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ISOTOPES OF NEPTUNIUM AND PLUTONIUM

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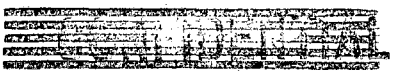

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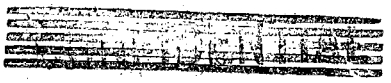

ISOTOPES OF NEPTUNIUM AND PLUTONIUM

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I. INTRODUCTION

Within the past few years there has been a rapid increase in the number of nuclides that have been identified in the region of the atomic table above lead. Characterization of these has allowed a partial mapping of the nuclear energy surface, and significant trends have become apparent. Perlman, Ghiorso, and Seaborg[1] have shown that certain regularities exist in decay by alpha particle emission. Consideration of the energies involved in transitions by alpha and beta particle emission has allowed calculation of the energies available for electron capture decay, which may not be measured; Thompson[2] has shown certain regularities in this system also.

The work described in this dissertation originated in an effort to identify previously unknown isotopes of neptunium and plutonium and to characterize a few that were known for extension of the nuclear energy surface. Two new light plutonium isotopes and one heavy neptunium isotope were found in the course of these investigations, and have been assigned to Pu^{232}, Pu^{235}, and Np^{241}, while a contribution to the data on the modes of decay of Pu^{234}, Np^{234}, and Np^{236} has also been made. All of these were produced by the bombardment of uranium with helium and deuteron ions from the 60-inch cyclotron of the Crocker Radiation Laboratory and the 184-inch cyclotron of the University of California Radiation Laboratory. Separation of these fractions from fission products required the development of rapid chemical procedures in addition to the standard procedures that have been in use.

The chemical and experimental methods are described in the first section of the dissertation and the results of the bombardment work are described for each nuclide. The experimental data indicate excellent agreement with the expected results and do aid in clarifying the structure of the energy surface.

II. EXPERIMENTAL METHODS

A. Preparation of Targets

All of the bombardments considered in this paper utilized uranium as target material. In the majority of cases the uranium was available as U_3O_8, though in the case of U^{233}, the stock was usually kept in nitrate solution.

For experiments on the 184-inch cyclotron, a weighed amount of oxide is placed in a small platinum envelope which is clamped on the probe and inserted various distances into the acceleration tank to intercept particles of the desired radius and hence energy. The targets for the 60-inch cyclotron are small platinum dishes which are held in a water-cooled holder placed in front of the port through which the deflected beam emerges. An adherent layer of oxide may be formed in the dishes by scoring the bottom, adding the powdered oxide and a drop of perchloric acid, fuming to dryness, and igniting.

In cases where a thin uniform film is desired or only a small quantity of uranium in solution is available, ammonium uranyl phosphate may be precipitated, slurried with water, dried slowly on platinum target foils, and gently flamed. This film is very adherent to cleaned pre-ignited platinum and seems to hold very little water of hydration, so there is none of the spattering which occurs when an attempt is made to evaporate most uranium solutions and salts.

Both of these methods produce targets that are readily soluble in nitric acid, so there is no delay in the chemical procedures.

B. Chemical Procedure

The chemistry of plutonium and neptunium has been described amply,[3] but a discussion of the procedures for rapid separation of tracer amounts of these elements from fission product mixtures is in order. The potentials, precipitations, and oxidizing or reducing agents discussed below may be found by reference to Seaborg, Katz, and Manning.[3]

All of the actinides have similar carrying properties when in corresponding oxidation states, so they may be treated as a group. When in the +3, +4, and +5 states, all will follow lanthanum chemistry, and lanthanum fluoride, precipitated from acid solutions, is used often as a specific carrying agent. Only the +4 states will carry on zirconium phosphate from acid solution, while the +6 statesof the other actinides resemble uranium, and will not carry with either zirconium or lanthanum from acid solution.

It is obvious that by changing oxidation states and alternately carrying and scavenging with a given precipitate, fairly complete decontamination may be obtained. The problem then reduces to stabilizing a specific oxidation state rapidly, and is dependent upon the rates of reactions and potentials. In aqueous solutions plutonium may exist in +3, +4, +5, and +6 states; the potentials between all of these range from -0.9 to -1.1 volt in 1M nitric or hydrochloric acid, so the rates of oxidation and reduction primarily determine the state. Neptunium, on the other hand, has more divergent potentials; for example, in 1M HCl at 25°: Np^{+4} $\underline{-0.74}$ NpO_2^+ $\underline{-1.14}$ NpO_2^{++}.

The +3 - +4 and +5 - +6 couples are rapid and reversible, but the +4 - +5 couple is normally slow so that extreme conditions must be imposed to shift across these states, although a few one-electron agents are rapid

under certain conditions: specifically, iodide ion in warm hydrochloric acid greater than 5M reduces plutonium almost completely to the +3 state and neptunium to the +4 state within two minutes; ferrous ion stabilized by hydrazine will rapidly reduce plutonium to a +3 - +4 equilibrium and neptunium to predominately +4 in 1-2M HNO_3; and ceric ion in nitric acid will rapidly oxidize plutonium and neptunium to the +6. In addition, for the reversible couples, nitrite ion in nitric acid solutions stabilizes Pu^{+4} and Np^{+5}. Bromate and permanganate have been used also as oxidizing agents in some cases. Obviously many combinations of precipitations may be designed, and many were used in the experiments in this paper. Since the products sought were often short lived, the primary consideration was the rapidity of the operation, and often more complete separations were discarded for being too slow. Eventually short standard procedures evolved, which will be described.

Uranium was the target material in all bombardments, usually as the oxide, but occasionally as the metal. The oxide is dissolved in nitric acid, and the metal is dissolved in hydrochloric acid with the addition of nitric acid to oxidize the uranous ion to uranyl. The solutions are centrifuged to remove insoluble material and the supernatants diluted to 2M hydrogen ion and subjected to the following procedures which are suitable for 1 g or less of uranium when the work is done in 15 ml centrifuge cones.

For plutonium, Pu^{239} tracer is added as well as 0.5 mg lanthanum and 2.0 mg zirconium carriers and a few drops of a 0.1M $FeCl_2$ - 0.5M $N_2H_4 \cdot 2HCl$ mixture, and the solution is warmed one minute to reduce all plutonium to the +3 and +4 states. Nitrite ion is added to stabilize the +4 state, and phosphoric acid is added to precipitate zirconium phosphate, which is centrifuged and carries the plutonium. This precipitate is washed twice with water containing H_3PO_4 and HCl, and then slurried with 1 1/2 ml concentrated HCl plus two drops of HI. This mixture is heated for two minutes

which reduces the plutonium to +3 and strips it from the zirconium phosphate. Lanthanum carrier (0.2 mg) is added and the slurry diluted to 2M HCl; hydrazine is added to reduce the I_2 formed by air oxidation and the slurry digested for two minutes, whereupon the zirconium is reprecipitated with phosphoric acid and centrifuged. The supernatant is made 1M in HF and the LaF_3, which carries the Pu^{+3}, is digested two minutes, centrifuged, and washed. This completes the cycle, which may be repeated if desired by dissolving the LaF_3 with saturated H_3BO_3 and concentrated HNO_3 (which also oxidizes the Pu^{+3} to Pu^{+4}), diluting to 2M HNO_3, adding zirconium and carrying Pu^{+4} with the phosphate precipitation. The chemical yield of Pu^{239} tracer is 85-90 percent per cycle. Note that there are two specific separations from neptunium: precipitation of plutonium with the zirconium phosphate from the NO_2^- - NO_3^- solution, and scavenging of neptunium with zirconium phosphate from the Cl^- - I^- solution.

Neptunium may be separated by a procedure which is similar in sequence, but employs different oxidation states. The same target solution and carriers as for plutonium is used, but Np^{237} tracer is added. The neptunium is first reduced to Np^{+4} with 1 ml of the ferrous-hydrazine mixture in the hot solution and carried on zirconium phosphate. The washed precipitate is slurried and heated with concentrated nitric acid and a small amount of solid ceric salt (sulfate or nitrate), which oxidizes the neptunium from +4 to +5 and +6 and strips it from the phosphate. Lanthanum carrier (0.1 mg) is added, the slurry diluted to 2M HNO_3, and additional phosphoric acid precipitates zirconium and ceric phosphate, removing the oxidizing agent. The supernatant is treated with nitrite which reduces the Np^{+6} formed to Np^{+5}, and then HF is added to precipitate cerous and lanthanum fluoride which carries the Np^{+5}. The chemical yield of Np^{237} tracer is 80 percent in this sequence.

It must be emphasized that the fractions isolated in these two procedures are not radiochemically pure, since any element present in colloidal form or which splits on a precipitation may not be eliminated except by an excessive number of cycles, so in every case some method of final purification was needed. Several extraction methods are available, but they are not all completely selective; in any case, none of them offer the decontamination factors available with ion exchange methods. In 12 and 13M HCl on a Dowex-50 column, the +3 transuranium elements elute rapidly at essentially the same time,[4] while Np^{+5} elutes even more rapidly. Both neptunium and plutonium may be purified on a 6 cm x 2 mm column of Dowex-50 colloidal resin in 15 to 20 minutes, so this method was used.

The LaF_3 obtained from the chemical procedures is dissolved in HCl and H_3BO_3 for plutonium, and HNO_3 and H_3BO_3 for neptunium; this solution is diluted and $La(OH)_3$ precipitated with NH_4OH and centrifuged. The washed precipitate is dissolved and saturated with HCl gas to keep the volume to a minimum, and this solution is put on the top of the column which has had 12M HCl passing through it. The flow rate is maintained by air pressure, and when the solution containing the activity has passed into the resin, more 12M HCl is introduced at the top of the column and the flow resumed. Drops are collected on glass and platinum plates as desired, and the samples dried for counting. In many cases, for examination of soft particles, these samples were volatilized from a tungsten filament and caught on platinum sample plates.

