitation is absent.

A typical curve from which the areas denoting intensity were measured is shown in Fig. 7. In all of them equally smooth curves could be drawn through the points denoting the observations. The angular settings noted are purely relative. Actually in all cases the angles corresponding to the peaks of the curves were found to give with reasonable accuracy the values of  $\lambda$  for the  $K\alpha_1$  and  $K\beta_1$  lines. In Fig. 8 is given a curve showing for the copper-nickel

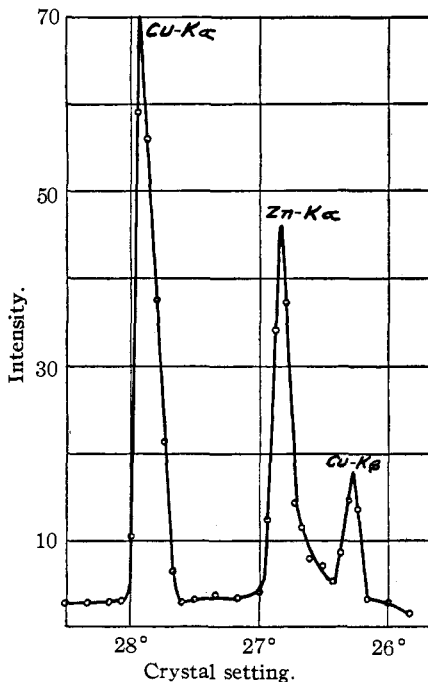


Fig. 7.—Intensity curves for copper-zinc alloy containing 64.5 atomic per cent. of copper; slits, 0.30 mm.

alloys the relation between composition and relative intensity. Theoretically, the latter should be proportional to the atomic per cent. Actually, the effects of crystal reflectivity and of absorption by air and chamber window act to increase slightly the relative intensity of the radiation from the elements of higher atomic number. It is for this reason that in the copper-nickel alloys the relative intensity of the copper radiation runs somewhat high. The curve of Fig. 8, however, is typical of a calibration curve which could be used in analyzing an unknown. For the same reason,

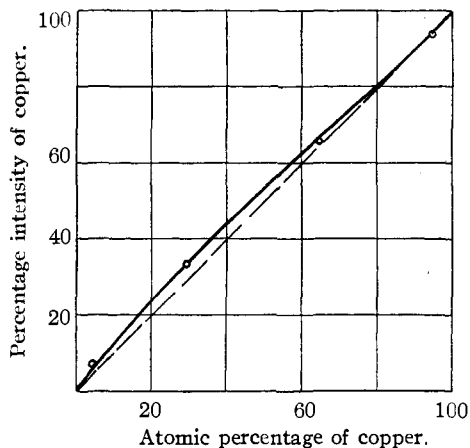


Fig. 8.—Relation between intensity of  $K\alpha$  doublet and composition for copper-nickel alloys.

the relative intensity of the copper radiation from the copper-zinc alloy should be lower—the values obtained in our analysis are therefore somewhat too high.

The other case for which mutual excitation should be absent occurs for two elements whose atomic numbers are remote. Molybdenum and iron were selected and three different compositions were examined. Unfortunately, they had been made up in small samples and bad segregation had evidently occurred. Simply a resetting of the sample led to a different relationship of intensities, al-

though for any one setting good agreement was found on repetition. The results are, therefore, of no value analytically, but they are given in Fig. 9 for an alloy to which 9.3 atomic per cent. of molybdenum had been introduced, to show the differences for the two  $K\alpha$  doublets. That of iron is of such long wave length, 1.932 Å., that the continuous radiation in its neighborhood is very low, whereas that of molybdenum at 0.708 Å. is near the peak in the continuous radiation curve. The intensity of the molybdenum radiation is essentially very much greater than that of iron for equal amounts of each because of its higher reflection from the crystal and greater transmission of the air and chamber window.

As illustrative of the case in which strong mutual excitation is present, the iron-nickel alloys were chosen. The  $K\alpha_1$  line of nickel is at 1.654 Å.,

TABLE III

RELATION BETWEEN COMPOSITION AND INTENSITY OF  $K\alpha$  RADIATION FOR IRON-NICKEL ALLOYS; SLITS SET AT 0.90 MM.

