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The Isotopes of Neptunium

L. B. Magnusson

March 31, 1949

Berkeley, California

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L. B. Magnusson

March 31, 1949

To be declassified as a thesis

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The Isotopes of Neptunium

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Abstract

Evidence is presented for three new, light neptunium isotopes formed by deuteron bombardment of U^{233}, U^{235}, and U^{238}. Np^{231} has a half-life of ca. 50 minutes emitting alpha particles of 6.28 Mev energy. An upper limit of 100 may be placed on the electron capture/alpha emission decay ratio. Np^{233} decays predominantly by electron capture with a 35 minute half-life. Np^{233} has an alpha decay half-life of three years with alpha particles of 5.55 Mev energy. A 13-minute x-ray period indicating electron capture is attributed to Np^{232}. Alpha-particles from Np^{232} have not been positively observed.

Approximate cross sections for formation of various neptunium isotopes by (d,xn) reactions at 15-100 Mev are calculated. At least as many as nine neutrons may be ejected. The cross sections are low, of the order of 10^{-3} barn by reason of fission competition. The (d,n) reaction remains prominent at all bombarding energies suggesting that stripping of the proton from the deuteron with low excitation is the principal reaction mechanism. The total cross section for formation of neptunium isotopes does not seem to change much with larger bombarding energy, although other spallation reactions become prominent. From a qualitative kinetic picture it is concluded that the large spallation yields involving emission of charged particles are formed mainly at the expense of fission whereas the total neptunium yield is not greatly dependent on deuteron energy over the range 15-100 Mev. Np^{231} could not be formed in yield comparable to that for the heavier isotopes indicating that fission competition is markedly greater at low mass numbers.

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The Isotopes of Neptunium

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I. Introduction

A new field, that of the transuranium, synthetic elements, was opened with the discovery of an isotope of neptunium, element 93, by McMillan and Abelson in 1939.[1,2] Through its property of decay by β^--particle emission, this isotope, mass number 239, retains unique importance in the transmutation of macro amounts of U^{238} to elements of higher atomic number. Following the discovery of Np^{239} and concurrently with investigations of other transuranium isotopes, a rapid advance in knowledge of the radio-properties of neptunium isotopes was made during the next several years. By 1945 six neptunium isotopes were known and well characterized. More recently, evidence has been obtained for three new, very light neptunium isotopes.

A necessary preliminary achievement was the determination of some of the chemical properties of neptunium so that it could be separated from other elements, particularly its neighbors, uranium and plutonium. On the basis of chemical properties Seaborg, McMillan, Wahl, and Kennedy[3,4] thus were able to identify a two day beta emitter as a new neptunium isotope formed in deuteron bombardments of uranium. The mass assignment of 238 was proved by yield considerations.[5,6]

A very long-lived, alpha-particle emitting neptunium isotope was found a year later,[7] Np^{237}, formed by the β^-decay of U^{237}. Np^{237} has been produced in macro amounts and hence is the most important isotope for chemical studies of the element.[8,9] The possibilities for producing lighter neptunium isotopes from uranium were virtually

exhausted at this point since the 16 Mev deuterons of the 60-inch Berkeley cyclotron were not energetic enough to knock out more than three neutrons in a (d,xn) type reaction on U^{238}. Deuteron bombardment of U^{235} was expected to produce light neptunium isotopes but the small abundance of U^{235}(less than 1%) in natural uranium precluded any identification of the products over the background activity of the heavier neptunium isotopes produced from U^{238}.

Milligram quantities of U^{233} and U^{235} became available in 1944 and lighter neptunium isotopes were soon produced in cyclotron bombardments. James, Florin, Hopkins, and Ghiorso[10] identified Np^{236}, Np^{235}, and Np^{234} as products of deuteron bombardments of U^{235}. Np^{234} was also made by deuteron bombardment of U^{233} and its mass assignment confirmed by neutron fission measurements of the uranium daughter.[11] Since the initial discoveries, a variety of means of production have been observed.