The advantages of the column procedure are that carrier free samples are obtained and that estimates of the contamination and identification of the activity may be made by comparison on each sample plate between the total activity and the associated alpha tracer. Where more time is available, much better column separations may be obtained by dissolving the $La(OH)_3$

precipitate with 0.5M $HClO_4$ and absorbing the activity with a small amount of resin. This resin is transferred to the top of the column, and the narrow band of activity created by this method gives elution characteristics greatly improved over the procedure described for rapid bombardment separations.

C. Recovery of Uranium Target Solutions

An important aspect of bombardment work in the heavy region is the recovery of the target material. Only limited amounts of U^{233} and U^{235} were available, and they must be accounted for at all times. Several recovery processes have been used, but the best and most convenient small scale batch operation utilizes anion exchange resin, specifically Dowex A1 or A2.

The supernatant solutions from the chemical procedures contained mixtures of anions, including nitrate, nitrite, phosphate, fluoride, sulfate, and chloride. Both the fluoride and phosphate interfere in normal recovery methods but may be eliminated with anion resin. To avoid corrosion of the glass apparatus, solutions containing fluoride are first evaporated to a reduced volume with sulfuric acid to eliminate excess HF. In any case the solution ready for recovery is fortified with HCl gas and heated to decompose excess nitrate which attacks the resin, and finally saturated with HCl.

The resin bed is prepared in a sintered glass filter funnel by using graded wet resin and washing with 10M HCl. Under saturated conditions the resin will absorb its own weight of uranium, but this would mean a loss upon washing, so a factor of ten in the volume of resin is always allowed to ensure against such losses. The uranium chloride recovery solution is allowed to flow through the resin bed, and washed with ten column volumes of 10M HCl to remove all other anions, while the uranium chloride complex is visible as a narrow yellow band at the top of the column. The column may be washed with 6M HCl to remove some fission products absorbed in 10M

HCl without appreciably moving the uranium band.

The uranium is then removed from the column with 0.1M HCl; a small amount seems to hydrolyze within the resin globules and may be removed by repeating with a small volume of 10M HCl and more 0.1M HCl. After this process, the next problem is the removal of the remaining fission product cations. The uranium chloride solution is partly evaporated to reduce the volume and to eliminate excess HCl, then a few milligrams of ferric ion is added to act as a scavenge, and ammonium uranate is precipitated with ammonia. This precipitate is slurried several times with ammonium carbonate solution and a few drops of ammonia (to prevent the formation of colloidal ferric hydroxide), and the uranate dissolves with formation of the uranyl carbonate complex, while the ferric precipitate holds the hydroxide insoluble fission products. The supernatant may then be acidified with hydrochloric acid and boiled to remove carbonic acid, whereupon ammonium uranate is reprecipitated with ammonia, filtered and ignited to U_3O_8. Alternatively the ammonium uranate can be dissolved in dilute nitric acid to form a stock solution which is radiometrically analyzed.

To ensure against losses, the various residues are always concentrated, reworked and checked for uranium content by activity. With reasonable care, the yield of purified uranium should be 99 percent.

III. MEASUREMENT OF RADIATION

A. Instruments

In the discussion of individual neptunium and plutonium isotopes, frequent reference will be made to certain radiation detection instruments. In order to avoid repetition, some of the pertinent characteristics of each of these instruments will be described first and the instruments referred to by name in the subsequent discussions.

The Geiger counters used are argon, xenon, or chlorine-argon filled bell-shaped detecting tubes with thin mica windows. The argon tubes count all the electrons that penetrate the tube window, but have a low efficiency for electromagnetic radiation, ranging from 1 percent for 15 Kev x-rays down to 0.2 percent at 100 Kev and thereafter increasing about 1/2 percent per Mev. The xenon tubes also count all the electrons but have an efficiency for electromagnetic radiation which varies from four times that of the argon tubes at low energies to about twice that of argon tubes above 1 Mev. The chlorine-argon tubes have half the efficiency of the argon tubes, but can handle much higher counting rates than either of the others, and are much more stable. As a result, each type has been used for specific measurements: the argon tube for electron measurements where minimum x-ray interference is desired; the xenon tube where maximum electromagnetic radiation counting efficiency is needed; and the chlorine-argon tube for following the decay of samples where high counting rates are available and a counter stable over a long period of time is required.

Alpha particles were detected in ionization chambers and recorded on standard scalers. For resolution of a mixture of alpha emitters, the 48 channel pulse analyzer is used. This instrument measures the total ionization produced by an alpha particle and sorts these pulses electronically to register successive short intervals of the energy spectrum on 48 fast mechanical registers.

For direct observation of L x-rays and soft gamma-rays in the heavy elements, a xenon-filled tube operating in the proportional region was connected to the pulse analyzer; this combination allows resolution of the L_α, L_β, and L_γ groups.

For special purposes a windowless methane proportional counter has been valuable. Only alpha particles are counted at a plateau of 3500-4000

volts on this counter, but if the voltage is raised to 5000 volts, essentially all particles register including Auger electrons and the nuclear recoils from alpha emission. The counting of Auger electrons is of greatest value, since high counting efficiencies for electron capture decays result.

Estimates of conversion electron energies and of beta energies were made on a magnetic "bender," a crude beta-ray spectrometer of poor resolution but high geometry, designed for low activity samples.

B. Interpretation of X-ray Measurements

The problem of the counting efficiencies for the radiations from electron capturing nuclides has assumed importance in determining partial alpha half-lives for comparison with the alpha systematics. In branching decay, the number of alpha particles may be precisely determined, but the calculation of the electron capture disintegration rate rests ultimately on complete knowledge of the decay scheme and counting efficiencies of the accompanying radiations. Since these are unknown in the majority of cases, approximations must be made that will minimize the errors.

Direct counting of the K x-rays, as a method of determining the number of disintegrations, falls into error since many of the heavy elements undergo considerable L electron capture; in addition, internal conversion of the gamma-rays following decay may produce more than one K x-ray per disintegration. The L x-rays offer an approach, since an L electron vacancy is produced for every K_α x-ray and every K x-ray Auger conversion in the L shell. The K_α groups are 80 percent of the K x-rays emitted in the heavy region.[5-7] Auger conversion occurs primarily in the L shell and is measured to be 10 percent for astatine.[6] If this figure (10 percent) is generally applied to the heavier region, there should be emitted 0.9 K x-rays or 0.7 K_α x-rays per K electron vacancy. Then there are 0.8 L electron vacancies

per K electron vacancy: 0.7 from the K_a x-rays and 0.1 from the K Auger conversion. Hence for cases without gamma-ray conversion, the number of L electron vacancies will range from 0.8 for a pure K electron capture to 1.0 for a pure L electron capture; thus the assumption of one L electron vacancy per disintegration will not lead to an error greater than 20 percent from this source, in estimating electron capture disintegration rates. However, the situation is complicated by the occurrence of gamma-ray internal conversion since every conversion, whether in K or L shell, will produce an additional 0.8 to 1.0 L electron vacancy. Auger conversion of the L x-rays[7] introduces a factor of 0.5, so that one-half of the actual number of vacancies corresponds to the number of detectable L x-rays.

Thus for typical cases, the factor to be applied to the number of L x-rays detected, in order to calculate the number of electron capture disintegrations, will range, for example, from 2 for a K and L electron capture decay with no converted gamma-rays to 1/2 for the case where three completely converted gamma-rays follow the capture. These are extreme cases, and in most heavy electron capturing nuclides with unknown decay schemes, the assumption of one detectable L x-ray per disintegration should not be in error more than a factor of two. In many cases some estimate may be made of the amount of conversion, and a closer approximation will result. In the reports on the nuclides considered in this paper, these assumptions are indicated.

IV. RESULTS AND DISCUSSION

A. The Nuclide Pu^{234}

This isotope of plutonium was first observed by Hyde, Studier, and Ghiorso.[8] Some attempts have been made to characterize it by Perlman, O'Connor, and Morgan[9] who measured the half-life as $8.5^{\pm}$ hour and the alpha particle energy as 6.2 ± 0.1 Mev, and confirmed the mass assignment

by observing the growth of U^{230} and its decay series. The object of the present investigation was to measure the alpha particle energy more accurately and to determine the relative rate of electron capture in order to calculate the partial half-life for alpha particle emission for comparison with the systematics of alpha radioactivity relating energy and half-life.[1]

This isotope may be produced by the $U^{233}(\alpha,3n)Pu^{234}$ reaction, utilizing helium ions from the 60-inch cyclotron, or by the $U^{235}(\alpha,5n)Pu^{234}$ reaction with helium ions from the 184-inch cyclotron. Both methods were used, the choice depending upon the quantities of target material available. Plutonium fractions were chemically isolated and the energy of the alpha particles remeasured on the pulse analyzer as 6.19 ± 0.01 Mev by comparison with standards of known alpha energy.

The half-life obtained from several bombardments by following the decay of this alpha peak on the pulse analyzer was 9.0 ± 0.5 hours.

The electromagnetic radiations were counted through beryllium and lead absorbers in efforts to observe the K x-rays and any harder electromagnetic radiation; none could be detected with the small amounts of activity available. As a result, the L x-rays were measured for abundance and followed for decay on the xenon proportional tube and xenon filled Geiger tube to show their association with Pu^{234} (Fig. 2A). Under the conditions of measurement, the counting efficiency of the L x-rays on the xenon proportional tube was 1 percent and on the Geiger tube, 0.5 percent.[10] From these counters the number of L electron vacancies per alpha particle emission is about 35, corrected for the 0.5 Auger conversion factor. The discussion on the x-rays associated with electron capture indicates that a branching ratio of 35 for electron capture to alpha particle emission is a maximum, since any internal conversion will give more L vacancies per alpha particle. As measured on

the windowless methane counter, there are 20 electron counts per alpha particle; this value is a minimum branching ratio since we should never observe a counting rate corresponding to greater than the disintegration rate unless there are highly converted gamma-rays delayed more than 2.4×10^{-6} seconds (counter dead time) so that more than one count per disintegration would be possible. The true value for the branching ratio therefore should be between 20 and 35.

