Neutron Deficient Isotopes of Praseodymium

A THESIS

submitted in partial fulfilment of the
requirements for the degree of Doctor
of Philosophy in the Faculty of Graduate
Studies and Research of McGill University.

by

C.E. Dahlstrom

Radiation Laboratory,
August, 1953

TABLE OF CONTENTS

Summary

A new isotope Pr^{137} has been discovered, its half-life measured as 1.5 ± 0.1 hours, and its positron end point energy as 1.7 ± 0.1 Mev. For Pr^{138} (2.0 hours) a previous tentative mass assignment has been confirmed, and two conversion electrons with energies of 262 ± 5 Kev. and 299 ± 5 Kev. have been found associated with its decay. These electrons appear to be K and L conversions from a 300 Kev. transition in Ce^{138}.

The assignments were made in the following manner. Cerium oxide targets were irradiated with protons of energies up to 90 Mev. The neutron deficient praseodymium isotopes so produced were chemically separated from the cerium and dispersed according to mass on copper foil collectors in a mass spectrograph. X-ray film transfers from the foils located the positions of the radioactive isotopes. These isotopes were then cut from the foils for individual half-life measurements. The identification of previously known Pr^{139} (4.5 hours) determined the masses of the other radioactive isotopes. The beta particle energies were obtained by analysis of the unseparated radioactive isotopes in a beta spectrometer.

Acknowledgements

The research was supervised by Dr. J.S. Foster, director of the Radiation Laboratory. His constant encouragement and valuable suggestions were greatly appreciated.

The methods involved in the chemical separation were due largely to Dr. A.L. Thompson of the Radiation Laboratory staff. Mr. J. Hilborn gave valuable assistance with the beta spectrometer runs. The use of Dr. R.E. Bell's gamma spectrometer was also greatly appreciated.

The members of the Radiation Laboratory machine shop, under the supervision of Mr. S. Doig, aided in some of the modifications made to the mass spectrograph. Necessary glass blowing was performed expertly by Mr. R. Lorimer.

The work was performed with the assistance of a Studentship and a Fellowship from the National Research Council of Canada.

I. INTRODUCTION

The McGill 82 in. synchro-cyclotron accelerates protons up to energies of 100 Mev. Thus, it is an excellent tool for producing (p,xn) reactions. Protons in the beam of the synchro-cyclotron enter the nuclei of the target material and commonly remain there. The excess energy is lost, in part, by the evaporation of neutrons from the newly formed compound nucleus. This process therefore tends to form neutron deficient isotopes of the next element on the atomic scale.

Since relatively little work has been done on the radioactive isotopes of the rare earth elements, this appeared to be an especially promising field of research. With the available energy one may expect new isotopes from any rare earth target. In this region of scarce information new data on rates of decay, energies and types of radiations are of special interest. In the present work praseodymium was the element chosen for investigation.

A method of elimination is often used to assign a mass number to a particular activity. By investigating the activity formed from bombardment of targets of neighboring elements with suitable energies, and with different particles, the possible isotopes may be eliminated until one likely one remains. This method is presently not available at McGill. In such cases chemical extractions may sometimes be performed on the element under study and the extracted sample may contain a known daughter activity. If the mode of decay is known a mass assignment may then be made to the activity in question.

An alternative and, indeed, more certain way is to use a mass spectrograph. The activity under study is dispersed according to mass on the collector of the mass spectrograph. The positions of the various radioactive isotopes present are found by detecting their radiations with a photographic plate or a counting device. Once the mass scale has been calibrated mass assignment to a given isotope is definite. Furthermore, half-lives as well as energies and types of radiations from the separated isotopes may be studied if sufficiently strong sources are obtained on the spectrograph collector. With efficient counting devices it is not difficult to get good half-life values from weak sources, but determination of the radiation energies requires more intense activities. However, even if only the half-life can be assigned to a particular isotope by the mass spectrographic method the problem is much simplified.

Indeed, this makes possible a detailed study of the unseparated isotopes with more conventional equipment. The beta spectrum of the unseparated isotopes, as obtained on a beta spectrometer, gives accurate values for the energies of any conversion electrons present. Measurements of the rates of decay of these conversion electron peaks then shows them to be due to isotopes of particular mass numbers. The mass spectrograph tells us the mass of the lightest isotope formed in a particular bombardment. For the praseodymium isotopes studied, at least, the lightest isotope is associated with the highest positron end point energy. This energy can therefore be obtained from the beta ray spectrum.

Similarily, analysis of the unseparated isotopes with a gamma spectrometer gives the energies of the various gamma rays emitted. Measurements of the rates of decay of the gamma ray peaks associates each one with an isotope of a particular mass number.

A mass spectrograph was available in the Radiation Laboratory for this purpose. Furthermore, praseodymium is particularly adaptable to this type of investigation. Therefore, it was decided to use the mass spectrographic technique in studying the neutron deficient isotopes of praseodymium.

II, THE MASS SPECTROGRAPH

1. Mass Spectrographic Analysis of Radioactive Isotopes

Early investigations by Dempster(1) indicated that the success of the mass spectrographic method depended on the ionization efficiency of the type of ion source used. In his experiment, a 4 mg. sample of uranium having an activity of 2.5 x 10^{-4} curies due to fission products was analyzed in a double focusing mass spectrograph using a spark source. An activity of only 12 counts per minute was deposited in the fission mass range on the photographic plate. This implied a loss factor of 10^7 to 10^8 in the analysis. Although the spark source is able to produce ions of every solid element most of the sample is evaporated as neutral atoms. Furthermore, the ions produced by this source have an energy spread of about 1000 volts.(2) This makes a double focusing mass spectrograph necessary, reducing the efficiency still further.

Fortunately, the hot filament ion source was known to have a much greater ionization efficiency, at least for a few elements. In addition, the ions produced have an energy spread of only 0.2 volts,(2) allowing this source to be used with a simple direction focusing spectrograph. In this type of source a compound of the element to be analyzed is coated on a tungsten filament. On heating the filament in vacuum a portion of the sample is evaporated as ions. These ions are accelerated and collimated into an ion beam by suitable arrangements of focusing plates and collimating slits.

The early work of Richardson(3) had shown that a large fraction of the atoms evaporated from heated salts of the alkali metals were ions. The salts were heated on a tungsten filament and ionization appeared to depend on the fact that the work function of the tungsten was greater than the ionization potentials of the alkali elements. In 1935, Blewett and Jones(4) observed ion emission from the heated salts of Ba, Ir, Y, and Ce. In 1947, Hayden(5) extended the use of the hot filament source to include most of the rare earth elements. His article lists those compounds which have been used successfully with the hot filament source, along with the types of ions emitted and their ionization efficiencies. Table I is a partial list of these compounds.

TABLE I

Compound	Types of Ions Emitted	Ionization Efficiency %
$Ba(NO_3)_2$	Ba^+	0.02
$La(NO_3)_3$	LaO^+	16
$Ce(NO_3)_3$	CeO^+	0.12
$Pr(NO_3)_3$	PrO^+	12
$Nd(NO_3)_3$	NdO^+ (99%), Nd^+ (1%)	1
$Pm(NO_3)_3$	PmO^+ (95%), Pm^+ (5%)	0.5

Hayden was able to assign masses to radioactive isotopes of Y, Ru, Ce, and Pm by analyzing them with a mass spectrograph using a hot filament source. The radioactive isotopes, along with the stable isotopes of some element introduced as a mass standard, were collected on a photographic plate. If the half-lives of the radioactive isotopes were less than 10 hours their positions were determined by scanning the photographic plate with a lead slit and geiger counter arrangement. After a suitable length of time the photographic plate was developed and showed the positions of both the stable and radioactive isotopes in the sample. The masses of the known stable isotopes determined the masses of the radioactive ones. If the half-lives were greater than 10 hours it was found more efficient to expose the photographic plate containing the radioactive isotopes to a second photographic plate for a suitable length of time. The first plate then showed both the radioactive and stable isotopes while the second plate showed only the radioactive ones. The application of successive transfer plates indicated those isotopes which decayed away quickly and those that decayed slowly, from which approximate half-lives were determined.

Gransden(6) extended the method to the isotopes of lanthanum. In his experiments, the separated isotopes were collected on dural foils instead of photographic plates and the positions of the radioactive isotopes determined by X-ray transfers from the foils. The hot filament source was found so efficient for lanthanum that a geiger counter was used on the separated isotopes to determine half-lives and radiation energies. Maclure(7) later used this method to study radioactive isotopes of Sr, In, and Ga.

The main advantage of the mass spectrographic technique is that the mass assignment to a particular activity is certain. In addition, in the cases where sufficiently strong sources are obtained on the mass spectrograph collector, interpretation of the decay curves of the separated isotopes is greatly simplified.

There are two main disadvantages. The first is the inefficiency with which the mass spectrograph operates. In most cases only a very small fraction of the sample element on the filament becomes ionized. For praseodymium, one of the best ion emitters, this fraction is 12%. A more serious loss occurs due to the inefficiency of ion collection in the spectrograph. The geometry of the ion source is such that only a small fraction of the total number of ions formed passes through the entrance slit into the analyzing chamber. Even in the analyzing chamber losses occur due to scattering of ions from residual gases and from the analyzing chamber walls. For the instrument used in the present work only 1 in 500 of the total number of ions formed is able to reach the collector.

The second disadvantage is the length of time required to complete the isotope separation. The hot filament ion source requires that the samples to be analyzed have a mass of less than 100 micrograms. This usually involves a lengthy chemical separation of the sample element from the target material. The actual isotope separation in the mass spectrograph increases the time still more. Hence the technique is not applicable to short lived isotopes. As a general rule, isotopes with half-life less than 0.5 hours cannot be detected by the mass spectrographic method.

2. Physical Characteristics of the Mass Spectrograph

The mass spectrograph used for the present work has been described by Maclure.(7) Figure 1 is a photograph of the complete instrument. Figure 2 is a schematic diagram of the main components.