At the beginning (June, 1948) of the research reported in this paper, qualitative trends in stability with mass number and the radiation characteristics of the neptunium isotopes were clearly apparent. Neptunium exhibits the general instability of heavy elements of odd Z, only one configuration of nucleons, that in Np^{237}, being stable toward both electron capture and β^- decay. Neptunium isotopes with mass numbers above 237 are β^- unstable, and those with mass numbers below 236 are unstable to electron capture. Np^{236} decays by β^- emission.

We can obtain little information from these data, however, about the effect of mass number on the energies and half-lives for decay by alpha-particle emission. The neutron deficient isotopes Np^{234} and

Np^{235} decay predominantly by electron capture. No alpha particles from Np^{234} have been observed. James reports that Np^{235} has an alpha branching decay of about 0.1%.[12] The corresponding half-life for decay by alpha-particle emission of about 10^3 years, compared to the 2×10^6 year half-life for Np^{237} indicates that the alpha half-lives may shorten rapidly with decreasing mass number. It is of interest to determine whether the alpha decay process becomes sufficiently rapid with decreasing mass number to compete with the rates of decay by electron capture. The energy measurement of an alpha decay process, moreover, can be made unambiguously in contrast to electron decay processes. Work in this laboratory has revealed new systematic trends in alpha decay energies with mass number and it seemed likely that studies of light neptunium isotopes would yield additional information.[13]

The isotopes Np^{232} and Np^{233} had undoubtedly been produced in the 22 Mev deuteron bombardment of U^{233} but had not been identified.[11] The half-lives were thought to be too short for detection or possibly so close to that of Np^{236}, Np^{238}, or Np^{239} as to escape resolution.

This dissertation will report results obtained from deuteron bombardments at energies ranging from 15-100 Mev of U^{233}, U^{235} and U^{238}. Data have been obtained for three new isotopes, Np^{233}, Np^{232}, and Np^{231}. Relative yields for all the neptunium isotopes have been determined for a number of the bombardments. New information on the radiations of Np^{237} and Pa^{233} will be presented. The chemical and radiometric methods employed are discussed in sections V and VI.

II. The Isotope Np^{231}

A. Production.

Appreciable yields of protactinium isotopes from the (d,xn) type reaction, in which as many as seven neutrons were ejected, on Th^{232} with very high energy deuterons in the 184-inch cyclotron[14] suggested that similar bombardment of uranium might give significant yields of light neptuniums.

A process for extracting radioactively pure neptunium within an hour or two after the end of bombardment was devised and applied to a series of 100 Mev deuteron bombardments of natural uranium(metal). The neptunium fractions from these bombardments contained short-lived alpha activity. Examination of the neptunium with the alpha pulse analyzer within a few minutes after purification revealed a new alpha activity with an alpha energy of about 6.3 Mev. Pulse analyses at intervals, furthermore, revealed the growth of an alpha decay chain or series which was recognized as the series of short-lived alpha emitters[14] following the alpha decay of Pa^{227}. The following series was indicated:

$$Np^{231} \xrightarrow{\alpha} Pa^{227} \xrightarrow{\alpha} Ac^{223} \xrightarrow{\alpha} Fr^{219} \xrightarrow{\alpha} At^{215} \xrightarrow{\alpha}$$
$$Bi^{211} \xrightarrow{\alpha} Tl^{207} \xrightarrow{\beta^-} Pb^{207}$$

The parent-daughter relationship of Np^{231} and Pa^{227} was confirmed by repeated chemical separations of protactinium from the neptunium and measurement of the 38-minute decay of Pa^{227} in the protactinium fraction. The half-life of the Np^{231} parent was estimated to be of the order of one hour.

No alpha activity attributable to Np^{232} and Np^{233} was observed in these bombardments. The electron and electromagnetic radiation seemed

to be entirely from the neptunium isotopes of mass number greater than 233. There was so much Geiger activity from the heavier neptunium, in fact, that ionization caused by electrons and electromagnetic radiation interfered with the alpha pulse analyses of Np^{231}. The relatively small numbers of alpha counts from Np^{231} also suggested that the (d,7n), (d,8n), and (d,9n) reaction yields from U^{238} were very low. Increasing the energy of the deuteron did not seem to improve the yields of the light neptuniums relative to the heavy ones.