The methane counter has an efficiency of approximately 30 percent for heavy x-ray emitters with few converted gamma-rays,[11] so that the 20 electron counts per alpha particle for Pu^{234} would indicate a disintegration rate of about 60 electron captures per alpha particle emission if this isotope had no conversion electrons. However, this is considerably larger than the maximum figure of 35 obtained for the x-rays, hence soft conversion electrons must be present. Every conversion electron will increase the efficiency on the methane counter and reduce the calculated branching ratio toward the minimum value of 20; in addition, each conversion will produce another L electron vacancy which will reduce the maximum ratio of 35 obtained from the x-rays. The corresponding correction factors to be applied to the methane counter value and the x-ray value are not self-consistent with the assumed counting efficiencies; however, agreement may be obtained within the errors involved.

The best estimate of the branching ratio which results is about 25 electron captures per alpha particle emission, which leads to a partial alpha half-life of 9.7 days. This value and the measured energy are in agreement with the systematics.[12]

It may be noted that absorption curves on the low level of Geiger activity available did indicate the presence of some conversion electrons (Fig. 2B); however, the normal counting arrangement introduces about 10 mg/cm^2

of absorber over the sample, including window thickness, air gap, and a thin beryllium absorber to stop the alpha particles. This amount of absorber is sufficient to stop all particles below 80 Kev, which correspond to the conversion electrons of gamma-rays up to 190 Kev, so there may be a very appreciable amount of soft electrons as the methane counter indicates.

B. The Nuclide Pu^{232}

This isotope of plutonium has a high neutron deficiency and was expected to have a short half-life so that discovery of it was contingent upon the rapid separation of plutonium fractions from the bombarded material. Since the practical methods of formation of this light mass isotope are the reactions $U^{233}(\alpha,5n)$ and $U^{235}(\alpha,7n)$, which require a high energy, only the helium ions from the 184-inch cyclotron could be utilized. Because of the large specific activity of U^{233}, U^{235} was used as target material almost exclusively to reduce the necessary alpha decontamination factor.

The plutonium fraction from a bombardment with 150-Mev alphas showed a collateral series on the pulse analyzer resembling the U^{228} series reported by Meinke, Ghiorso, and Seaborg[13] but which decayed with a half-life estimated as 22 minutes instead of the 9 minutes reported. The isotope Pu^{232} was expected to have an energy close to that of U^{228}, so the activity was tentatively assigned to Pu^{232}, the alpha peaks being unresolved.

Bombardments at various energies showed that the maximum yield occurred with about 110-Mev helium ions, and more bombardments were made at this energy in order to confirm the assignment and to obtain a better half-life of 36 ± 2 minutes.

Uranium fractions were separated from a small amount of Pu^{232} activity and these fractions were observed to decay on the pulse analyzer with the 9-minute half-life expected for the U^{228} series, thus confirming the mass

assignment. The U^{228} series observed by Meinke et al. was always complicated by the presence of other uranium series, and the energies reported were subject to considerable error. The series produced by Pu^{232} was uncontaminated and the 36-minute half-life allowed more time for measurement. Improvements in the pulse analyzer made possible the resolution of the Pu^{232} and U^{228} alpha peaks (Fig. 3C), and the measurement of the energy of each as well as the other members of the series. The best values are Pu^{232}, 6.58 Mev; U^{228}, 6.67 $\pm$ 0.02 Mev; Th^{224}, 7.13 $\pm$ 0.02 Mev; Ra^{220}, 7.43 $\pm$ 0.03 Mev; Em^{216}, 8.01 $\pm$ 0.03 Mev. Pulse analyzer curves of the Pu^{232} series, of the U^{228} daughter series, and the resolution of the Pu^{232}-U^{228} alpha particle peak are shown in Fig. 3A, B, and C, respectively. The decay of the parent and daughter series are shown in Fig. 4A and B.

Direct observation of the associated Geiger activity did not offer an approach to the amount of electron capture decay of Pu^{232} since Pu^{235}, which decays by electron capture with a 25-minute half-life, was present in all bombardments forming Pu^{232}, and the half-lives were unresolvable. The only possibility of determining the branching ratio rested upon isolating the electron capture daughter, Np^{232}, which has been assigned by Magnusson, Thompson, and Seaborg[14] as a 14-minute electron capturing isotope. No short lived L x-rays were observed in several experiments, but the low counting yield of x-rays and correction for decay of the Np^{232} during separation allowed placing only a limit of less than 60 for the EC/α branching ratio.

C. The Nuclide Pu^{235}

No evidence for Pu^{235} had been found in earlier work, so an experiment was designed to favor its discovery. Closed energy cycles give a value of 1.28 Mev for the transition energy to be expected in electron capture (see Fig. 1), and from this, an estimate of the half-life as 10 to 40 minutes.

This isotope of plutonium can be made by the two reactions: $U^{233}(\alpha,2n)Pu^{235}$ and $U^{235}(\alpha,4n)Pu^{235}$. Since a short half-life was expected, a bombardment of maximum intensity was desired; hence the 60-inch cyclotron, which has a beam intensity about ten times that of the 184-inch cyclotron, was utilized with U^{233} as the target, although the U^{233} alpha activity required special care in handling. With the 37-Mev helium ions available, Pu^{234}, Pu^{235}, and Pu^{236} are all produced. To reduce the Pu^{234} formed in the bombardment and to maximize the yield of Pu^{235}, the helium ion beam was decreased in energy by absorption. Since the maximum yield for the $(\alpha,2n)$ reaction and the threshold for the $(\alpha,3n)$ seem to occur at 28-30 Mev, 0.002 inches of tantalum absorber was placed over the U^{233} target dish to reduce the energy of the incident particles to this value. An early version of the shortened chemical procedure was used, which gave counting samples off the ion exchange column one hour after bombardment. The elution curve showed a Geiger activity which followed the Pu^{239} alpha tracer peak exactly (Fig. 5A). The samples were combined for counting and followed for decay, some points being taken with absorbers to obtain an estimate of the radiations. The best half-life obtained from the data is 26 ± 2 minutes (Fig. 5B). The radiations appear to be primarily L x-rays, with a small amount of harder radiation; there are few, if any, conversion electrons with energy greater than 100 Kev. It is interesting to note that the few points taken have a close similarity to the corresponding absorption points for 410-day Np^{235} which decays primarily by L electron capture.[15] The estimated partial alpha half-life of Pu^{235} is long, and the alpha energy is expected to lie between Pu^{234} and Pu^{236}. Pulse analysis of samples containing the 26-minute activity showed a small alpha peak from Pu^{234}, which contained no detectable amount of a short lived activity on the low energy side.

Pulse analysis of the radiations observed with the xenon proportional tube showed the characteristic L_α, L_β, and L_γ groups of a heavy element, which in conjunction with the column run determines that this is a plutonium isotope with all of the expected properties. Therefore, the assignment is made to Pu^{235}, since Pu^{234} and Pu^{236} are known, and since no other plutonium isotopes can be made in appreciable quantities.

D. The Nuclide Np^{234}

This isotope of neptunium was first observed by James, Florin, Hopkins, and Ghiorso[16] in a bombardment of U^{235} with deuterons, and later observed in bombardments of U^{233} with deuterons[8] and Pa^{231} with helium ions.[17] The half-life was reported as 4.4 days and the isotope was reported to have a characteristic hard gamma-ray of 1.9 Mev. The estimated cycle energy for the total transition is 1.9 to 2.0 Mev (Fig. 1), which means that the transition yielding the 1.9-Mev gamma-ray is an extremely low energy electron capture process to be competing well with decays to less highly excited states of the product nucleus. It became of interest, therefore, to confirm this gamma-ray energy and also to determine as much of the decay scheme as possible.

The isotopes Np^{234} and Np^{236} were produced by deuteron bombardments on U^{235} (99.94 percent) by the (d,3n) and (d,n) reactions, respectively, and the samples were examined after the decay of Np^{236}. The first measurements were made with beryllium absorptions and an argon Geiger tube in order to reduce the effect of the large number of L x-rays. Two well defined conversion electron groups could be resolved at 0.7 Mev and 0.3 Mev with a relative abundance of two to one, respectively (Fig. 6A). Lead and silver absorptions on the xenon tubes showed that the electromagnetic radiations observed were primarily L x-rays and the hard gamma-rays. The intermediate

region is in such low intensity that it is difficult to resolve, however, there appear to be present K x-rays and a small amount of more energetic electromagnetic radiation; these have a composite half-thickness of 250 mg/cm^2 of lead (Fig. 6B), which corresponds to 160 Kev. The low counting efficiency of electromagnetic radiation between 100 and 500 Kev allows considerable radiation of intermediate energy to be present even when the observed intensity is low. The normal assumptions for these efficiencies indicate that the Np^{234} samples emitted L x-rays, K x-rays plus gamma-rays less than 1 Mev, and hard gamma-rays in the proportion 100 to 60 to 40, respectively. Measurements on the hard gamma-ray gave half-thicknesses of lead ranging from 16 gm/cm^2 upward to impossible values, and it was presumed that this was due to secondary radiations. Measurements on the beta-ray spectrometer by O'Kelley when a large Np^{236}-Np^{234} sample became available showed conversion electrons from 0.803 Mev and 0.44-Mev gamma-rays as well as a few at energies corresponding to 0.18 Mev and 1.42 Mev (Fig. 7). To show that the hard gamma found in lead absorptions in reality was 1.42 Mev which should have a half-thickness in lead of only 12 gm/cm^2, duplicate absorption measurements were made on the 1.33-Mev gamma-ray from Co^{60}. The half-thickness values from this were also 16 gm/cm^2 and up, so it seems most likely that there is a single hard gamma of 1.42 Mev in Np^{234} and that absorption by lead as a method for determining the energy of hard radiation is widely in error. Correlation of the numbers of electrons and x-rays shows that Np^{234} emits electrons of 0.3 Mev and 0.7 Mev in proportion of 0.5 percent and 0.9 percent of the L x-rays, respectively.

