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**THE X-RAY SPECTRA OF POLONIUM
ATOMIC NUMBER 84**

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ABSTRACT

Two samples, each containing an estimated 10 curies (2 mg) of polonium-210, were purified by vacuum distillation and evaporated onto oblique sections of X-ray targets made of copper. Four lines of the K series and ten lines of the L series of the X-ray spectrum of polonium were recorded with a one-meter transmission crystal spectrograph and a 25-centimeter Bragg spectrograph, respectively. Measured wavelengths agree approximately with values predicted by extrapolation of Moseley's law and with those claimed by Hulubei. Decay of polonium-210 (half life = 138 days) and growth of lead-206 (stable) were observed over a period of 180 days.

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THE X-RAY SPECTRA OF POLONIUM ATOMIC NUMBER 84

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INTRODUCTION

The element polonium, or radium F, was first discovered in 1898 by Marie Curie in her studies of the radioactivity of pitchblende and chalcocite.¹ Its atomic number of 84 was later established by measurement of two lines of its L X-ray spectrum.² Until recently, no record of the K spectrum and only incomplete information of the L spectrum³ could be found in the literature.⁴ This lack of information was largely caused by the scarcity of the natural element with its short half life of 138.26 days.⁵

SAMPLE PREPARATION

The high specific activity of polonium made it necessary to employ elaborate health precautions when handling this material. All operations in the preparation of these samples were performed in a special hood provided with an independent air supply and operated under a slight negative pressure with respect to the room in which it was located. All operations were performed through sealed glove ports, the gloves having freedom of motion by being attached to long, large, Vinylite gauntlets.

The polonium to be used for these experiments was electroplated from a hydrochloric acid solution onto platinum gauzes.⁶ Each gauze carried approximately 10 curies of material. The high vapor pressure of polonium⁷ permitted the application of a fractional volatilization technique⁸ to purify the polonium from impurities deposited during the electroplating process and from any lead that had accumulated as a result of radioactive decay.

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Platinum gauzes carrying a total of approximately 30 curies of polonium were inserted as far as possible into the all-quartz purification tube shown in Figure 1, and the tube was attached to a vacuum system. No special care was exercised in the transfer operation to protect the polonium from the air. Previous experience⁹ had shown that any polonium oxide present decomposed readily during the first volatilization step. After the tube was evacuated to 5×10^{-6} millimeters of mercury, the region surrounding the gauzes was heated strongly with a hand gas-oxygen torch. As this heating proceeded, the pressure rose, and the polonium distilled from the gauzes and condensed in the form of a mirror on the cooler portions of the tube. The local heating was continued until the quartz tube started to soften and collapse. Poor thermal contact between the quartz tube and the gauzes prevented the gauzes from reaching more than a dull red heat. The flame was removed, and pumping was continued until the pressure had again reached 5×10^{-6} millimeters of mercury. The tube was then sealed from the vacuum system at Seal-Off No. 1.

Purification⁹ was accomplished by placing this sealed tube in a furnace with the capillary end and a portion of the next section protruding from the furnace. By bringing the furnace to $500^{\circ} \pm 20^{\circ}\text{C}$ and maintaining that temperature for 90 minutes, the more volatile impurities and polonium were distilled into the capillary tube, leaving the less volatile impurities behind. The less volatile materials were eliminated by sealing the tube at Seal-Off No. 2. The remaining section of the tube was then reversed and placed in a smaller furnace. By keeping this furnace at 300°C for 30 minutes, the more volatile impurities were distilled away from the polonium and were isolated by sealing at Seal-Off No. 3.

TARGET COATING

The apparatus used to coat the copper X-ray target is shown in Figure 2. The standard Pyrex taper and ball joints were lubricated with Apiezon "N." Six screws held the copper target to a hollow brass block that had been soft soldered to the copper end of a Housekeeper seal. A 1/8-inch Neoprene washer lightly lubricated with Apiezon "N" was placed between the target and the brass block to obtain a vacuum seal.

Current for the resistance furnace wound with No. 34-gauge platinum wire was transmitted to the interior of the apparatus through doubled No. 14-gauge copper wire. These heavy leads were sealed into the side arms with Apiezon "W" wax. The interior flexible leads were soft soldered to these leadins and were insulated with porcelain beads. By separating the two parts of the 50/30 ball joints, the furnace could be loaded and re-

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FIGURE 1. POLONIUM PURIFICATION TUBE

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Figure 2

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assembled without disturbing any of the adjustments. The double set of ball joints on the lower portion of the apparatus permitted exact lateral positioning of the furnace orifice on the X-ray target face. The orifice was positioned vertically three to four millimeters from the target face by raising or lowering the furnace. The all-quartz volatilization furnace is shown in Figure 3.