The mass spectrograph is a Nier sector type instrument,(8) in which the ion beam is deflected through an angle of 90° after acceleration. The radius of curvature of the ion path in the magnetic field is 6 inches. In the mass 150 region the dispersion along the collector is approximately 1.5 millimeters per mass unit. The resolving power is of the order of 200.

The analyzing chamber consists of a 1.25 in. diameter copper tube, 19 in. in length. The central portion is flattened to 0.5 in. and bent into a 90° arc on a 6 in. radius. The two straight portions of the copper tube each terminate in a cylindrical chamber for the ion source and collector. The chambers are closed by brass plates making vacuum seals against O-rings, to facilitate loading and removal of samples.

The curved section of the analyzer tube fits into the 9/16 in. gap between the two iron pole-pieces of the magnet. The shape of the pole-pieces is identical to those used by Graham, Harkness, and Thode.(9) A magnetic field of 3000 gauss is supplied by 10 permanent magnets placed at intervals around the sides of the pole-pieces.

A plate holder, marked P in figure 2, is designed to hold a 1 in. x 3 in. Ilford Q3 mass spectrograph plate and is mounted on an insulating base in the collector chamber. For radioactive samples a copper foil is used in place of a photographic plate. To satisfy the focusing conditions for the sector type instruments the plate holder, apex of the magnetic field, and the beam defining slit all lie in a straight line. The plate holder makes contact through a kovar seal to the input of a direct current amplifier.(9) The amplifier is useful in monitoring the intensity of the ion beam and indicates when ion emission commences and is completed. It is also necessary when adjusting the various ion source voltages for maximum ion current.

The ion source is of the hot filament type. The 0.001 in. x 0.03 in. x 0.75 in. tungsten ribbon filament is mounted in the 1/8 in. gap between two half-moon plates marked T in figure 2. The filament is under slight tension to prevent buckling while heated. It is connected to an adjustable positive voltage supply. Direct current from a selenium rectifier circuit heats the filament to the necessary temperature. A repelling plate R is placed 5/32 in. behind the filament. Normally, it is about 10 volts more positive than the filament. However, the praseodymium samples used required a filament temperature high enough so that electron emission from the filament became important. These electrons were attracted to the repelling plate, causing one of the resistors in the potential dividing system to be partially shunted. Thus the filament potential varied with its temperature and caused considerable spread in the ion beam energy. This was eliminated, without causing any noticeable change in the ion current intensity, by maintaining the filament and repelling plate at the same potential. Two half-moon focusing plates, F_1 and F_2, are placed 5/32 in. in front of the filament. The gap between these plates is 1/8 in. wide. Their potentials may be adjusted individually to focus the ion beam on the entrance slit. The 0.015 in. x 3/8 in. entrance slit S is 9/32 in. in front of the focusing plates and is kept at ground potential. All the metal parts of the ion source are made of 0.020 in. chromel A sheet and are insulated from each other by pyrex spacers. All the potentials are supplied from a single 500 to 2000 volt regulated power supply.

The spectrograph was originally evacuated through two 7/8 in. diameter tubes connected to the analyzing chamber proper. To evaporate and ionize a sample of praseodymium from the ion source filament a temperature exceeding 1000° C is required. At this temperature considerable gas is evolved from the filament and neighboring components. For this reason the pumping leads were changed to 1¼in. diameter tubes connected directly to the ion source and collector chambers. Two 3-stage oil diffusion pumps, backed by single Welch rotary forepump, are used to evacuate the system. A sufficiently low pressure (10^{-5} mm. of Hg.) may be obtained approximately 45 minutes after turning on the pumps.

Considerable difficulty arose from oil deposits which collected on the inner walls of the analyzing tube. These deposits evidently formed insulating surfaces which badly deflected the ion beam. Since no cold traps are used in the pumping lines some vapor from the oil diffusion pumps is able to get into the analyzer tube and condense there. The new arrangement of pumping leads should reduce this effect considerably. To further improve this the analyzer tube was thoroughly cleaned and gold plated to 0.0001 in. thickness. The gold surface should prevent any corrosion of the inner walls of the analyzing tube. In addition, the oil in the diffusion pumps was changed from Silicone DC-702 to Octoil-S. These measures vastly improved the shape of the lines formed by the spectrograph as well as the ion collection efficiency.

3. Operation of the Mass Spectrograph

A nitric acid solution of the element whose isotopes are to be separated is pipetted onto the front surface of the tungsten filament. This operation is carried out under a heat lamp to speed evaporation. The material on the filament then is a solid nitrate of the sample element. Effort is made to keep the samples less than 10 micrograms to avoid an unduly long time to complete the isotope separation. The filament is then installed in the mass spectrograph and the system evacuated. When the pressure is approximately 10^{-5} mm. of Hg. the filament is slowly heated with the direct current supply until the direct current amplifier indicates that ion emission has started. During the warming up of the filament the nitrate sample is converted to oxide. By taking about 15 minutes to heat the filament better resolved lines and more efficient ionization have been obtained. If the sample is greater than 10 micrograms it is necessary to give it a "breaking in" period. If this is not done, at least for radioactive samples, badly blurred and curved lines result. For this reason the accelerating voltage is initially set to focus the isotopes present near one end of the ion collector. With this accelerating voltage, ion current is collected until the filament appears to be emitting steadily. During this period the focusing plate potentials are set to give maximum ion current. The focusing plate potentials usually differ by several volts to compensate for misalignments in the ion source. The average potential of the focusing plates is very important in obtaining maximum ion collection efficiency. This setting must be made empirically. For stable praseodymium, which requires an accelerating potential of 675 volts, the focusing plate potentials must be approximately 550 volts to obtain maximum ion current.

When the ion current has become steady the accelerating potential is changed to focus the isotopes present near the center of the collector. The filament temperature is then set to give the desired ion current and left until the sample is depleted. A 10 microgram sample of stable praseodymium is able to maintain an ion current of 10^{-9} amperes for 30 minutes. This gives a total spectrograph efficiency of 1 in 5000. That is, for every 5000 praseodymium atoms on the filament only one reaches the collector.

Careful alignment of the ion source components is necessary to obtain high ion currents. The ion beam defining slit, in particular, must be accurately positioned to prevent scattering of the ion beam from the walls of the analyzer tube. Cleanliness of all parts is of utmost importance. The metal parts of the ion source are periodically cleaned in boiling Royalene and, after each run, are rubbed with fine emery paper. The pyrex spacers are cleaned periodically in a hot acid bath and rinsed thoroughly with distilled water.

III. A SURVEY OF PREVIOUS STUDIES

Aston(10) found the stable isotope of praseodymium to occur at mass 141. In 1935 Amaldi and associates(11) bombarded Pr^{141} with neutrons and produced two activities with periods of 19 hours and 5 minutes, respectively. The 19 hour activity was found to emit beta particles whose intensity was reduced to one-half by 0.12 gm/cm^2 of Al. In the same year Marsh and Sugden(12) repeated the experiments and attributed the 19 hour activity to Pr^{142}. In 1938 Pool and Quill(13) measured the period of the short lived activity as 3.5 minutes and found it to be a positron emitter. They assigned this activity to Pr^{140}. These activities were confirmed by Wu and Segre(14) in 1942. They gave 18.7 hours as the period of Pr^{142} and reported that it emitted only electrons with a maximum energy of 2 Mev. In the same year Dewire, Pool, and Kurbatov(15) produced Pr^{142} by the reactions Pr^{141} (d,p), Ce^{142} (p,n), and La^{139} (α,n). After chemical purification the decay curve for Pr^{142} gave a half-life of 19.3 hours. The negative beta ray spectrum was studied with a magnetic spectrometer and found to have an end point of 2.14 Mev. A weak 1.9 Mev. gamma ray was also found associated with this period. The same investigators also produced Pr^{140} by the reaction Pr^{141} (n,2n) and measured its half-life as 3.4 minutes. Cloud chamber measurements yielded an upper limit of 2.4 Mev. for its positron spectrum.

More recent work has been reported by Stover,(16) at Berkeley. Cerium metal was bombarded with protons of energies of 10, 20, and 32 Mev. from the linear accelerator. At 10 Mev. (p,n) reactions on Ce^{142} and Ce^{140} gave the 19.5 hour and the 3.5 minute activities reported previously. At 20 Mev. a 4.5 hour activity appeared. A chemical extraction showed the daughter product of this activity to be the previously known Ce^{139}(140 days).(17) This allowed the 4.5 hour activity to be assigned with certainty to Pr^{139}. The ratio of positron emission to K capture was given as 0.06:1. A beryllium absorption experiment gave 1.0 Mev. as the maximum positron energy. This result was verified by a magnetic counter sweep. Lead absorptions indicated a 1.0 Mev. gamma ray in addition to K X-rays and annihilation radiation.

At 32 Mev. a 2.0 hour activity appeared and was assigned to Pr^{138} on the basis of relative yields and threshold energy. Thus the element appeared certain but the mass assignment needed confirmation. A beryllium absorption experiment and the magnetic counter sweep both indicated a positron with a maximum energy of 1.4 Mev. In addition, a 220 Kev. conversion electron was reported. Lead absorptions showed gamma rays of 0.16 Mev. and 1.3 Mev.

besides the usual K X-rays and annihilation radiation. Thirteen percent of the decays were by positron emission and the remainder by electron capture.

IV. EXPERIMENTAL PROCEDURE AND RESULTS

1. Irradiations

Cerium, the target element, has the following stable isotopes; Ce^{142} (11.1%), Ce^{140}(88.5%), Ce^{138} (0.25%), Ce^{136} (0.19%). The neutron deficient praseodymium isotopes which are produced should therefore be mainly the result of (p,xn) reactions on Ce^{140}, with a smaller contribution from Ce^{142}. Ce^{138} and Ce^{136} would not be expected to contribute in significant amounts unless at least one of them has an abnormally high proton capture cross-section.