Since the Auger conversion coefficient of the L vacancies is 0.5, the transitions to the excited state yielding the 1.42-Mev gamma-ray occur in about 20 percent of the electron capture decays, also the sum of the three gamma-rays at 0.18, 0.44, and 0.80 Mev is likewise 1.42 Mev suggesting

the cascade emission of these as a parallel path for decay of the excited state. In any case there is a large excess of L x-rays, so that even at the large transition energy available the amount of L electron capture is of the same order of magnitude as K electron capture.

E. The Nuclide Np^{236}

This isotope of neptunium was discovered by James, Florin, Hopkins, and Ghiorso,[16] by observing the growth of Pu^{236} alpha particles into a neptunium fraction isolated from a U^{235} target that had been bombarded with deuterons. Later experiments on the rate of growth of the Pu^{236} and the direct decay of the neptunium fraction gave a half-life of 21-22 hours. Excessive amounts of Np^{238} and Np^{239} in all samples prevented the determination of the radiations. The closed-energy cycles indicated that Np^{236} should capture electrons as well as emit beta particles (Fig. 1), and show that the beta energy would be a valuable check point for extending the cycles into the heavier elements.

Bombardments were performed on enriched U^{235} (94 percent) in attempts to characterize this isotope, but in every case the Np^{238-9} yield predominated and it was not until a few hundred milligrams of 99.94 percent U^{235} became available that samples free of Np^{239} could be prepared. A short bombardment with 18-Mev deuterons on the 60-inch cyclotron produced a few thousand counts of radioactively clean Np^{234} and Np^{236}. Beryllium absorptions using an argon Geiger tube were taken immediately after the bombardment on the Np^{234-6} mixture, and also after the Np^{236} had decayed. When the second series of absorption points were corrected for the decay of Np^{234} and subtracted from corresponding points of the first absorption, a differential absorption curve for Np^{236} resulted, which gave a range of 180 mg/cm^2 of beryllium, or about 0.5 Mev. Later bombardments with 14-Mev deuterons produced a sample of Np^{236} free of Np^{234}; the beryllium absorption curve is shown in Fig. 8A.

Subsequent bombardments which yielded more activity allowed "bender" curves to be taken which, when analyzed by a crude Kurie plot, also gave a beta energy of 0.5 Mev.

Eventually sufficient activity was produced for direct measurement of the beta spectrum on the beta-ray spectrometer, by O'Kelley (Fig. 7).

These runs showed that the beta spectrum was complex, with two beta groups and a conversion electron present. A Kurie plot of the beta spectrum showed that these groups had end-points at 0.51 and 0.36 Mev and an abundance of 60 percent and 40 percent, respectively, of the total beta emissions. The K, L, and M conversion electrons of a 0.15-Mev gamma-ray were also seen, equal in total abundance to the low energy beta group. When the decay of this isotope was followed through 1 g of beryllium, which absorbs all of the electrons and 1/3 of the L x-rays, an excessive amount of electromagnetic radiation was observed to be associated with the 22-hour isotope; in addition, the spectrometer data showed an excessive amount of L Auger electrons. With the sample free of Np^{234}, the radiation was characterized by silver absorptions as entirely L x-rays and K x-rays with no detectable amount of the 0.15-Mev gamma-ray (Fig. 8B).

The relative activity of beta particles, L x-rays and K x-rays as observed on a xenon counting tube was 12.6, 1.25, and 0.15. The beta particles were counted through a total of 10 mg/cm^2 of absorber, including air gap and window thickness, and from the integrated spectrum O'Kelley estimates that this will stop 40 percent of the electrons, at the low energy portion of the spectrum. The corrections for this and the counting efficiency of the x-rays give the relative abundances emitted of each as 100 beta-rays, 130 L x-rays, and 110 K x-rays. If the standard 0.5 Auger conversion factor for L electron vacancies and 1 K x-ray and 0.5 L x-ray per K electron vacancy is assumed as an approximation, the 40 K x-rays and 20 L x-rays from the converted gamma-ray may be subtracted from the observed activity and a total decay

scheme may be postulated by crediting the remaining 70 K x-rays and 110 L x-rays to electron capture. This gives a ratio of total electron capture to beta particle emission of 2. In addition, the 110 L x-rays are equivalent to 220 L electron vacancies; if 70 are credited to the K electron capture, then the L/K electron capture ratio is also 2 (Fig. 9).

The assumed efficiencies and conversion factors for x-rays together may easily be in error by ±20 percent, so the absolute values are not too accurate; however, the ratio of two between electron capture and beta emission is probably not far wrong. The methane internal counter offers corroboration of this since the ratio of activity on this instrument to the total beta particles corrected to 100 percent geometry is 1.5 for thin samples. Actually the beta decays should never register with 100 percent yield since the geometry factor is 50 percent when the sample is mounted on a flat plate. However, comparison with the other beta emitters indicatesthat back-scattering of soft particles and the additional emission of conversion electrons in this case should give a counting yield of 70 to 80 percent. If the excess activity above the beta activity in the samples is credited to electron capture, with a normal counting yield of 30-40 percent for cases with no converted gamma-rays, then the ratio of electron capture to beta emission again is 2 or 3.

F. The Nuclide Np^{241} and Search for Isomers of Np^{238} and Np^{239}

An activity which is tentatively assigned to Np^{241} has been identified as a result of bombardments seeking heavy neptunium isotopes. From a closed energy cycle it was estimated that Np^{241} should be unstable with respect to beta emission by about 1.2 Mev and hence should have a half-life of about 0.5 hours. The cycle here was perhaps more subject to error than most since two sides of the energy cycle were estimated (Fig. 1).

U^{238} was utilized as target material, and an attempt was made to produce Np^{241} by the (a,p) reaction, using 35-Mev helium ions from the 60-inch cyclotron. Since Hyde and Studier[18] have recently identified 7-minute Np^{240}, any new activity in the neptunium fraction from the uranium bombardment would very likely be due to Np^{241}.

A short chemical procedure was used, and neptunium fractions from the bombardment showed the presence of a short lived isotope, with half-life about one hour, which was coincident with the Np^{237} alpha tracer in a resin column elution curve (Fig. 10). Later bombardments gave some data on the beta energy and gamma-rays, and the better half-life of 60 $\pm$ 2 minutes (Fig. 11).

Absorptions with beryllium yielded a rough value of 0.7 Mev for the beta particles (Fig. 12A) and showed the presence of a large amount of L x-rays, indicating gamma-ray conversion. The presence of the L x-rays was confirmed by direct observation on the proportional tube and pulse analyzer.

Attempts to obtain samples for the beta-ray spectrometer failed to produce sufficient activity to define the beta energy, but did show the presence of a highly converted gamma-ray of about 0.1 Mev. A sample was placed on the "bender" and the resulting plot of activity versus magnet current indicated that the beta spectrum was complex. An approximate Kurie plot of the spectrum would indicate two beta groups of about 0.5 and 0.9 Mev. In an effort to find additional gamma-rays, a sample was followed for decay through different thicknesses of lead, and the one hour line resolved from each curve. These were interpolated at a common time to correct for the decay between successive absorption points, and the gamma energy was estimated as 0.8 Mev from the resulting half-thickness value, which is about the same value obtained from a differential lead curve (Fig. 12B).

The assignment to Np^{241} was not certain, since the activity might be a short lived isomer of Np^{238} or Np^{239}. Since two other odd-odd nuclei in this region ($_{91}Pa^{234}$ and $_{95}Am^{242}$) have isomers, it may be suspected that $_{93}Np^{238}$ might also. Bombardments with 9-Mev protons and 18-Mev deuterons were made on the 60-inch cyclotron and neptunium fractions isolated rapidly. These showed little activity other than with the 2-day Np^{238} and Np^{239} half-life expected, and contained none with the one-hour half-life. Since this activity is not made by deuterons, the mass number must be greater than 239, and from Hyde and Studier's assignment, it is not 240. In addition, the cross section calculated from the activity produced was about 10^{-3} barns which is about normal for an (a,p) reaction in this region, thus the best assignment of this activity is to Np^{241}.

The proton and deuteron bombardments also allowed limits to be set on the atom yield of short lived isomers of Np^{238} and Np^{239}. The maximum yield in a proton bombardment of an isomer with half-life 5 minutes or longer is 1 percent, relative to normal Np^{238}. The limit on the yield from a deuteron bombardment ranges from 0.05 percent for a 20-minute half-life to 3 percent for a 5-minute half-life, relative to the $Np^{238-239}$ mixture.

G. Discussion

Although the data for each nuclide have been discussed with the experimental work, it may be well to summarize the results in terms of the heavy element systematics for alpha and beta decay processes.