B. Alpha energy of Np^{231}

Deuteron bombardments at 45-100 Mev of U^{235} gave improved yields of Np^{231} by the (d,6n) reaction. Figure 1 shows alpha pulse analysis data for the neptunium fraction at 9, 21, and 55 minutes after separation from protactinium. A collimator was placed over the sample for the 21 and 55 minute readings to give sharper definition of the peaks. The growth of Pa^{227} and its daughters to equilibrium with the Np^{231} is clearly apparent. Separate peaks for Pa^{227}, Ac^{223}, and Bi^{211} are not observed since the energies are about equal and the instrument was set at a low resolving power to bring the entire series within the register range. Fig. 2 shows one of the best resolutions of Np^{231}, Pa^{227}, Ac^{223}, and Bi^{211}. The Fr^{219} and At^{215} are beyond the range covered by the instrument in this run. The energies of the alpha particles from Pa^{227} and Ac^{223} are 6.46 and 6.64 Mev, respectively.[14] From these data the energy of the alpha particle from Np^{231} is 6.28 Mev.

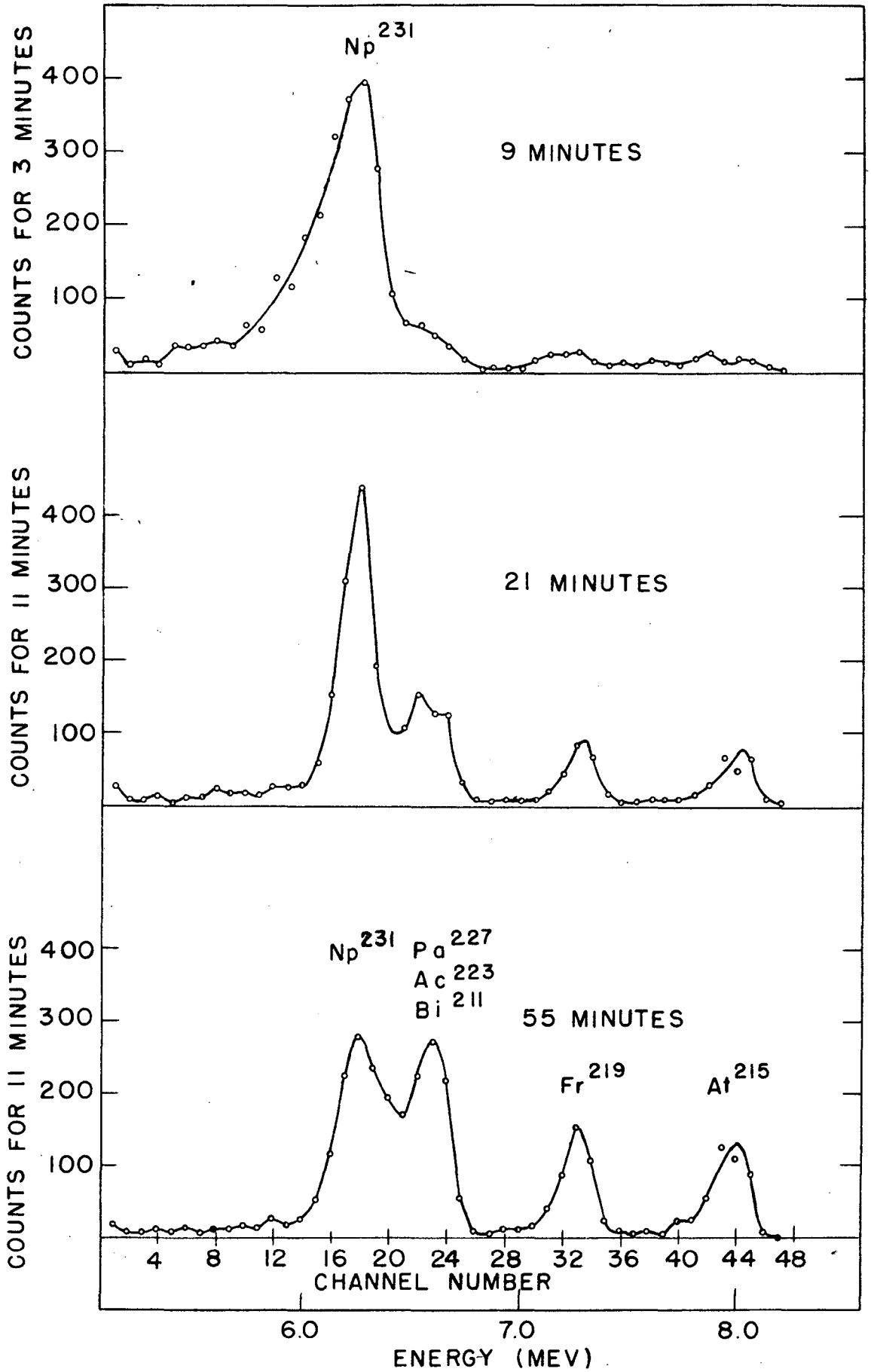

Fig. 1 Alpha pulse analyses of neptunium fraction at intervals after separation from protactinium. Sample not collimated for 9 minute reading. First reading taken 93 min. after end of 20 min., 45 Mev deuteron bombardment of U^{235}.