The cerium oxide target material was prepared by igniting ammonium hexanitrate cerate (obtained from G. Frederick Smith Co. as primary standard material). The ignition temperature was kept less than 300° C to avoid formation of an insoluble form of cerium oxide. Targets were prepared by packing about 15 milligrams of the cerium oxide powder into a 1/8 in. diameter tube formed from 0.001 in. dural foil. The free edges of the tube were clamped to a dural block which in turn was clamped to the water cooled internal probe of the cyclotron. This ensured that the insoluble form of cerium oxide was not formed by overheating during the cyclotron bombardment. Irradiations were carried out at proton energies ranging from 20 Mev. to 90 Mev. The duration of bombardments varied from ½ hour to 2 hours.

2. The Chemical Separation

The chemical separation of one rare earth element from another is normally a difficult problem because of their similar outer electron configurations. However, cerium differs from its immediate neighbors in that it may exhibit a valence of +4 as well a +3, the normal rare earth valence. The chemical separation of praseodymium from cerium therefore depends on oxidizing the cerium to its +4 valence state and precipitating it as a phosphate, leaving the praseodymium behind in solution.

After removal from the cyclotron the irradiated samples were subjected to the following chemical procedure.

(a) The cerium oxide was poured into a dry beaker and 1 cc. of concentrated nitric acid added. The mixture was stirred thoroughly to ensure complete wetting of the cerium powder. After addition of 1cc. of 30% hydrogen peroxide, the mixture was warmed gently, with stirring, until the cerium oxide was dissolved and the total volume reduced to 0.5 cc.

(b) The solution was cooled to about 20°C in a water bath and 10 milligrams of solid potassium bromate added to oxidize the cerium. Unless the cerium solution was cooled thoroughly complete oxidation did not occur. Thorough mixing of the potassium bromate with the cerium solution was essential. The mixture was then diluted to about 15 cc. with cool distilled water.

(c) Cerium phosphate was precipitated by adding 3 cc.

of 10% phosphoric acid. Warming the mixture to about 50° C. in a warm water bath helped to promote coagulation of the precipitate.

(d) The cerium phosphate was filtered on a fine glass sintered crucible. The filtrate usually contained about 50% of the total activity.

(e) The filtrate was made strongly basic by adding concentrated ammonium hydroxide. Precipitation of the rare earth hydroxides was ensured by heating the filtrate to the boiling point.

(f) The rare earth hydroxides were filtered out on a fine glass sintered crucible. The hydroxides were then removed from the filter by drawing several drops of concentrated nitric acid through it and rinsing with distilled water.

(g) The rare earth hydroxides were again precipitated as in step (e) and the solution centrifuged. The precipitate (about 20 micrograms) was always clearly visible in the tip of the centrifuge cone. It consisted largely of cerium left over from step (c) along with small amounts of lanthanum, praseodymium, and neodymium impurities in the target material. These stable elements acted as a carrier for the radioactive praseodymium.

(h) The precipitate was washed once with hot water, once with acetone, and dried thoroughly under a heat lamp. A gentle air jet was used to speed the drying.

(i) The precipitate was dissolved in 1 drop of concentrated nitric acid. It was then drawn up into micropipette and deposited in small drops on the front surface of the ion source filament. The loading of the filament was carried out under a heat lamp to speed the evaporation of the nitric acid solution.

The complete chemical separation normally took about one and one-half hours.

3. The Mass Separation

The loaded filament was installed in the mass spectrograph. A 2 1/8 in. x 1 in. x .002 in. copper foil was carefully rubbed with fine emery paper and inserted into the spectrograph plate holder to act as ion collector. The system was then closed and evacuated. After about forty-five minutes of pumping, when the pressure in the spectrograph was approximately 10^{-5} mm. of Hg., the ion accelerating potential was set at 750 volts. At this setting the praseodymium isotopes present were focused near the high mass end of the copper foil collector. The filament current was then slowly raised until ion current began to register on the output meter of the direct current amplifier. After adjusting the focusing plate potentials for maximum ion current the filament temperature was again slowly increased until the ion current was about 10^{-10} amperes. The praseodymium sample was then "broken in" at this temperature for about 10 minutes, or until the ion current appeared steady.

When the filament appeared to be emitting properly the accelerating potential was reduced to 700 volts. This focused the praseodymium isotopes near the center of the collector. The filament temperature was then set to give an ion current of about 2×10^{-10} amperes and left until the sample was depleted. This usually took another half hour.

The foil containing the active isotopes was then removed from the spectrograph and exposed for a suitable length of time to a piece of no-screen X-ray film. For the strongest sources exposures of 15 minutes were sufficient to sensitize the film. To bring out weaker lines exposures of several days were sometimes used. The X-ray film was laid directly on the front surface of the copper foil and gently pressed down. While in contact, three pin holes were made through both foil and film so that they could be placed in register later on.

After developing, the X-ray film showed lines corresponding to the positions of the active isotopes on the copper foil. If the foil contained sufficient activity it was again placed in register with the film and the positions of the active isotopes marked off on the foil with a pin point. The foil was then cut into narrow strips containing the individual isotopes. The rates of decay of these isotopes were then measured with a geiger counter.

If the foil contained rather weak activities a series of X-ray film transfers were taken from it. A rough value for the half-life of a given isotope could then be determined by noting the change in intensity of the lines produced by it on the X-ray films.

4. <u>Half-life Measurements</u>

All the decay curves were made using end-on Geiger-Muller tubes filled with 9 cm. of argon and 1 cm. of ethyl alcohol. The mica windows were 3 mgm/cm.^{2} thick. The tubes were mounted in a lead housing and connected to a scaling circuit.

Figure 3 shows the mass numbers of the radioactive isotopes detected at the various proton bombardment energies. The lengths of the lines indicate approximately the relative abundance of each isotope as estimated from the density of the image produced by it on the X-ray film.

(a) 20 Mev. Bombardment

This bombardment produced a single line on the X-ray film. This line was cut from the copper foil and its half-life measured with the geiger counter. The decay curve (Figure 4) shows the half-life to be 4.5 hours. Since there are no other isotopes of comparable half-life in this mass region, this isotope must be the Pr^{139} reported by Stover(16). This isotope then served to calibrate the mass scale.

(b) 40 Mev. Bombardment

Three fairly intense lines now appeared on the X-ray film. The heaviest isotope again gave the 4.5 hour half-life and therefore must be Pr^{139}. The isotope at mass 138 gave a half-life of 2.0 hours (Figure 5), confirming the previous mass assignment to this isotope(16). The 2.0 hour activity must be due to Pr^{138}. A new line also appeared at mass 137 and, after several days exposure, a fourth line at mass 135.

(c) 50 Mev. Bombardment

The line at mass 137 was now the strongest one present. On five different occasions it gave half-life values of 1.45, 1.45, 1.55, 1.60, and 1.60 hours. The period of this isotope was therefore set at 1.5 ± 0.1 hours. A typical decay curve is shown in Figure 6. No other known isotope of mass 137 has a period close to 1.5 hours. Therefore the 1.5 hour activity must be due to a new isotope Pr^{137}.

Pr^{138} and Pr^{139} were also present and again gave the 2.0 hour and 4.5 hour half-lives. After letting the Pr^{137} isotope decay for several days a second X-ray transfer still showed a faint line in this position. This is to be expected if the Pr^{137} decays into 36 hour Ce^{137}. A 16 hour exposure to the foil again showed a line at mass 135 and, in addition, a faint line at mass 133. A second X-ray exposure for 120 hours, directly following the 16 hour exposure, produced the mass 135 line in about the same intensity. Solving the decay equations then shows the half-life of the mass 135 isotope to be of the order of 20 hours.

(d) 60 Mev. Bombardment

Masses 139, 138, 137, and 135 were again present and mass 133 was now much stronger. In addition, a faint line appeared at mass 132. A 16 hour exposure to the isotope of mass 133 produced an intense line on the X-ray film. A second exposure for 48 hours, directly following the first, showed this line only very faintly. Thus the half-life of this isotope cannot be more than a few hours.

(e) 70 Mev. Bombardment

No new isotopes were dectected at this energy. Mass 132 was much stronger than in the previous bombardment. The isotopes with masses 133 and 132 were collected in sufficient quantity to get rough half-life values from the geiger counter. The value obtained for mass 133 was 3.8 hours, while mass 132 gave 4.7 hours. Neither of these values is accurate to more than ± 0.5 hours.

(f) 80 Mev. Bombardment

All the previous isotopes were again present, mass 132 now being the strongest. A faint line also appeared at mass131, but no indication of its half-life was obtained.

(g) 90 Mev. Bombardment

No new isotopes were detected at this energy.

5. Discussion of the Unassigned Isotopes

The production of the isotopes Pr^{139}, Pr^{138}, and Pr^{137} seems perfectly normal. Each one is formed at its expected threshold energy and their relative abundances change in an orderly manner. This does not appear to be true for the isotopes with masses of 135 and less. The Metropolis table of isotope masses(18) indicates that 40 Mev. is the minimum energy required to produce Pr^{135} from Ce^{140} by a (p,6n) reaction. This table also indicates that 50 Mev. is less than the threshold energy required to produce Pr^{133} from Ce^{140} by a (p,8n) reaction. The threshold for this reaction is 60 Mev. at which energy mass 133 is very intense. Furthermore, one would expect reactions in which such a high number of neutrons are evaporated to be relatively uncommon. One explanation could be that at least one of the stable isotopes Ce^{136} and Ce^{138} has a high proton capture cross-section.

It will be noted that the values given here for the half-lives of the isotopes with masses 135, 133, and 132 compare closely to those reported for lanthanum isotopes of the same mass numbers. These are La^{135} (19.5 hr.), La^{133} (4.0 hr.), and La^{131} (4.4 hr.). The absence of masses 136 and 134 fits the lanthanum scheme as well since their half-lives are 10 min. and 6.5 min., respectively, and are therefore too short to be detected by the mass spectrographic method. The appearance of mass 131 is also not surprising under this assumption, since La^{131} has a period of 55 min. Lanthanum isotopes could be produced from a cerium target by(p,2pxn) reactions. At the high bombardment energies used these reactions might become important. Lanthanum isotopes might also be formed as daughter products of cerium isotopes with the same mass numbers. Since the mass spectrograph discriminates strongly against cerium (Table I), only the lanthanum isotopes would be collected by the mass spectrograph in appreciable quantity. The cerium isotopes might be formed by (p,pxn) reactions or as daughter products of praseodymium isotopes.