The measurement of the partial alpha half-life of the even-even nuclide Pu^{234} does give excellent agreement with the systematics curve of alpha energy and half-life. Although the partial alpha half-life of Pu^{232} was not measured, the energy falls in line with the other plutonium isotopes in the graph of alpha energy versus mass number. For the even-odd nuclide Pu^{235},

the partial alpha half-life was expected to be of the order of three years,[12] since the odd nucleon causes the transition to be forbidden to some degree. With the small amount of 26-minute electron capture activity produced, no alpha particles were observed, as was expected from comparison of the half-lives.

In the electron capture decay of Np^{234} and Np^{236}, a large amount of apparent L electron capture was observed, in common with many such cases in this heavy element region; for Np^{234} the ratio L/K was about 1 and for Np^{236}, about 2, even though a comparatively high energy of transition is available. According to Rose,[19] these energies should give a ratio of L_I electron capture to K electron capture of 0.2 for allowed transitions. However, both of these isotopes are of the odd-odd type, which usually are forbidden to some degree in all decay processes. Any forbidden decay, specifically, parity change with $\Delta J = 0$ or 1 under the Gamow-Teller selection rules for beta decay,[20] will favor L_{II} and L_{III} electron capture in appreciable amounts. There has been no formulation of the theory for these heavy elements, but estimates based on the formulas of Marshak[20] for elements of lower atomic number would indicate that the ratios observed are not unreasonable.

Insufficient measurements have been made on Np^{241} to compare its transition energy with the estimation from closed energy cycles, but these are certainly not incompatable at the present time.

ACKNOWLEDGMENT

The work described in this dissertation was performed under the direction of Professor G. T. Seaborg. Mr. A. Ghiorso, Dr. R. A. James, Dr. K. Street, Jr., and Mr. G. D. O'Kelley aided in many of the experiments. I wish to thank Professor J. G. Hamilton, Mr. G. B. Rossi, Mr. T. M. Putnam, Jr., and their associates in the Crocker Radiation Laboratory for their cooperation in operating the 60-inch cyclotron; and Professor R. Thornton, Dr. D. C. Sewell, Mr. J. T. Vale, and the operating crew of the 184-inch cyclotron for their aid in the bombardments performed at the Radiation Laboratory of the University of California. This research was performed under the auspices of the U. S. Atomic Energy Commission.

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Figure

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   A. Beryllium absorption of the beta particles and electrons.
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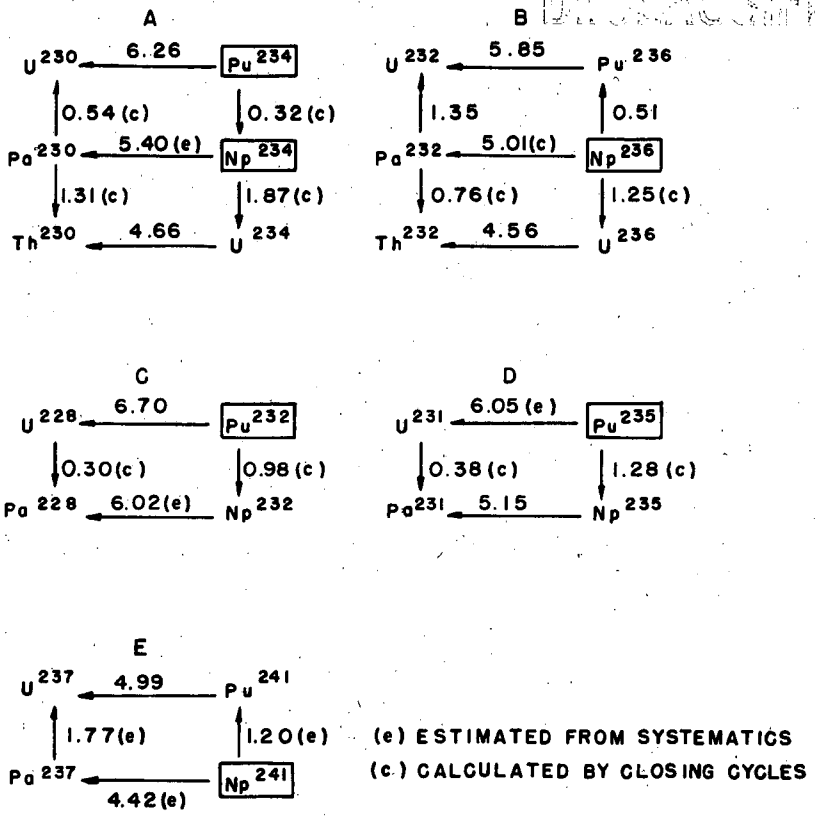