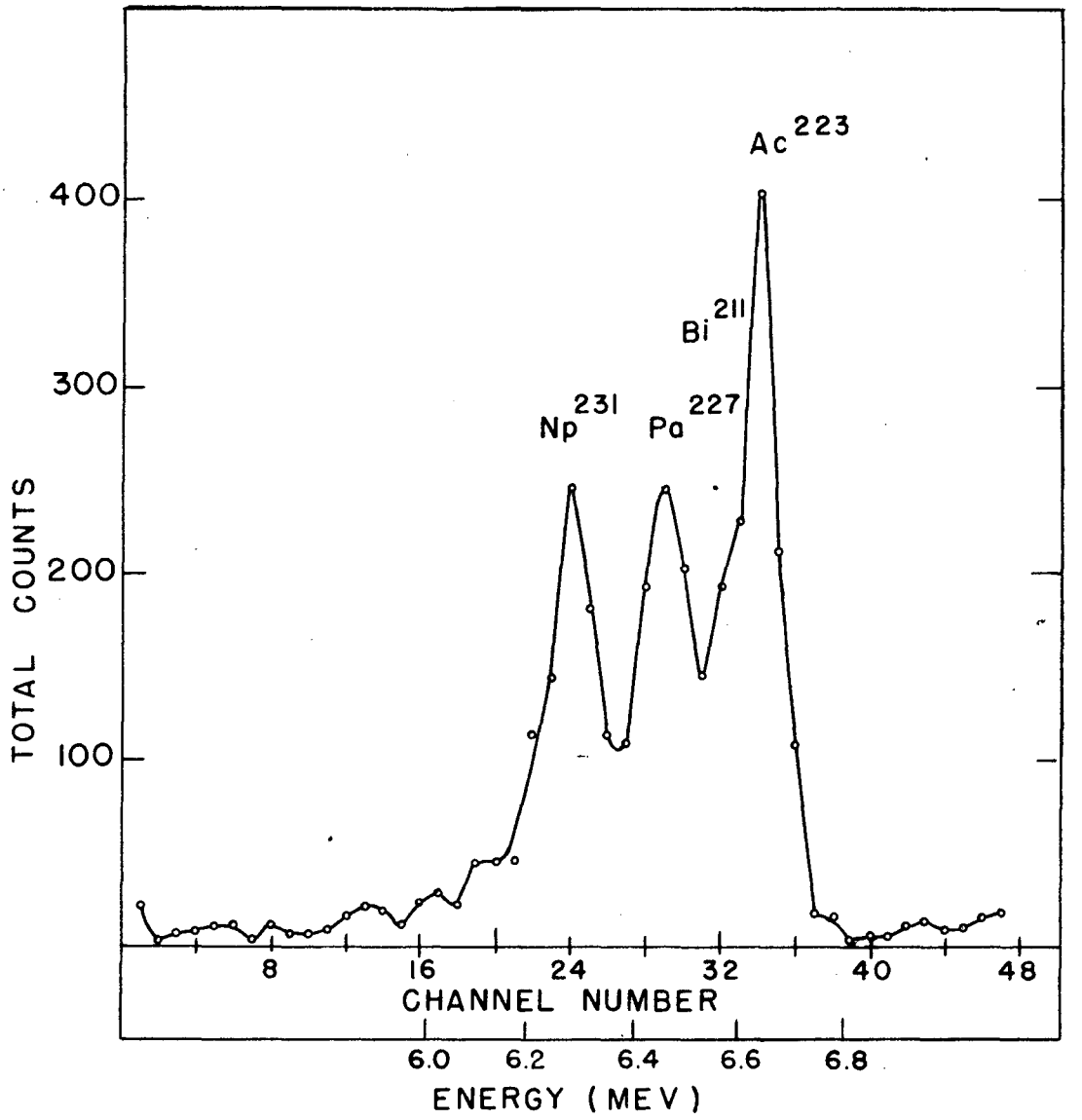

Fig. 2 Energy of the Alpha Particle from Np^{231}. 10 min. count taken 95 min. after separation from protactinium and 175 min. after end of 45 min., 45 Mev deuteron bombardment of U^{233}.

C. Half-life of Np^{231}.

The presence of its daughters by alpha decay obviously complicates measurement of the half-life of Np^{231}. The geometry and resolution of the alpha pulse analyzer, moreover, proved usually to be too uncertain and variable to permit following the decay of Np^{231} peak directly in the presence of near equilibrium amounts of the daughters. The best half-life values were obtained by pulse analyzing for Np^{231} in aliquots freshly purified from protactinium. The aliquot size was determined by pulse analyzing the samples for the Np^{237} tracer used in all runs. In some cases, small amounts of U^{234} and U^{235} contamination from the original target were present. Since U^{234} and Np^{237} have nearly the same alpha energies, the Np^{237} tracer content of these samples could not be determined accurately from pulse analysis. An internal tracer standard was therefore used, as an additional check, namely the Np^{236} always produced in the U^{235} bombardments. Accurate ratios of the neptunium contents of counting plates from the same bombardment could be obtained from individual pulse analyses for Pu^{236} on each of the plates after complete decay of the Np^{236}. Figure 3 (lines A and B) is a comparative semilog plot of the Np^{231}/tracer ratio decays obtained for Np^{231} samples from two different bombardments. Line C is data on the decay of Np^{231} measured in the presence of daughters by a series of pulse analyses which had unusually good resolution (as in Fig. 2). The slope of the lines is a measure of the Np^{231} half-life, the absolute values of the ratios having no significance. Included in the figure is an observed decrease in recoil Pa^{227} activity from an Np^{231} sample(line C). The half-life of Np^{231} is ca. 50 minutes.