Finally the lines observed might be due, at least partially, to new praseodymium isotopes. In such a case decay curves for the isotopes should yield new half-lives. The half-life curves obtained for the isotopes with masses 133 and 132 were toorough to decide for or against this hypothesis.

6. An Aluminum Absorption Experiment

On one occasion bombardment at 50 Mev. produced enough Pr^{137} to run an aluminum absorption curve on the separated isotope. A geiger counter measured the counting rate as a function of the amount of aluminum between the source and the counter window. This curve is shown in Figure 7. The low counting rate did not allow a correction to be made for any gamma background present. The curve was analyzed to give the maximum positron energy by the Bleuler and Zunti(19) method. In this method the unknown absorption curve is compared with the curve that would be obtained from a substance obeying exactly the Fermi theory of beta decay. Values of the absorber thickness which reduced the source intensity by factors of 2, 4, and 8 were determined from the Pr^{137} curve. A system of standard curves, published in the Bleuler and Zunti article, then gave values of the maximum positron energy for each of the three absorber thicknesses. For a simple allowed spectrum these values should all be the same. For Pr^{137} the values of Emax were found to be 1.8, 1.9, and 2.1 Mev.

7. Beta Spectrometer Procedure and Results.

The beta spectrometer used was a large ring focus instrument of the Slatis-Siegbahn type.(20) The magnetic field focuses electrons and positrons of a given energy (with a small energy spread) on an anthracene crystal. The light pulses from the crystal produce voltage pulses from a photomultiplier which in turn drives an amplifier and counting rate meter. The counting rate meter feeds an Esterline-Angus paper strip recorder. Thus a scan of the magnetic field produces a positron and electron energy spectrum on the Esterline-Angus paper strip. Alternately, the magnetic field may be set at a particular value and the change in intensity of electrons and positrons of a given energy measured as a function of time. The transmission factor of the instrument is 0.25% and its resolution is 2%. Measurements of beta particle energies may be reproduced to within 0.1% of eachother.

Sources were prepared in the following way. The cerium was removed from the irradiated target material in the same way as described in the section on chemical procedure. The filtrate containing the active isotopes was adjusted to a pH of 5.5 as indicated on a pH meter. Ammonia gas bubbling through the filtrate provided a fine control on the pH adjustment. The solution was then filtered through a No. 5 membrane type filter, obtained from membranfilter Gesellschaft, Sartorius-Werke A.G. and Co., Gottingen, Germany. The activity was collected on a 1/8 in. diameter spot in the center of the filter by clamping it in a special platinum plated brass holder. At a pH of 5.5 about 90% of the activity was removed by the filter. If the solution was actually made basic a dark blue filtrate was obtained. These filters were then mounted directly on the source holder of the beta spectrometer.

At a bombardment energy of 40 Mev. a scan of the beta spectrum showed strong conversion lines at 262 ± 5 Kev. and 299 ± 5 Kev. Weak conversion lines were observed at 119 ± 5 Kev., 760±10 Kev., and 1005 ± 10 Kev. The positron end point energy was estimated as 1.7 ± 0.1 Mev. Stover(16) gives the maximum positron energies of Pr^{139} and Pr^{138} as 1.0 Mev. and 1.4 Mev., respectively. Since the mass spectrograph results showed that only three isotopes were formed in any abundance during the 40 Mev. bombardment, 1.7 Mev. must be the maximum positron energy of Pr^{137}. The decay of the 262 Kev. conversion electron peak was followed for about 2 hours. It decayed with a half-life of 1.9 hours (Figure 8) and so must be associated with the decay of Pr^{138}. The positron background comprises only 15% of the total height of the electron peak. Thus the true period of this conversion electron will not differ much from the observed value.

A run at 50 Mev. again showed the strong 262 Kev. and 299 Kev. conversion electrons. The weak line at 119 Kev. was also observed but the 760 Kev. and 1005 Kev. lines had disappeared. A portion of this beta spectrum is shown in Figure 9. The decay of the 299 Kev. peak was followed for 5 hours and gave a half-life of 2.1 hours (Figure 10). Therefore this electron is also a result of the decay of Pr^{138}.

Since both the 262 Kev. and 299 Kev. conversion electrons are due to the decay of Pr^{138} it seems probable that they are the K and L internal conversions from an energy transition of the daughter Ce^{138} nucleus. The critical X-ray absorption energies for the K and L shells of Ce^{138} are approximately 40 Kev. and 6 Kev., respectively.(21) Adding these values to the electron energies gives 302 Kev. and 305 Kev. for the Ce^{138} transition energy. The close agreement between these two values tends to confirm the assumption regarding the orgin of the 262 Kev. and the 299 Kev. conversion electrons. The small irregularities on the high energy side of the 299 Kev. peak (fig. 9) lends further support since the M and N shells might be expected to share in the conversion.

The K/L ratio calculated from the beta spectra is about 2.5:1. If the 299 Kev. peak is assumed too high due to contributions from other shells the ratio might be increased to 3:1. Curves published by Goldhaber and Sunyar(22) show that an E3 transition is most likely to give a K/L ratio of this magnitude. This article also indicates that the half-life of a 300 Kev. E3 transition would be of the order of several seconds. Thus the observed rate of decay of the conversion electron peaks would be essentially that of the parent Pr^{138}.

8. Gamma Spectrometer Procedure and Results

The gamma spectrometer used was constructed by Dr. R.E. Bell. Its main features are the following. A sodium iodide crystal is mounted directly on the light entrance window of a photomultiplier. Gamma rays which are absorbed in the sodium iodide cause it to scintillate, producing a voltage pulse on the output of the photomultiplier. The size of the voltage pulse is very nearly proportional to the energy of the gamma ray producing it. The photomultiplier feeds a single channel pulse height analyzer whose bias can be swept through the scale. The output of the pulse height analyzer feeds a counting rate meter which in turn drives an Esterline-Angus paper strip recorder. The paper drive of the Esterline-Angus meter also sweeps the bias of the pulse height analyzer. In this way a gamma ray energy spectrum is recorded on the paper strip. The energy scale was calibrated using the 662 Kev. gamma ray from Cs^{137}. The resolution of the spectrometer is estimated to be about 15%.

Sources were prepared in the same manner as for the beta spectrometer.

At a proton bombardment energy of 35 Mev., the gamma spectrum showed a series of broad peaks whose energies were measured roughly as 160 Kev. (2.3 Hrs.), 330 Kev. (2.0 hrs.), 550 Kev. (2.2 Hrs.), 850 Kev. (1.5hrs.), 1.1 Mev. (1.5 hrs.). The bracketed figures are the approximate half-life values obtained by measuring the decay rates of the various gamma ray peaks. A similar run at 50 Mev. yielded approximate gamma ray energies of 150 Kev. (1.5 hrs.), 250 Kev. (2.0 hrs.), 450 Kev. (1.5 hrs.), 700 Kev. (2.0 hrs.), 900 Kev. (1.3 hrs.).

In both runs the 35 Kev. X-rays from praseodymium were very intense and had to be blocked out by lead absorbers. The abundance of X-rays indicates that a great many of the decays are by electron capture.

V. CONCLUSIONS

A mass spectrographic analysis of the target material used showed traces of lanthanum, praseodymium, and neodymium impurities. Their abundance, however, was estimated to be less than 0.1%. Therefore, the chance of producing other elements than praseodymium by (p,xn) reactions would be negligible. At some of the higher bombardment energies used the cross-sections for (p,pxn) and (p,2pxn) reactions may not be negligible. Thus the proton bombardment of cerium might produce radioactive isotopes of both cerium and lanthanum as well as praseodymium. However, the 1.5 hour activity of the mass 137 isotope must certainly be due to praseodymium since the known half-lives of both Ce^{137} and La^{137} are much longer (36 hours and 400 years, respectively). Similar considerations apply to Pr^{138} and Pr^{139}. The half-lives of the isotopes of masses 135, 133, 132, and 131 could not be measured accurately enough to assign them to a particular element. However, the mass assignments made are certain for all of the isotopes detected since assignment of the 4.5 hour activity to Pr^{139} has been proven chemically.

Because of the inefficiency of the mass separations all of the half-life measurements are based on low counting rates. This introduces a correspondingly large statistical error in the results. Thus it is not possible to quote the half-life value for Pr^{137} to an accuracy better than 5%. The conversion electron energy measurements from the beta spectrometer results are consistent to within 1%. Due to the difficulty of judging the end point, the maximum positron energy for Pr^{137} is not accurate to more than 5%.

The conclusions to be drawn from the work reported here are the following.

(a) A new radioactive isotope Pr^{137} has been formed by proton bombardment of cerium. Its half-life is 1.5 ± 0.1 hours and it emits a positron with a maximum energy of 1.7 ± 0.1 Mev.

(b) A 2.0 hour activity produced by proton bombardment of cerium is due to Pr^{138}, confirming the previous tentative mass assignment. The decay of this isotope gives rise to two conversion electrons with energies of 262 ± 5 Kev. and 299 ± 5 Kev. These electrons appear to be the K and L conversions from a 300 Kev. transition in Ce^{138}.

BIBLIOGRAPHY

(1) A.J. Dempster, CP-1507, p.25, March (1944).

(2) M.G. Inghram, Advances in Electronics, 1, 219, (1948).

(3) O.W. Richardson, "The Emission of Electricity from Hot Bodies", Longmans, Green, and Co., p.196, (1916).

(4) J.P. Blewett and E.J. Jones, Phys. Rev., 50, 464, (1936)

(5) R.J. Hayden, MDDC-1546, September, (1947).