Loading of the furnace with the capillary containing the purified polonium was done in a helium-filled dry box. Manipulation was accomplished through glove ports. After making certain that the apparatus was completely flushed with helium, the tip of the capillary was broken off and the capillary placed in the furnace, open end downward. The apparatus was assembled, the stopcocks turned to maintain the helium atmosphere, and the apparatus removed from the dry box.

After attaching the furnace assembly to a vacuum system, the orifice of the furnace was carefully checked to insure that it was centered with respect to the face of the target. The furnace was then clamped in position and the apparatus evacuated to a pressure of 5×10^{-6} millimeters of mercury. The hollow target was cooled by filling the cavity back of the target and target holder with ice water.

The temperature of the furnace was raised slowly by adjusting a Variac in the heating circuit until the furnace windings were at an estimated 700°C . At this temperature the volatilization of the polonium onto the X-ray target was complete after five minutes. After cooling the furnace, the evacuated apparatus was removed from the vacuum system and placed in a helium-filled dry box where it was then dismantled in a helium atmosphere, which prevented oxidation of the polonium.

The target was removed from its holder in the coating apparatus and assembled to the X-ray tube target-holder with a new Neoprene gasket. After assembly was complete, the target was placed in a helium filled, gasketed, Pyrex pipe for transfer to the X-ray tube.

No method of determining the amount of polonium on the target was available. The physical size of the target prevented such an assay. It was assumed that between 10 and 15 curies were deposited.

K SPECTRUM

The X-ray tube, high voltage power supply, and transmission type spectrograph have been described in a previous report.¹⁰ Several modifications were made to extend the wavelength coverage of the spectro-

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OVEN MOUTH

RADIATION SHIELD

PLATINUM FURNACE
WINDING

SUPPORT ROD

VOLATILIZATION FURNACE

Figure 3

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graph. The X-ray tube target tip was reduced to 0.375 inch diameter to reduce the width of the undiffracted beam of X-rays which contribute to the central image. The remaining undiffracted beam was removed by interposing a narrow lead strip in front of the center of the crystal. The removal of the undiffracted X-ray beam was necessary to eliminate the effect of air scattering within the spectrograph. The crystal holder was modified by addition of a mechanical drive and indicating equipment to permit rotation of the crystal in increments as small as 20 seconds of arc. Mechanical changes were made in the slit assembly to permit location of the slit on the optical axis of the spectrograph in order to give slightly increased intensity and permit more exact measurement of wavelengths. Before the exposures were started, the loaded X-ray tube was maintained at a maximum pressure of 2×10^{-5} millimeters of mercury for 18 hours to outgas both the sample and the tube parts as completely as possible. Since adequate pumping speed was available and loss of sample by volatilization was a major consideration, no heat was applied during the outgassing period. Shortly after the high voltage was turned on, the pressure decreased to 5×10^{-6} millimeters of mercury and remained at this figure for the duration of the exposure.

To minimize target heating and consequent loss of material by sublimation, electron currents were limited to two milliamperes or a maximum power dissipation of 250 watts. All exposures were made at 120-125 kilovolts as follows:

Run	Material Age (days)	Exposure (milliampere-hours)
1	4	15
2	25	20
3	52	18

Densitometer tracings were made from two films each of Run No. 1 and No. 2 on a Leeds and Northrup recording microphotometer using a film travel of 5.00 millimeters per minute and a chart travel of $2\frac{1}{32}$ inches per minute. The distance from the slit to the film plane (36.960 inches) was converted to chart measurement units by multiplying by the factor 103.187. Tangent θ was determined from measurement of densitometer charts and the converted slit to film distance. Wavelengths were calculated by Bragg's Law. All wavelengths are based on $d_{100} \text{ CaCO}_3 = 3029.45 \text{ XU}$ so that all results are in X-units. Equivalent values in Angstroms may be obtained by multiplying wavelengths by 1.00203. Final data are presented in Table 1.

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TABLE I.

Line Identification	K Spectrum of Polonium		K Spectrum of Lead	
	Measured (XU)	Predicted (XU)	Measured (XU)	Previously Reported ¹¹ (XU)
K α_2	160.5 $\pm$ 0.3	160.89	170.0	170.0
α_1	155.6 $\pm$ 0.2	156.12	165.1	165.2
β_1	137.9 $\pm$ 0.3	138.28	147.4	146.1
β_2	133.0 $\pm$ 0.5	134.04	143.5	141.2

L SPECTRUM

The Bragg type spectrograph used for examination of the L spectrum of polonium has also been described.¹² This spectrograph was modified by addition of a slit assembly permanently mounted on the disposable X-ray tube so that the spectrograph would not become contaminated. The crystal oscillating mechanism was modified to include the drive motor inside the vacuum camera, thus eliminating the problem of vacuum leaks at the shaft seal. The rock salt crystal was oscillated $\pm 5^\circ$ about a median Bragg angle of 10° to record the whole spectrum at one setting. This gave a wavelength coverage of approximately 450 XU (Ag K absorption edge $\lambda = 484.48$ XU) to 1530 XU (Cu K α_2 $\lambda = 1541.1$ XU). The outgassing and start-up procedure used in the L spectrum experiments was identical to that described in the K spectrum experiments.