(e) ESTIMATED FROM SYSTEMATICS
(c) CALCULATED BY CLOSING CYCLES

FIG. 1

MU 1140

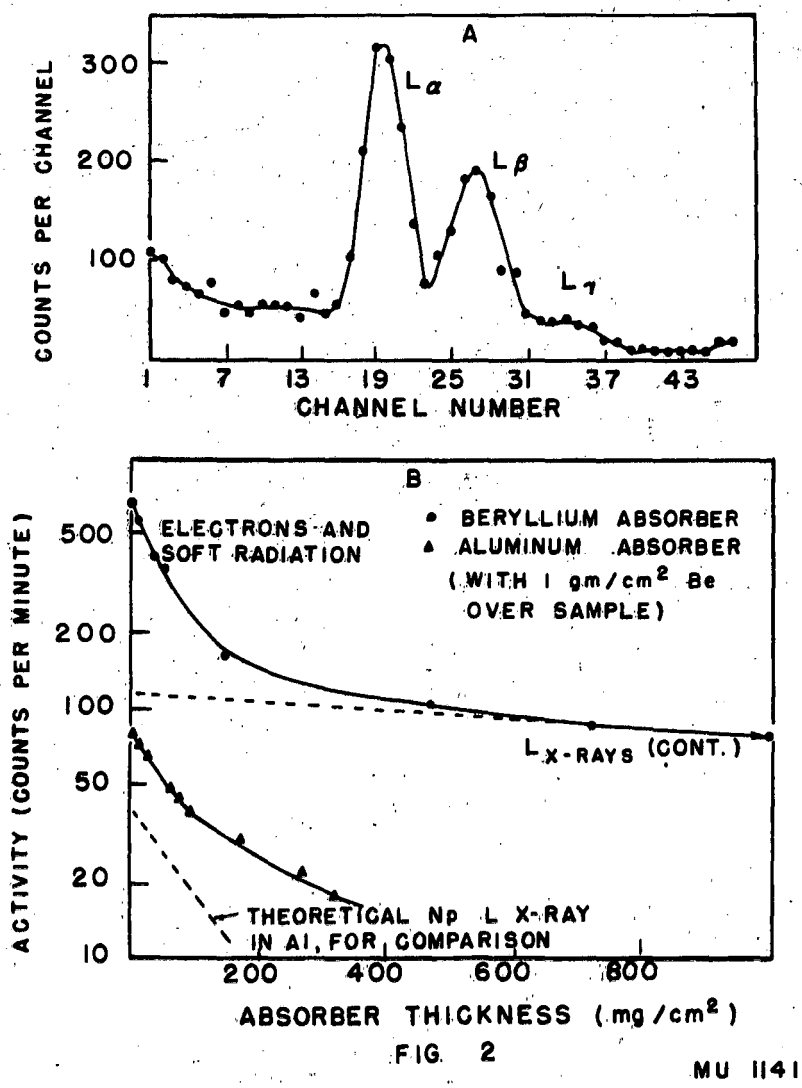


FIG. 2

MU 1141

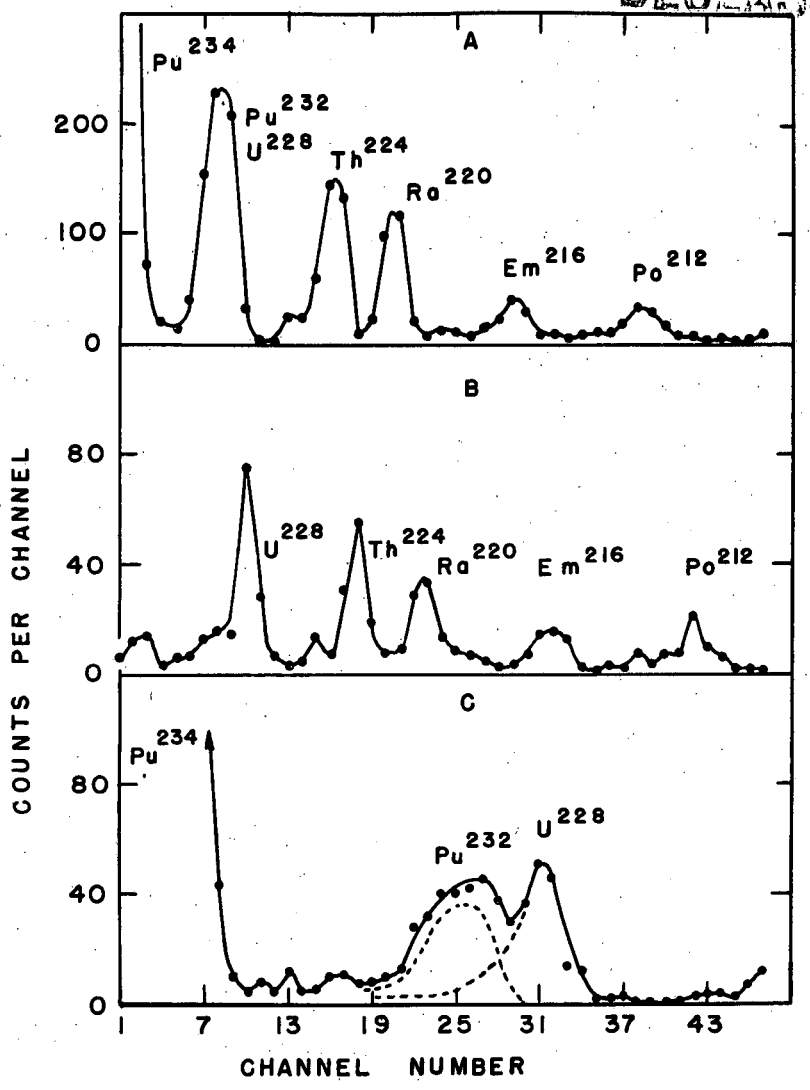


FIG. 3

MU 1142

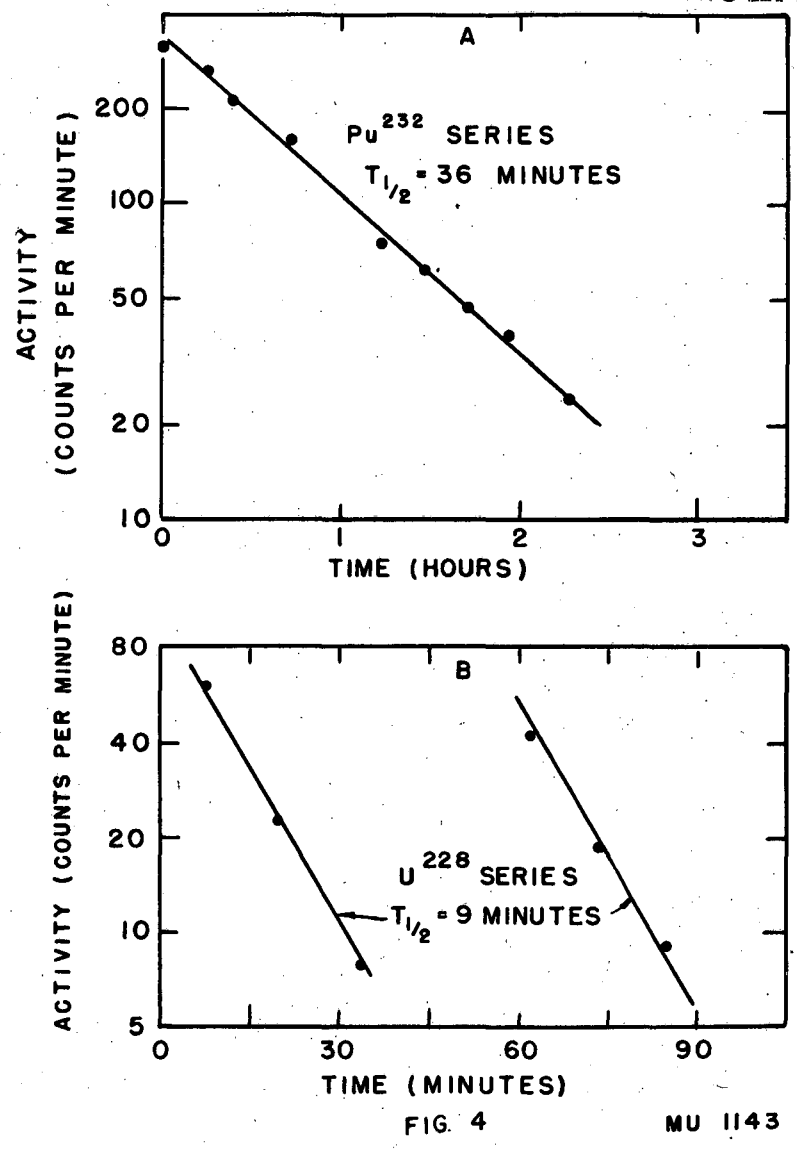


FIG. 4 MU 1143