(6) M.M. Gransden, "Properties of New Neutron Deficient Isotopes of Lanthanum", (Ph.D. Thesis. McGill University, April, 1951).

(7) K.C. Maclure, "Properties of Some Neutron Deficient Isotopes of Strontium, Indium, and Gallium," (Ph.D. Thesis, McGill University, August, 1952).

(8) A.O. Nier, Rev. Scient. Inst., 11, 212, (1940).

(9) R.L. Graham, A.L. Harkness, and H.G. Thode, J.Scient. Inst., 24, No.5, 119, (1947).

(10) F.W. Aston, Phil. Mag., 49, 1191, (1925).

(11) E. Amaldi, et. al., Proc. Roy. Soc., 149, 522, (1935).

(12) J.K. Marsh and S. Sugden, Nature, 136, 102, (1935).

(13) M.L. Pool and L.L. Quill, Phys. Rev., 53, 437, (1938).

(14) C.S. Wu and E. Segre, Phys. Rev., 61, 203, (1942).

(15) J.W. Dewire, M.L. Pool, and J.D. Kurbatov, Phys. Rev., 61, 564, (1942).

(16) B.J. Stover, Phys. Rev., 81, 8, (1951).

(17) D.E. Mathews and M.L. Pool, Phys. Rev., 72, 163, (1947)

(18) N.Metropolis, "Table of Atomic Masses", Institute of Nuclear Studies, Chicago, (1948).

(19) E. Bleuler and W. Zunti, Helv. Physica Acta, 19, 376,(1946).

(20) H. Slatis and K. Siegbahn, Phys.Rev., 75, 1955, (1949).

(21) R.D. Hill, E.L. Church, and J.W. Mihelich, Rev. Scient. Inst., 23, No. 10, 523, (1952).

(22) M. Goldhaber and A. W. Sunyar, Phys. Rev., 83, 906,(1951).