Composition atomic, % Fe....	91.7	91.7	64.8	64.8	55.5	22.6	5.9
Intensity, % Fe.....	87.8	87.7	67.8	68.4	60.8	26.6	6.9

just within the absorption edge of iron, 1.738 Å., at which its K radiation is excited. The results are given in Table III.

A typical set of curves is shown in Fig. 10 and the relation between all of the alloys is given in Fig. 11. The situation is rather complicated. The effect of crystal reflectivity and of absorption is to decrease the intensity of the iron, but for all alloys containing less than 80 atomic per cent. iron, the predominating effect on the intensity is the excitation produced by the nickel, accompanied, of course, by a partial absorption of the nickel

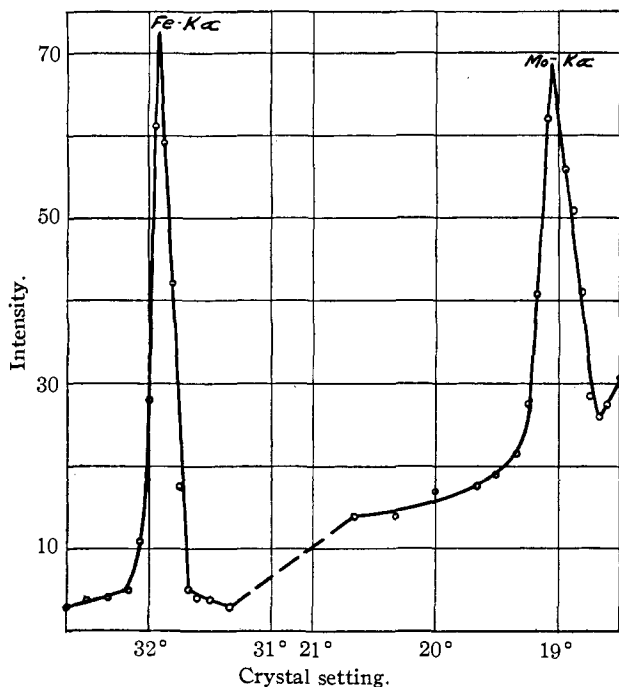


Fig. 9.—Intensity curves for molybdenum-iron alloy; slits, 0.40 mm.

radiation by the iron. In general, one would not expect this effect to be appreciable for small amounts of nickel. On applying the corrections for the first two effects and for that of voltage to the alloy containing 91.7 atomic per cent. iron, a value of 91.9% was obtained from the relative intensities.

**Experiments with Photographic Recording.**—Some experiments were also carried out on binary alloys with a Seemann spectrometer, using a crystal of sodium chloride and a wedge placed above it to form the slit. The opening of the spectrometer was placed 2–3 cm. from the window of the cathode ray tube, and the sample as before was right above the window, making a 10° angle with it.

The density of the lines on the film was measured for us by Mr. F. Ben-

ford of this Laboratory by means of a mercury lamp with a Fabry and Buisson microphotometer.

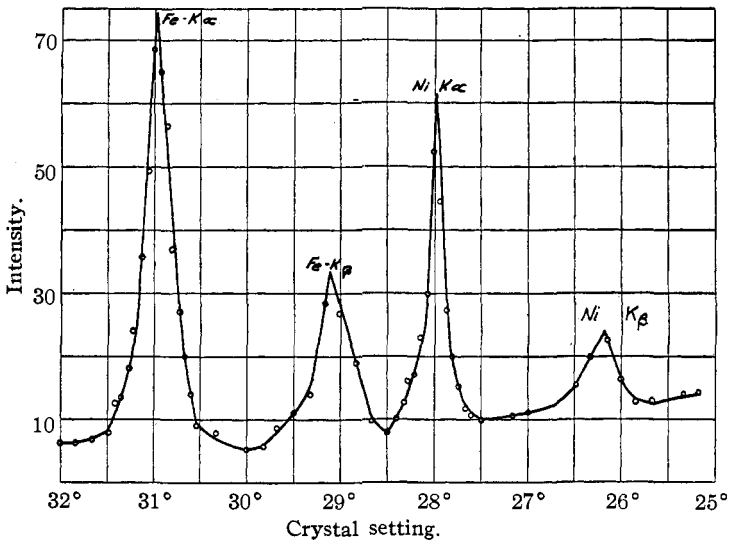


Fig. 10.—Intensity curves for iron-nickel alloy containing 64.8 atomic per cent. of iron; slits, 0.90 mm.