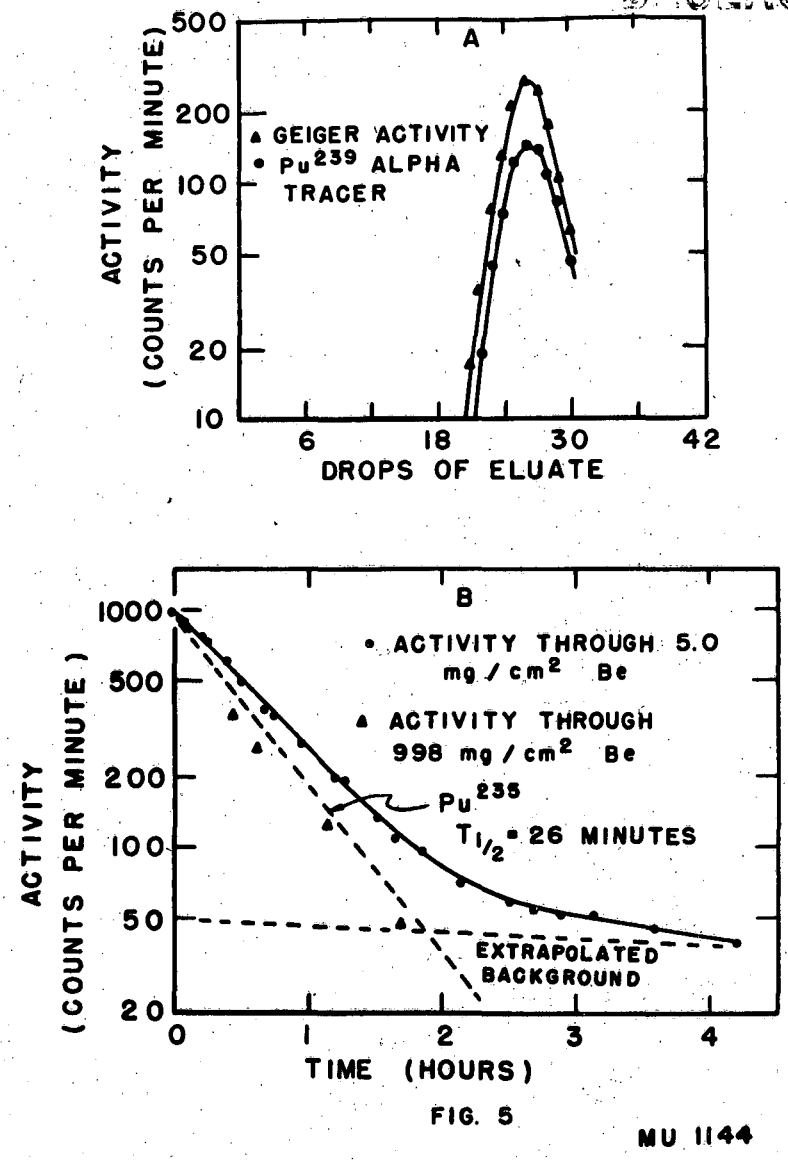


FIG. 5

MU 1144

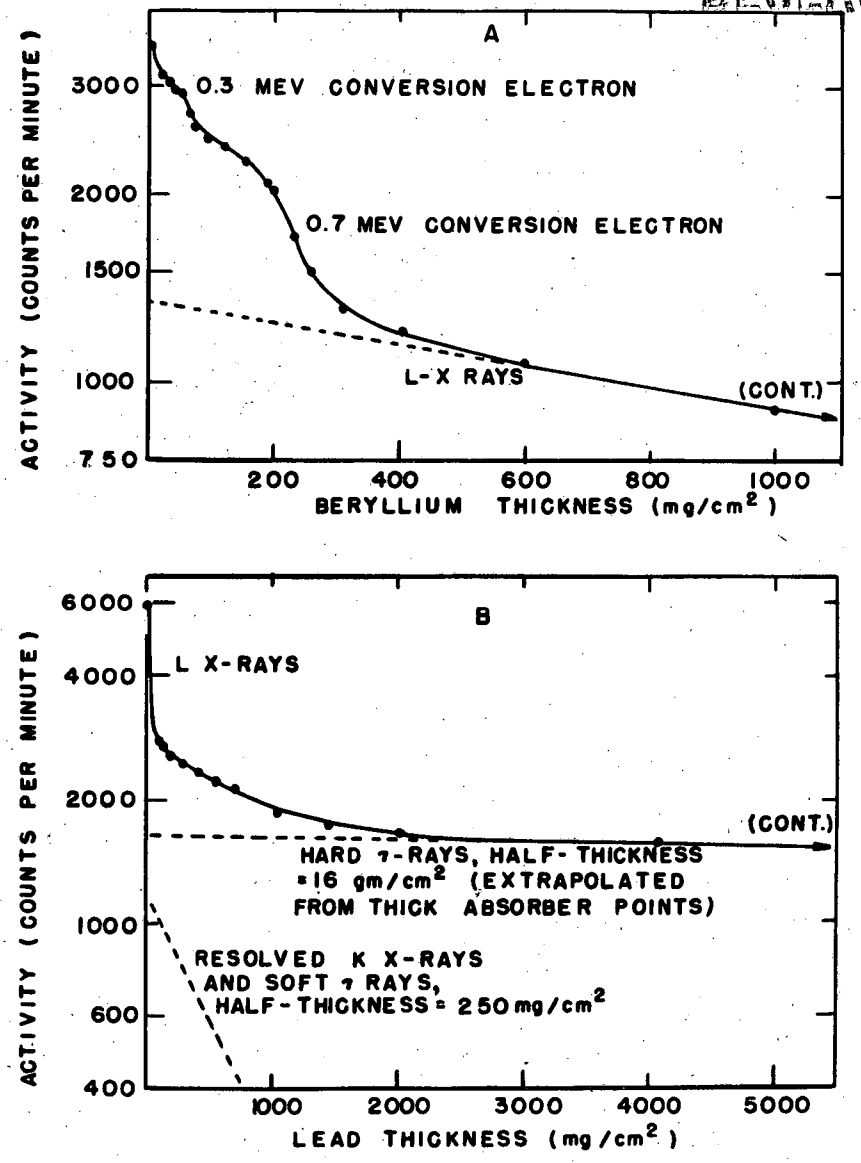


FIG. 6 MU 1148

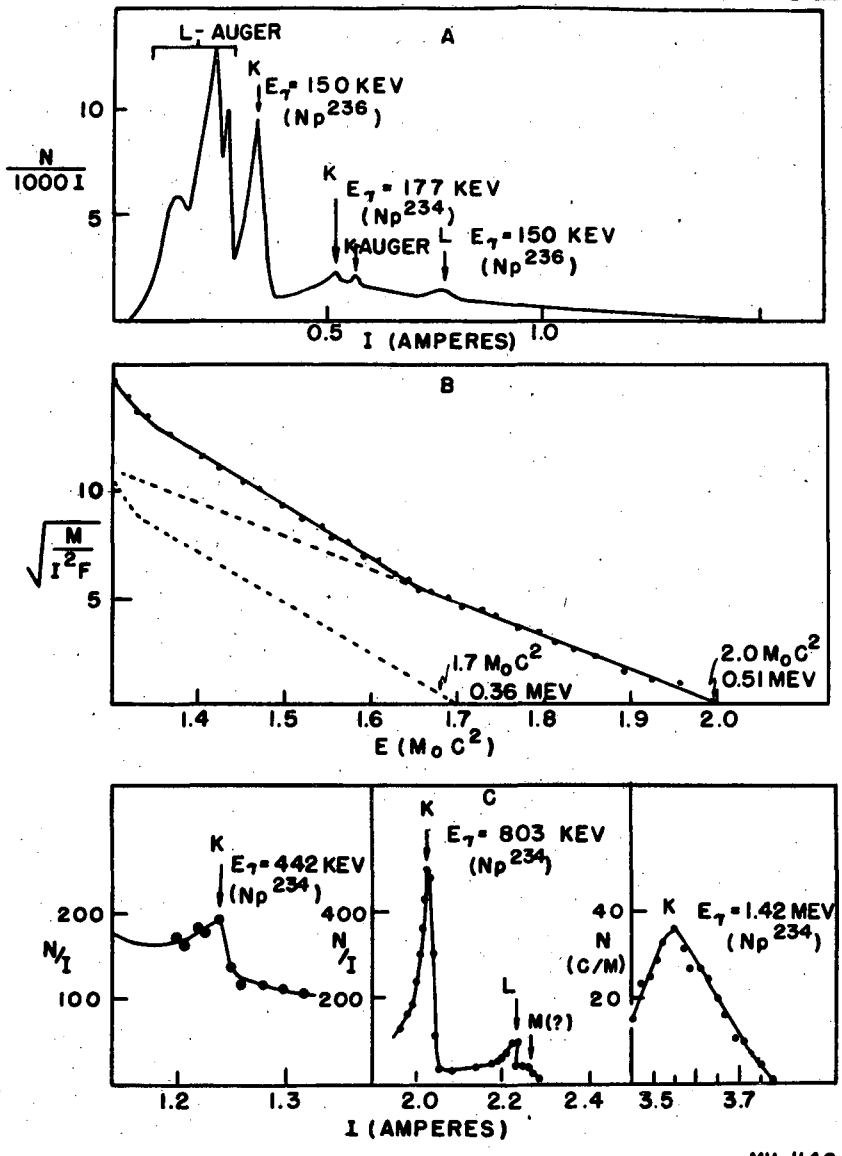


FIG. 7

MU 1146

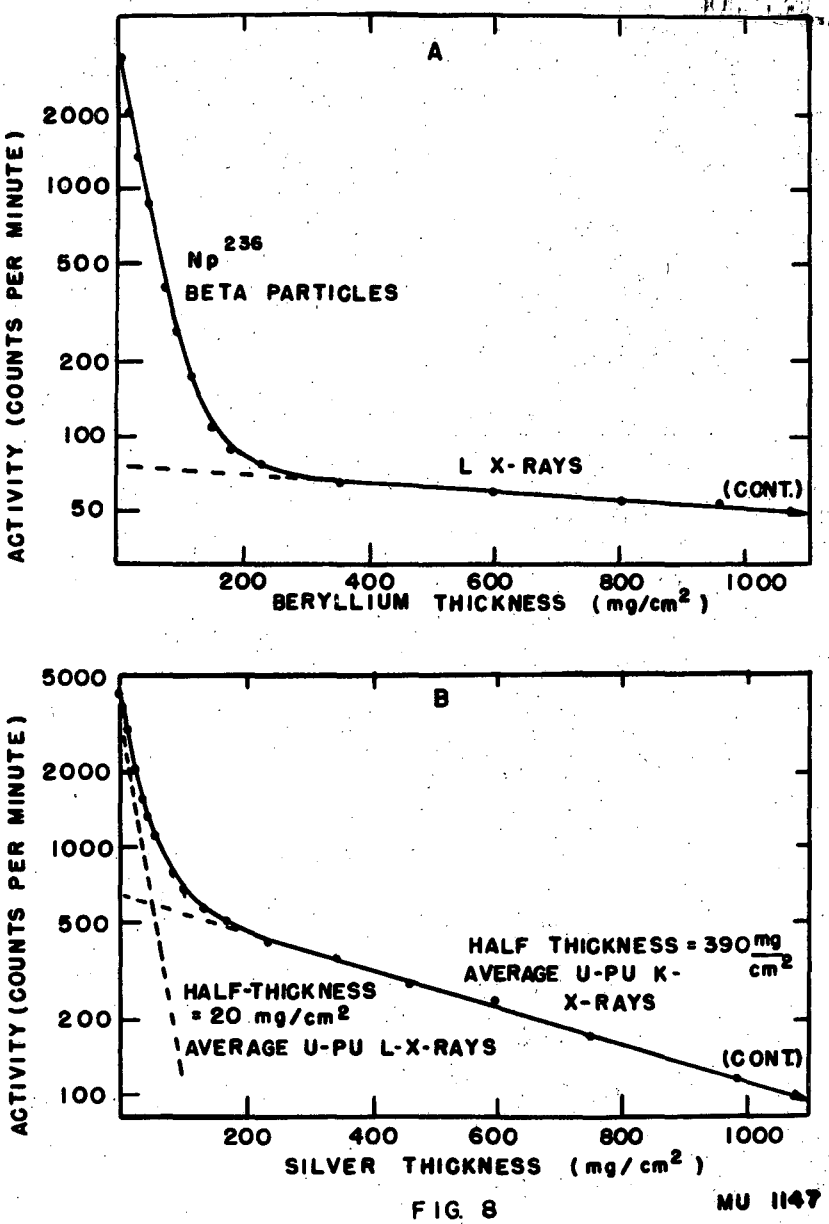
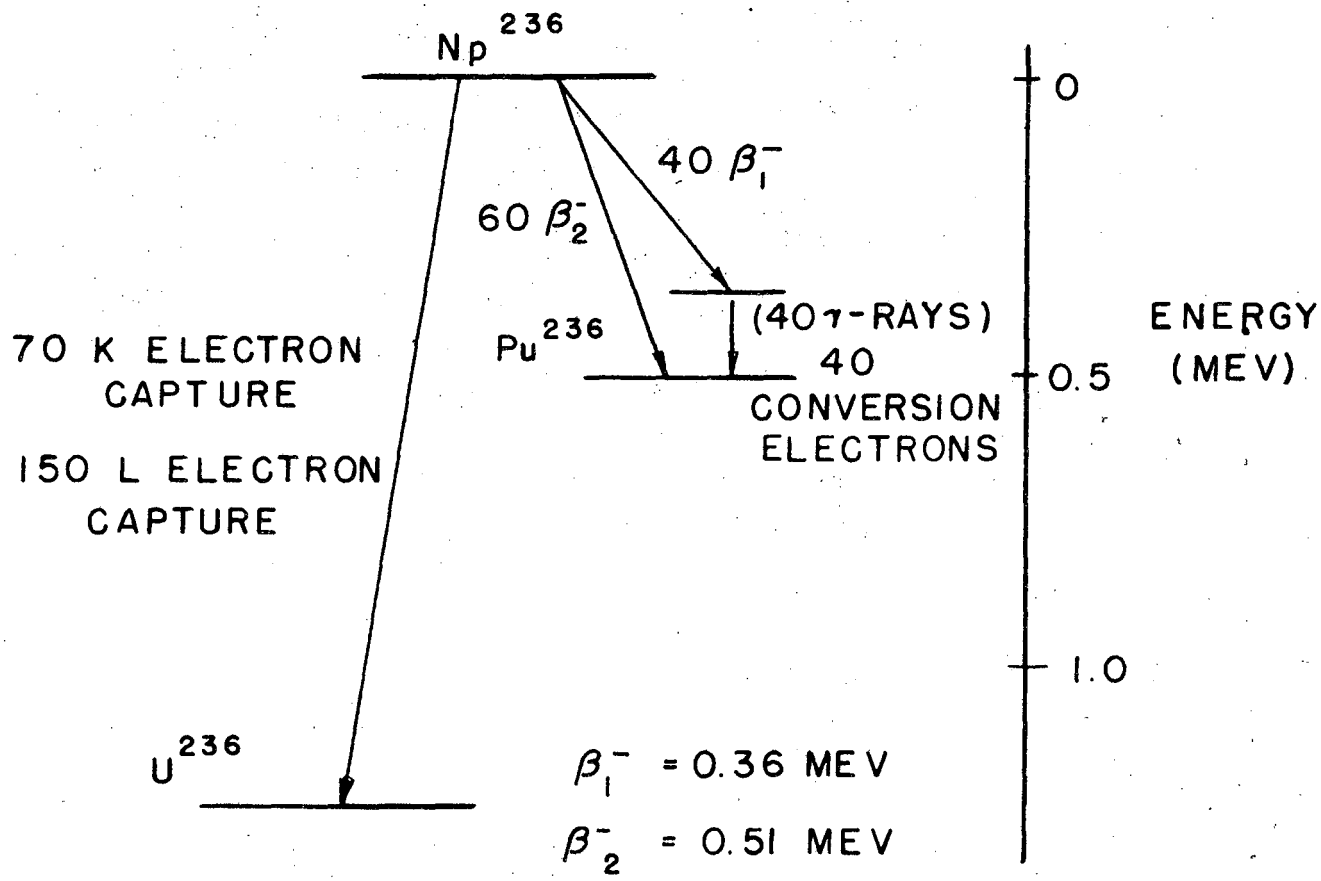