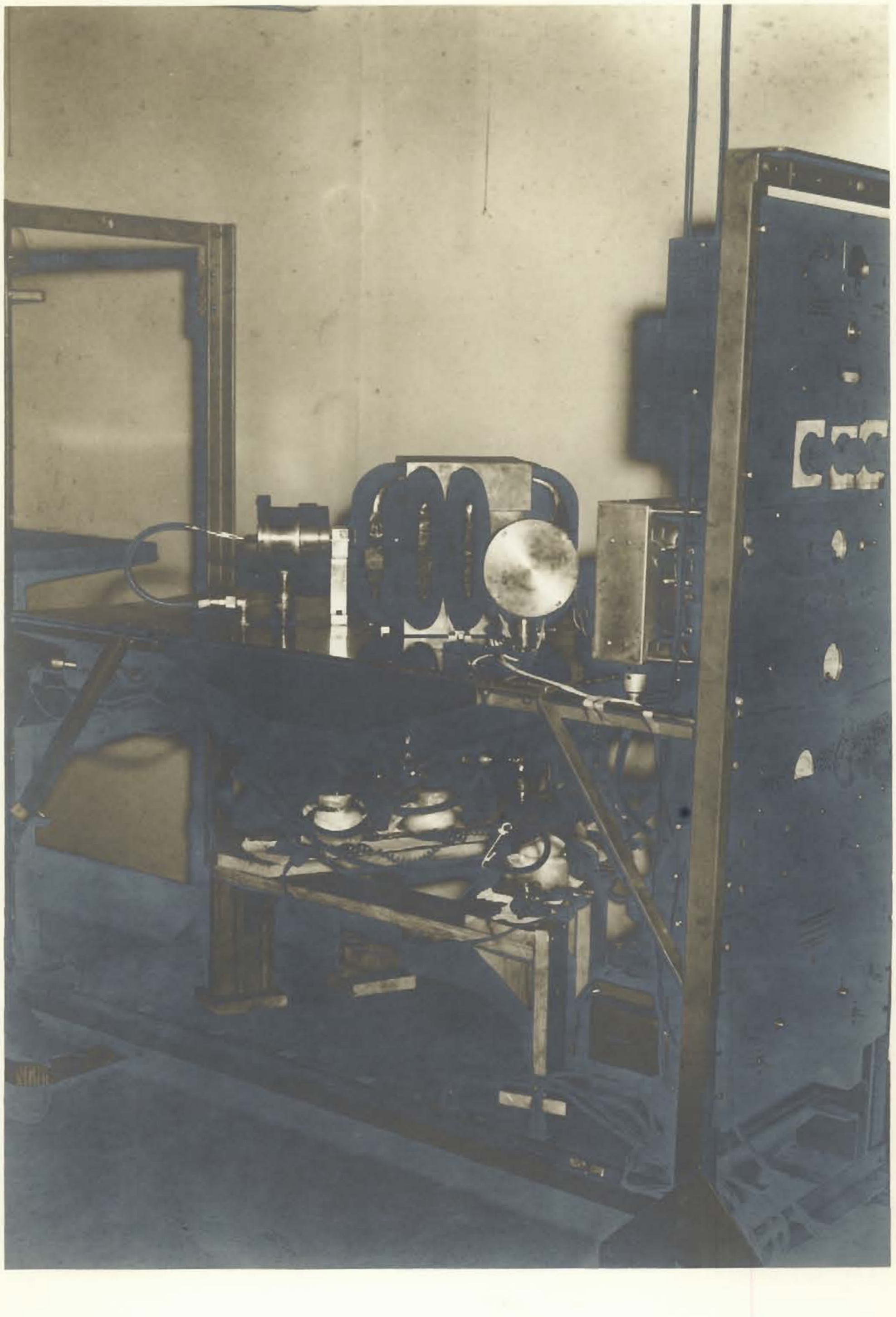

FIGURE I

THE MASS SPECTROGRAPH

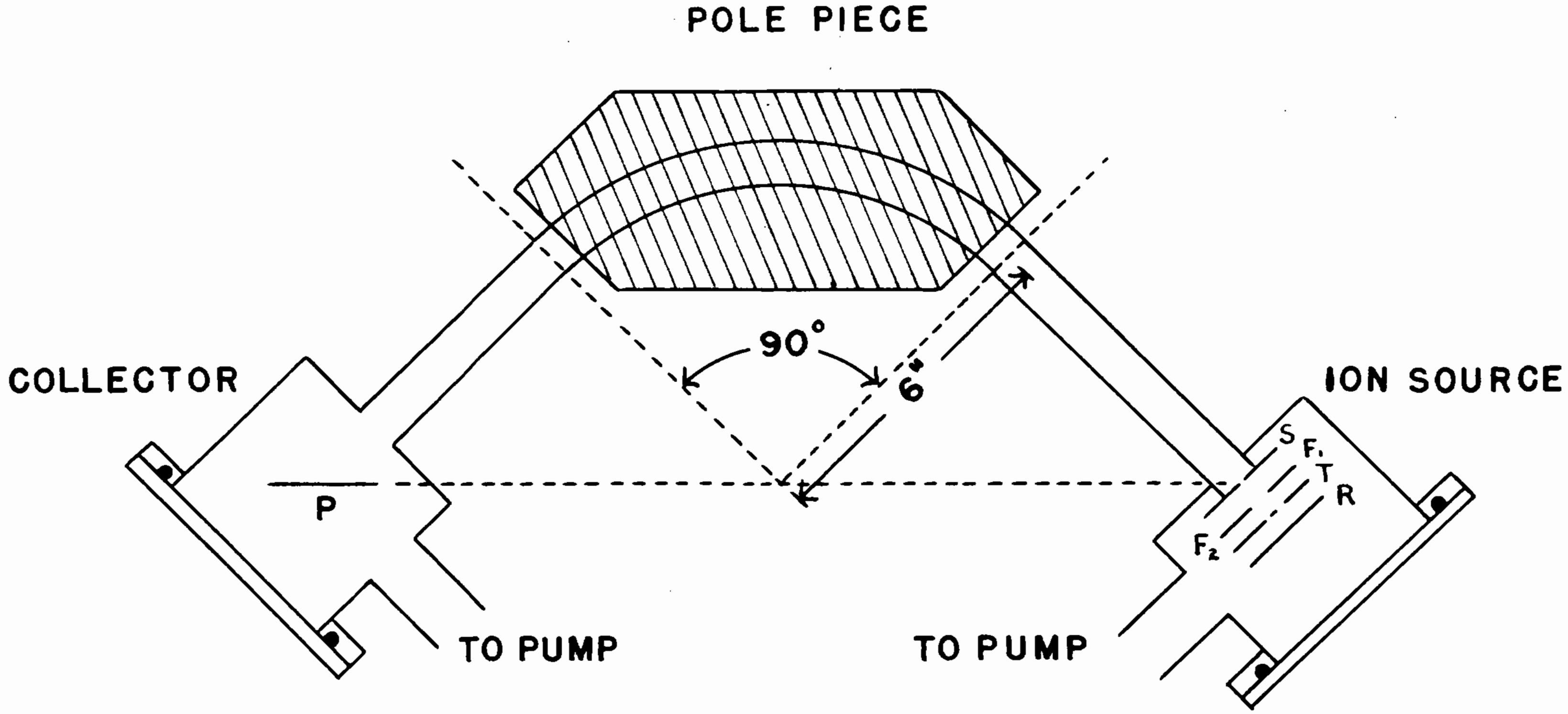

FIGURE 2
SCHEMATIC DIAGRAM OF THE MASS SPECTROGRAPH

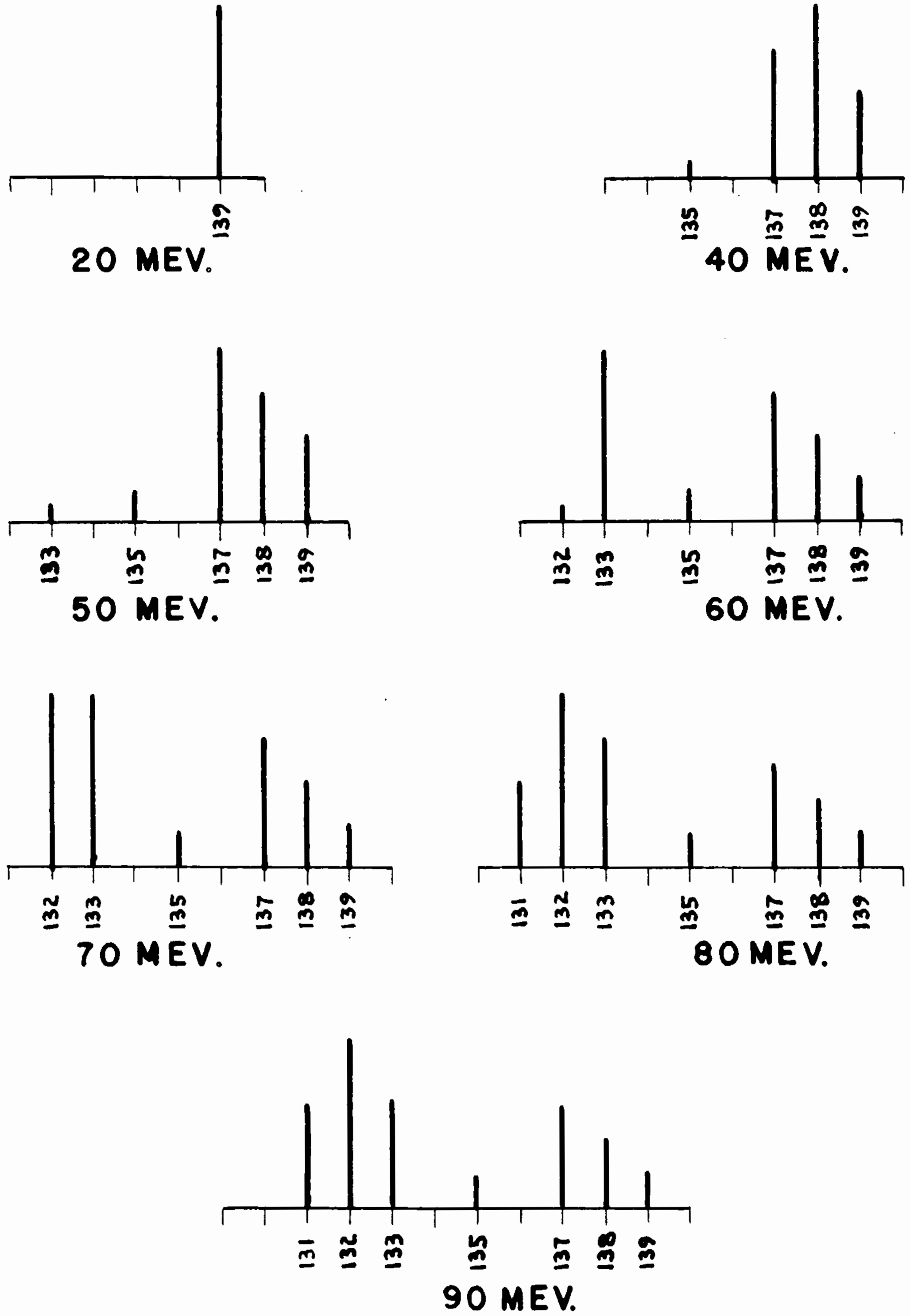

FIGURE 3

MASS NUMBERS AND RELATIVE ABUNDANCES OF

THE ISOTOPES DETECTED