With the cathode ray tube at 88 kv., experiments were made with various polished binary alloys. For those containing about equal parts of metals of adjacent atomic number, silver and cadmium and tin and anti-

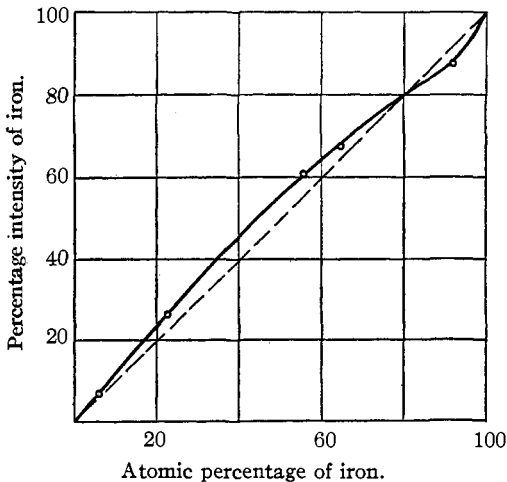


Fig. 11.—Relation between intensity of  $K\alpha$  doublet and composition for iron-nickel alloys.

mony, the spectrometer was oscillated over a  $3^\circ$  angle. At a slit width of 0.05 mm., sufficient to resolve the  $K\alpha$  doublet, the time of exposure to attain a line density in Briggs logarithms of 0.4 was eighty minutes at 0.3 ma. and 110 minutes at 0.2 ma.; with a slit of 0.50 mm., the time was reduced to forty and sixty minutes, respectively. For a single element the time required to attain the same density was sixteen minutes, using a  $1^\circ$  oscillation, a slit width of 0.05  $m\mu$  and a current of 0.2 ma.

Tests were made with the pure metals for various times to get the relation between photographic density and intensity of x-radiation, and also the relative photographic activity of the different metals. Applying this correction and the small ones for the reflecting power of the crystal and the voltage effect, a value of 59.6 atomic per cent. silver was found for a silver-cadmium alloy containing 60.2 atomic per cent., and 49.2 atomic per cent. of tin for a tin-antimony alloy containing 49.4 atomic per cent.

### Conclusion

The ionization method as applied to our present apparatus was capable of detecting qualitatively about 0.5% of an element, and quantitatively 3% or more. The apparatus as described is of a preliminary nature, but it serves to show the possible scope. Even with the present cathode ray tube, some simple and obvious changes would add greatly to the effective radiation. One is operation of the tube in a horizontal position so that the excited portion of the sample would have the shape of a vertical slit, thus introducing about three-fold more energy to the chamber. Another is operation at higher voltage.

The limit of sensitivity for the amplifying set likewise is many-fold greater than for that employed by us. Even the present one would be applicable for use with the x-ray tubes described by others for quantitative work, where the energy available is so great that very much smaller percentages could be detected.

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### Summary

1. The use of a cathode ray tube is described for exciting x-radiation of samples placed before its window, and also the use of an ionization chamber and an amplifying system for recording the intensity.

2. The variation in the intensity of the  $K\alpha$  doublet for Mo and Fe is shown to follow the relation  $I = c(V - V_0)^2$ , up to a voltage four-fold that of  $V_0$ , the exciting voltage for Mo, and eleven-fold for Fe. The exponent accordingly remains constant over a greater voltage range than has been observed in x-ray tubes.

3. The application of the cathode ray tube to the quantitative analysis of alloys is shown by both the ionization and the photographic methods.