In the first exposures, made at 80 KV, power dissipation was limited to 250 watts as previously mentioned to minimize loss of material by volatilization. Examination of the films shows, however, that much of the material must have been removed from the active part of the target in the first few hours of operation because exposures of increasing lengths were used and line intensity relative to background decreased markedly. Visual examination of the X-ray tube target through the glass tube wall confirmed this. When the excitation began, the material appeared to be in a spot approximately 1/4 inch in diameter; while after four exposures, the material covered well over half of the area of the 0.750 inch diameter target tip with bare copper showing in the center of the material. Local heating from the electron bombardment must have caused appreciable migration of the material.

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EXPOSURE DATA

Run	Material Age	Exposure (milliampere-hour)
1	30 hours	7
2	60 hours	9
3	90 hours	18
4	30 days	21
5	180 days	24

Because of the low contrast and broad lines, the microphotometer method of wavelength calculation was not applicable to most of these L lines. Wavelengths were calculated by measuring the film directly with a 10X Bausch and Lomb calibrated eyepiece in conjunction with a photographically reproduced millimeter scale. The following lines were used as standards of wavelength $\text{CuK}\beta_2$, $\text{PbL}\alpha_1$, $\text{PbL}\beta_1$, $\text{PbL}\gamma_1$, and the Ag K edge. Constants in the equation $\theta = md + \theta_0$, where θ is the Bragg angle and d is the distance from an arbitrary zero (θ_0 from the true zero), were derived and values of θ calculated for each polonium line. This procedure was followed for three films, and the reported wavelengths were calculated from these average values of θ by use of the Bragg Law (Table II). Wavelengths of the L lines are based on $d_{100} \text{ NaCl} = 2814.00 \text{ XU}$.

TABLE II

L SPECTRUM OF POLONIUM

Line Identification	Measured (XU)	Previously Measured ³ (XU)	Predicted ³ (XU)
L	1280.2 ± 0.4		
a_2	1123.7 ± 1	1123.29	1123.10
a_1	1112.2 ± 1	1111.52	1111.59
β_6	965.3		
β_2	927.0 ± 1.7	927.44	927.31
β_1	919.4 ± 0.7	919.89	919.79
β_3	905.8		
γ_1	784.5 ± 0.1	785.86	785.52
γ_2	769.9		
γ_3	762.0		

No corrections for index of refraction effects in the Bragg Law were necessary because the method of calculation is practically independent of such effects.

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Figure 4 is an energy level diagram of the K and L Lines constructed from data in Table I and Table II. The identification of the Po $L\beta_2$ line is based on this diagram.

Figure 5 shows reproduction of films taken from material 90 hours old and 180 days old. No lines of lead are observed in the spectrum of material 90 hours after purification, while after 180 days lead lines are very prominent.

It should be pointed out that the spectrum recorded 90 hours after purification showed faint but unmistakable $PbL\alpha_1$, α_2 lines. Assuming an initial sample of 10 curies, approximately 40 micrograms of lead is then detectable by this method. Previous experience has shown that samples of approximately 250 micrograms of molybdenum and ruthenium give intense K spectra with this spectrograph with much shorter exposures.

CONCLUSIONS

The growth of the Polonium decay product, lead-206, was followed by successive exposures at 20-day intervals. The lead lines were used for qualitative verification of the measured K wavelengths and as reference wavelengths in the reduction of data on the L series. As many as three X-ray films were loaded simultaneously for recording the more penetrating K spectrum, thus enhancing slightly the accuracy of K line measurements.

Agreement with predicted wavelengths in the case of the K lines is satisfactory since these calculated wavelengths are based on experimentally determined wavelengths of corresponding lines of other elements in the same atomic number region. Comparison of decay-product wavelengths as measured in this laboratory with those previously reported is an indication of the accuracy of these measurements. The differences of 1.3 XU in the case of $PbK\beta_1$ and 2.3 XU in $PbK\beta_2$ do not appear to be within experimental error as based on the measurement of polonium lines. The β_1 and β_2 lines of both polonium and lead are less accurate than the α_1 and α_2 lines because of their low intensity. Errors in polonium wavelengths, based on repetitive measurements of film and densitometer charts, are for a 95 per cent confidence interval.

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FIGURE 4. ENERGY LEVEL DIAGRAM OF K & L X RAY SPECTRUM LINES OF POLONIUM

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FIGURE 5 L SPECTRUM OF POLONIUM AND LEAD

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