FIG. 8



β_1^- = 0.36 MEV

β_2^- = 0.51 MEV

γ -RAY = 0.15 MEV

ELECTRON CAPTURE = 1.25 MEV (CALCULATED)

$$\frac{\text{TOTAL E.C.}}{\text{TOTAL } \beta^-} = 2$$

$$\frac{\text{L E.C.}}{\text{K E.C.}} = 2$$

Fig. 9

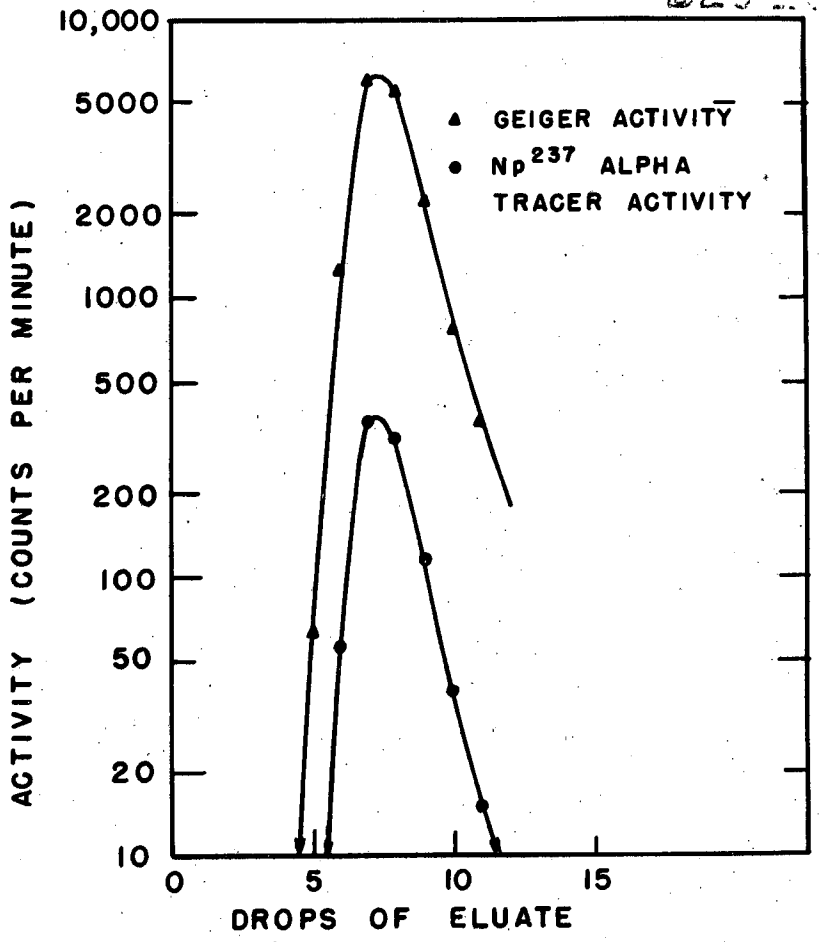
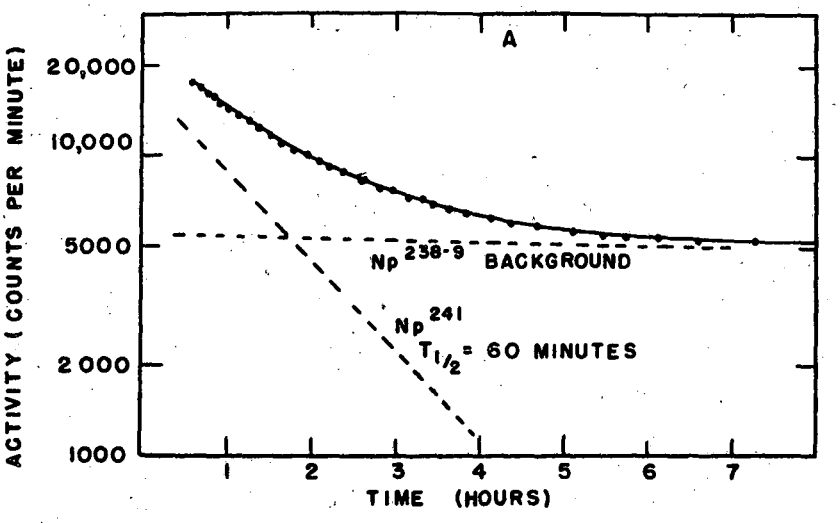


FIG. 10 MU 1149



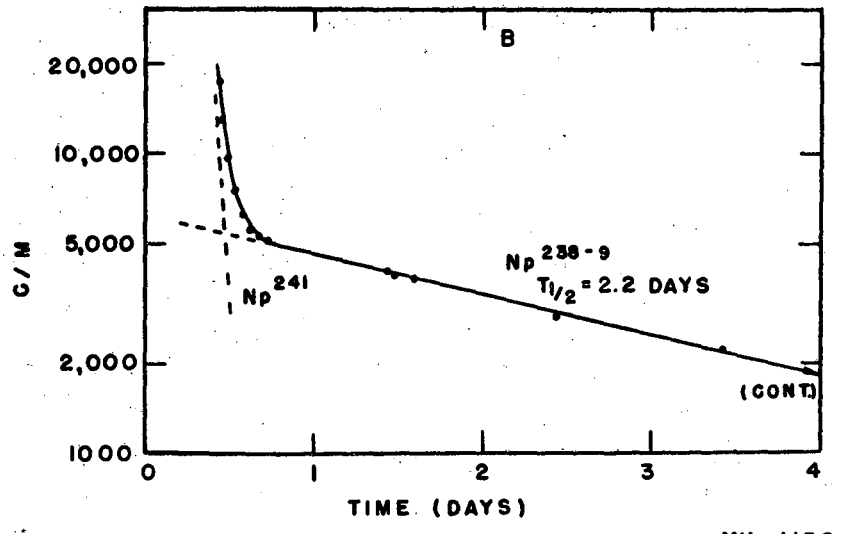
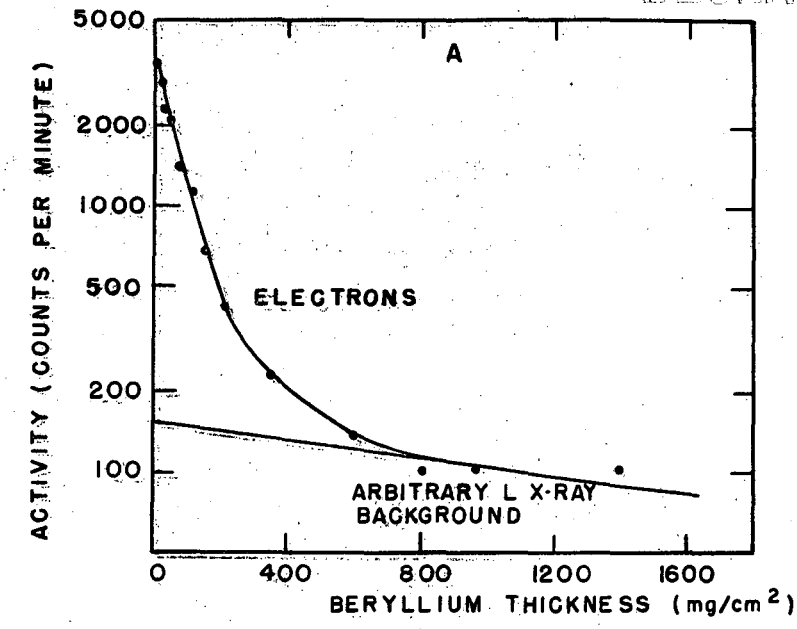


FIG. 11 MU 1150



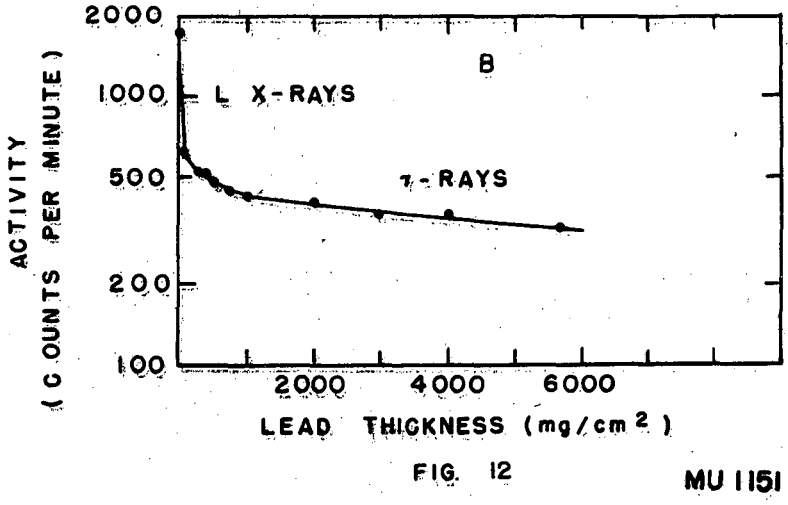


FIG. 12

MU 1151