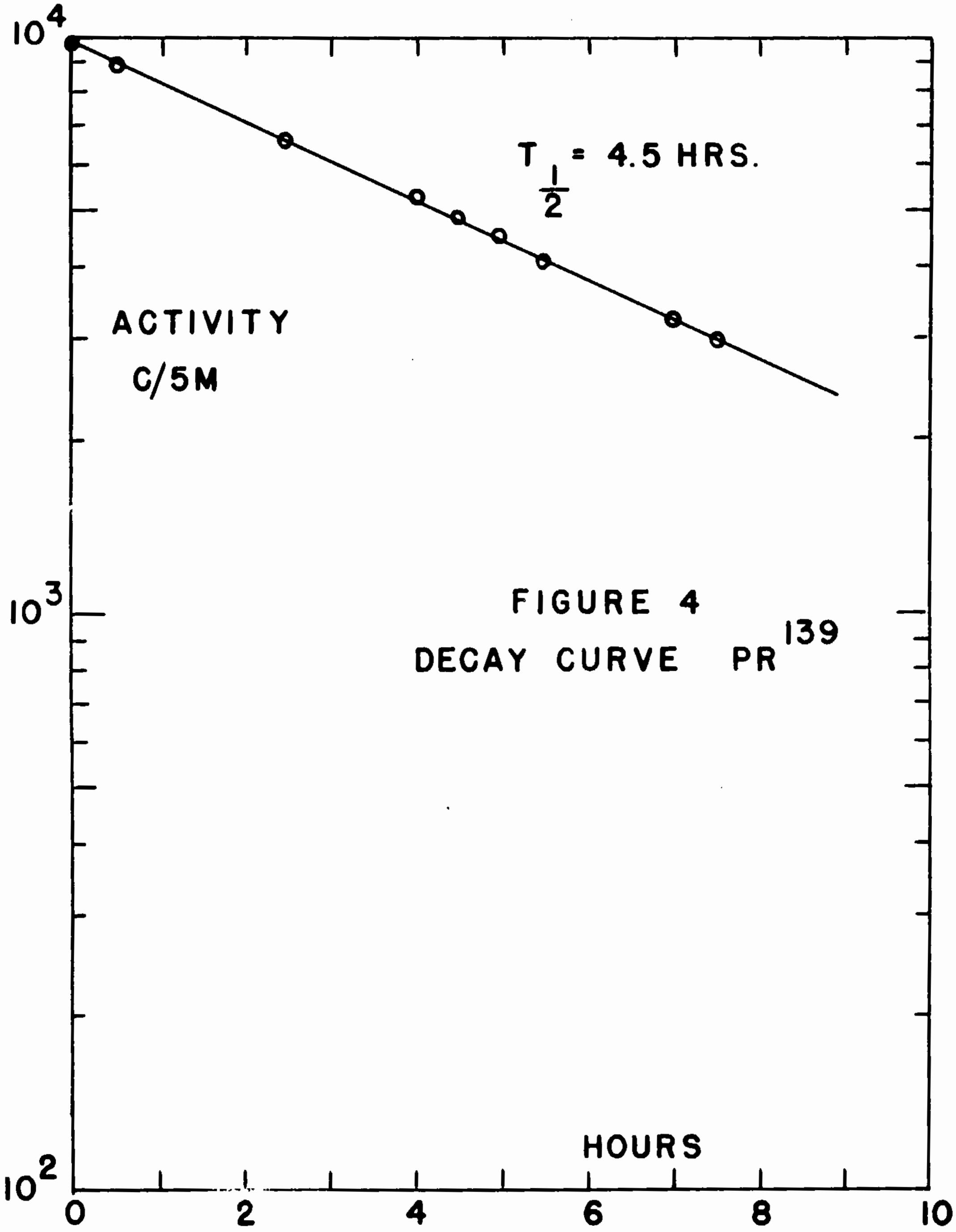

FIGURE 4

DECAY CURVE PR^{139}

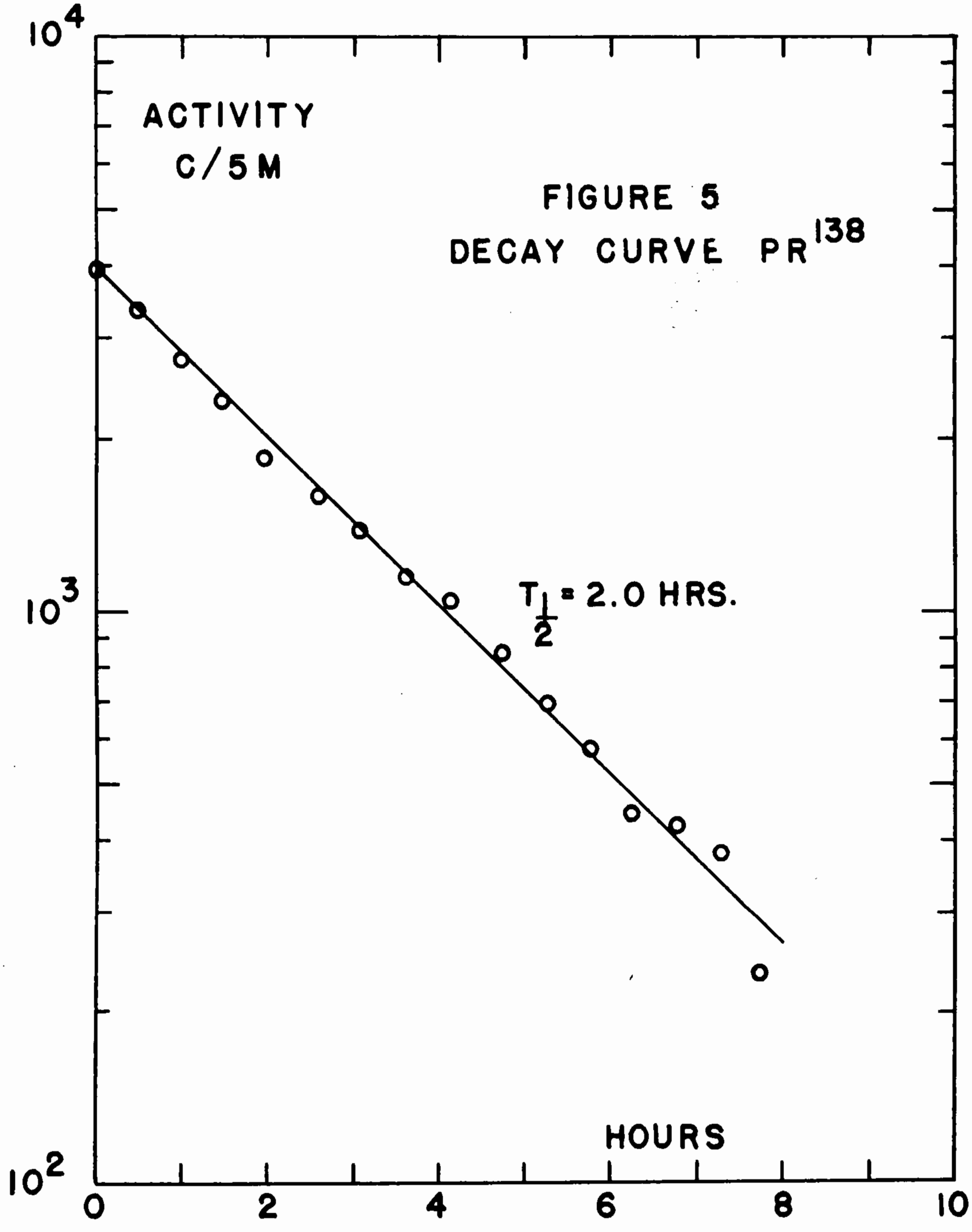

FIGURE 5
DECAY CURVE PR^{138}

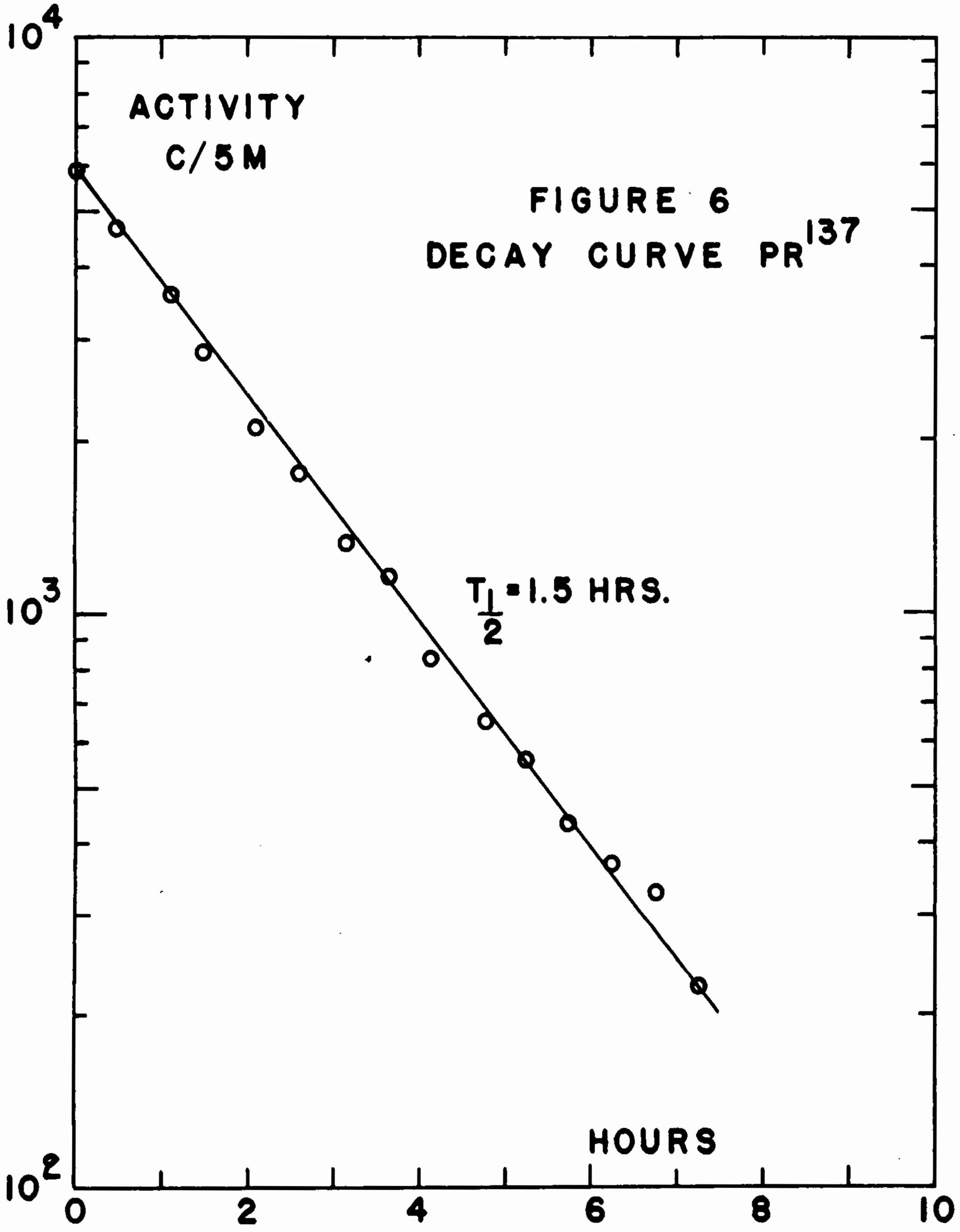

FIGURE 6
DECAY CURVE PR^{137}

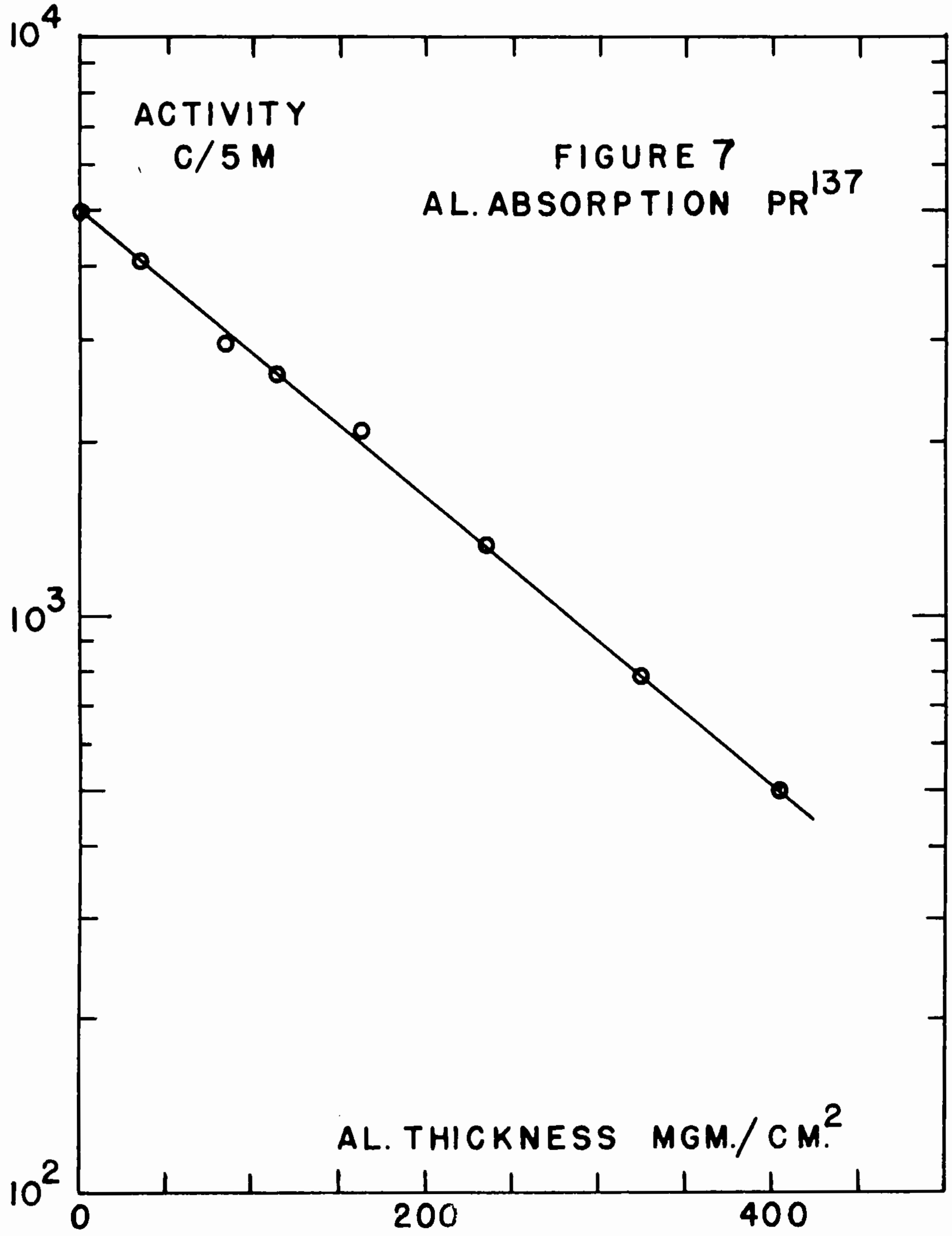

FIGURE 7
AL. ABSORPTION PR^{137}

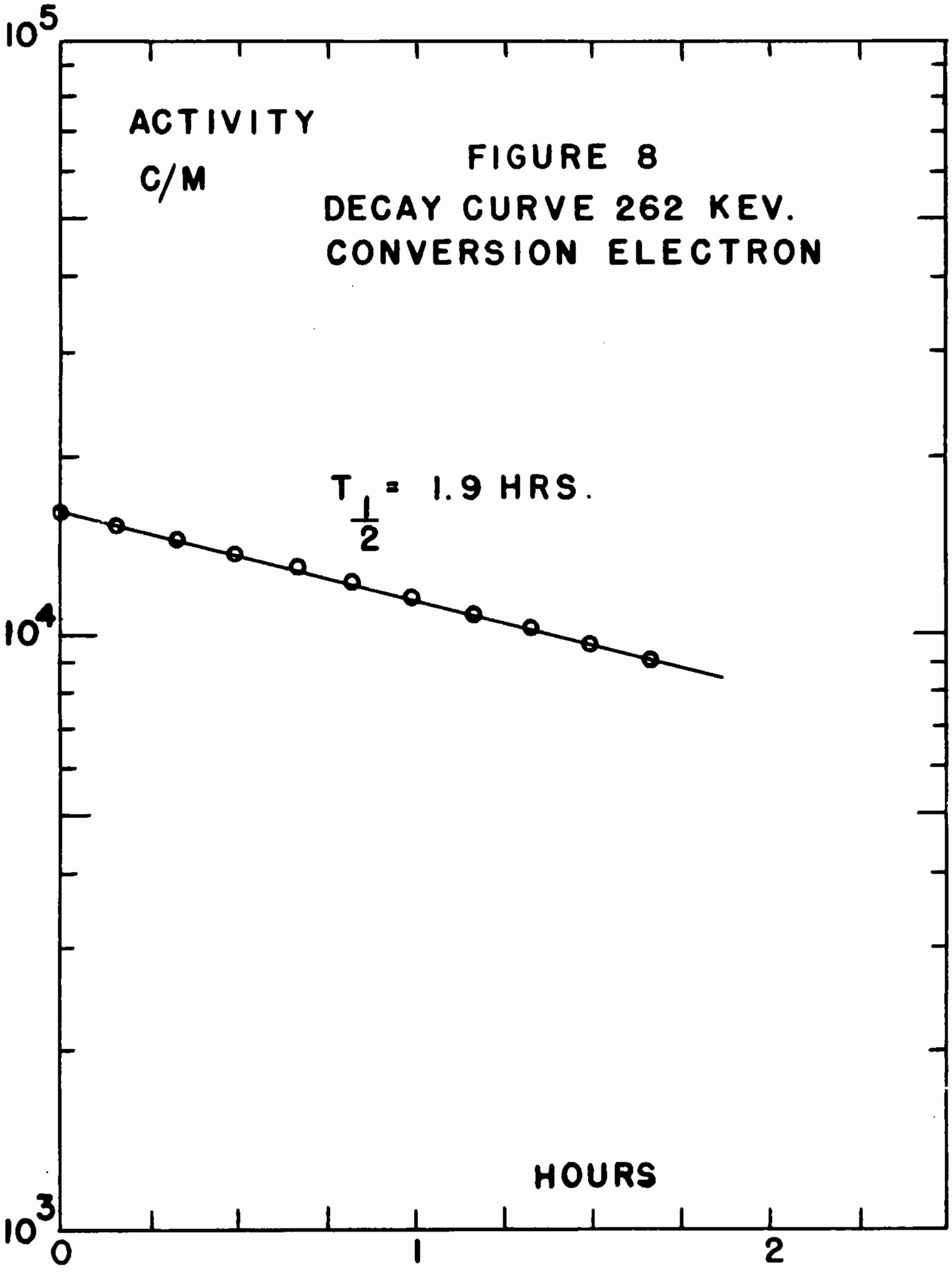

FIGURE 8
DECAY CURVE 262 KEV.
CONVERSION ELECTRON

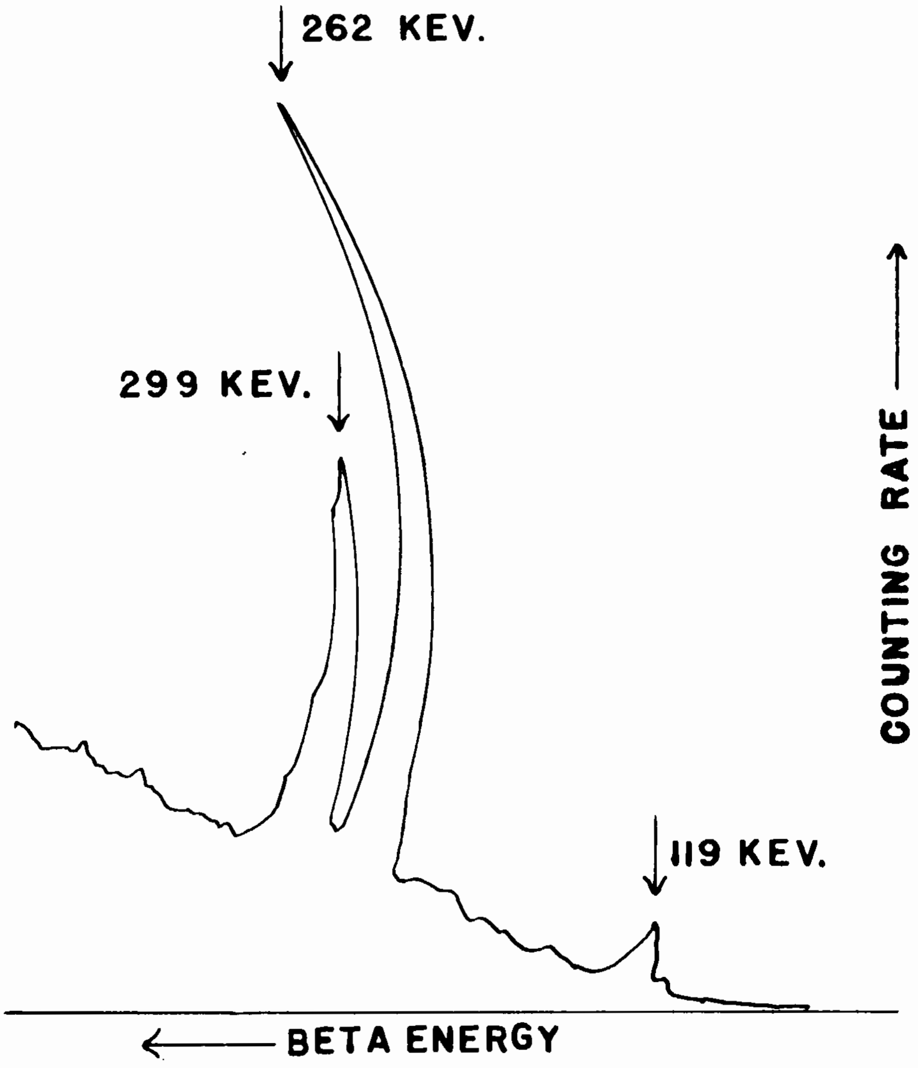

FIGURE 9

BETA SPECTRUM FROM RADIOACTIVE PR.

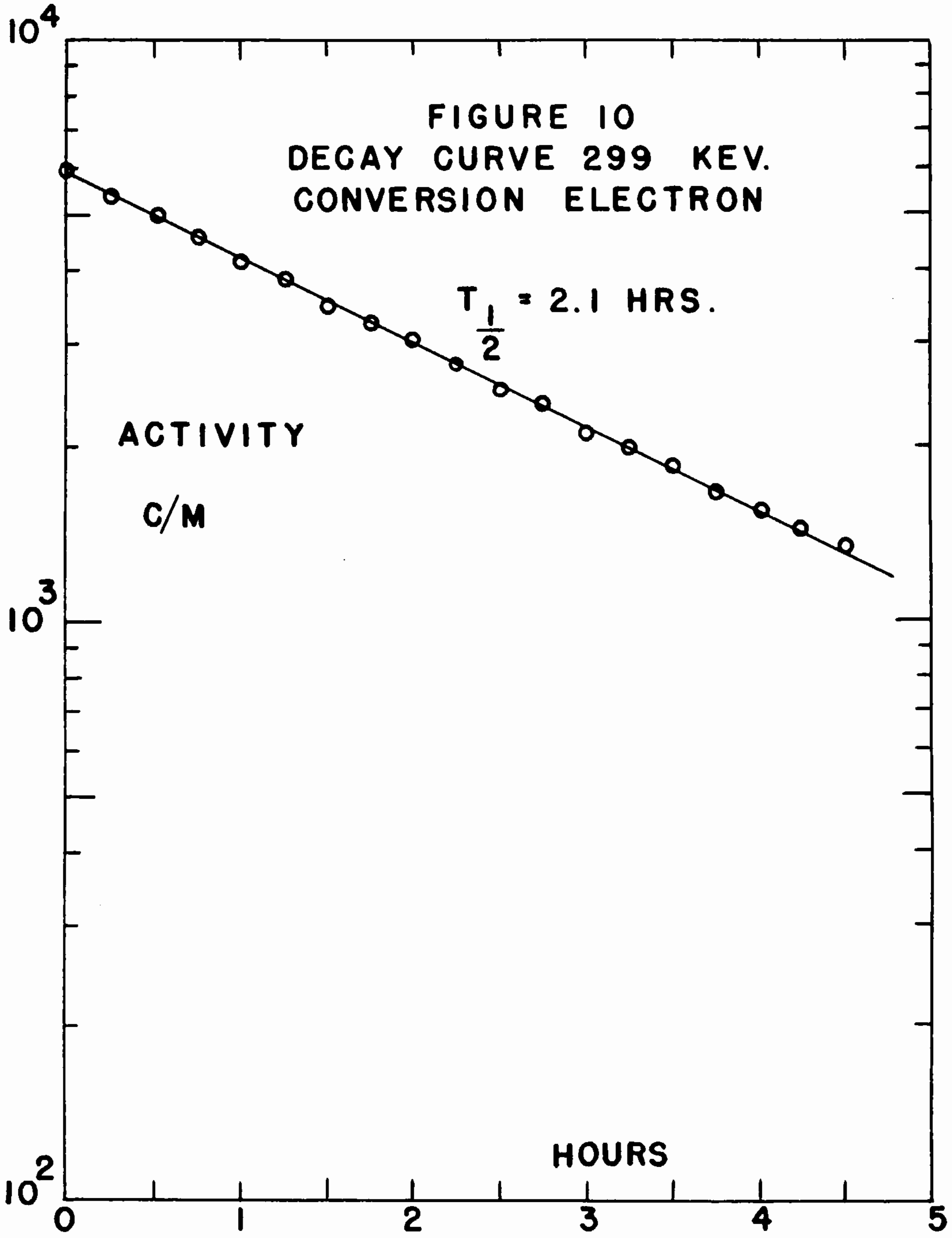

FIGURE 10
DECAY CURVE 299 KEV.
CONVERSION ELECTRON