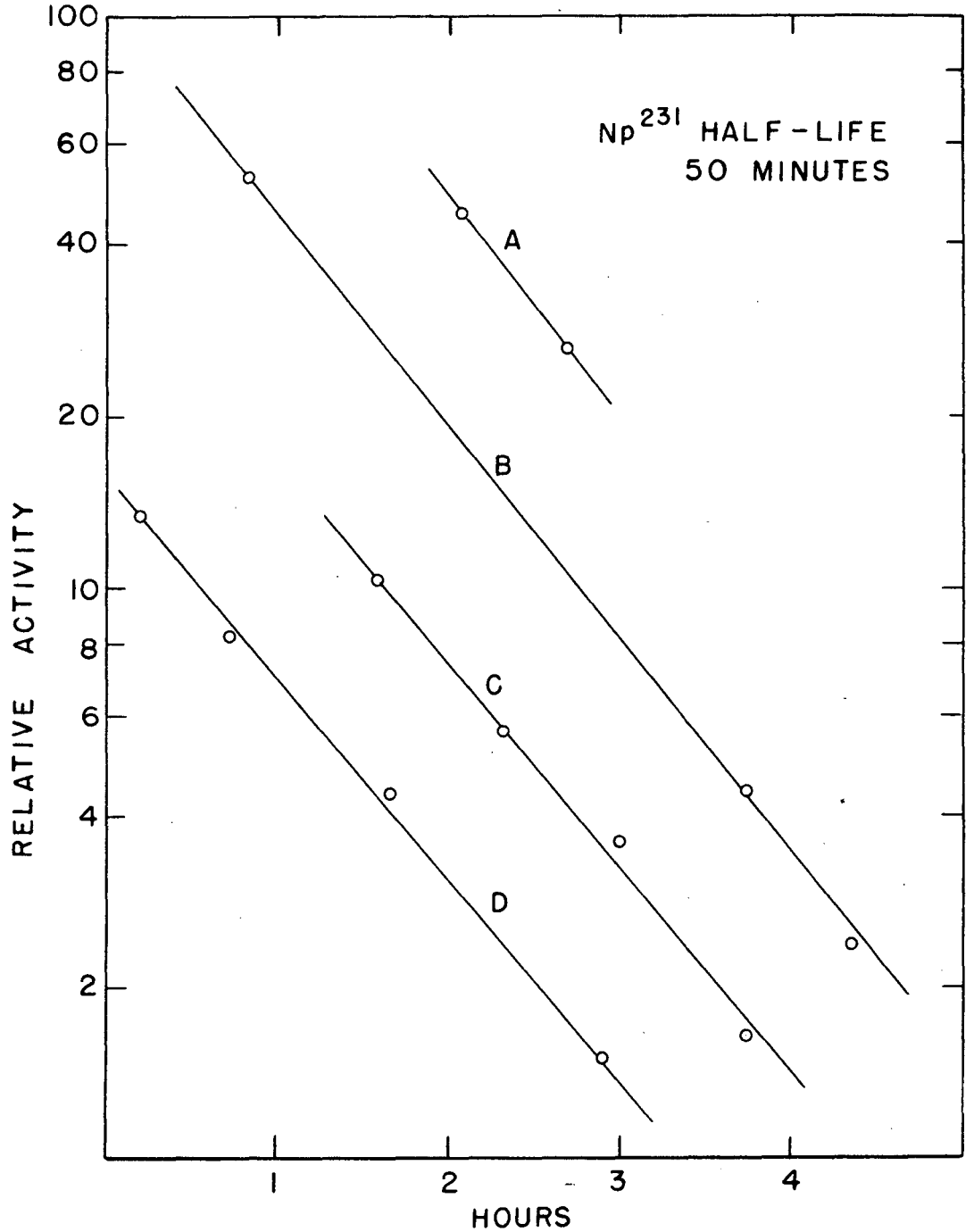

Fig. 3 Decay of the alpha activity of Np^{231}. Curves A and B from pulse analysis of Np^{231} separated from Pa. Curve C from Pa^{227} recoil atoms from Np^{231}. Curve D from pulse analysis of Np^{231} in presence of daughters.

Np^{231} is undoubtedly unstable to electron capture. The x-radiation characteristic of this process has not been directly observed. The daughter of Np^{231} electron capture decay is U^{231}, which also decays by electron capture with a 4 day half-life. The determination of the percent of Np^{231} electron capture decay by measurement of the number of U^{231} daughter atoms is accordingly very insensitive due to the low counting efficiency of x-rays, the factor of 10^2 for the relative half-lives, and, as will be seen later, the low yields of Np^{231}. A neptunium fraction was milked for U^{231} with U^{233} tracer after complete decay of the Np^{231}. The Geiger activity in the uranium fraction was only a little above counter background and was not positively identified as U^{231}. The poor sensitivity of the method allows us only to place an upper limit of 6×10^2 on the electron capture/alpha emission decay ratio from these data. From yield considerations an upper limit of ca. 10^2 is placed on the electron capture/alpha emission disintegration ratio.

III. The Isotope Np^{233}.

A. Production, half-life, and radiations.

No alpha particles from neptunium isotopes other than those from Np^{231} were detected in U^{233} and U^{235} bombardments with 45-100 Mev deuterons. Geiger activity of 35 minutes half-life was observed, however. The 35 minute activity was proved to follow Np^{237} quantitatively through the LaF_3, ether extraction, and TTA separations described in section V, and had the radiations expected for an isotope decaying by electron capture. Figure 4 shows decay curves for a sample of the 35-minute activity obtained from a U^{233} bombardment. The relatively large abundance of electromagnetic radiation is

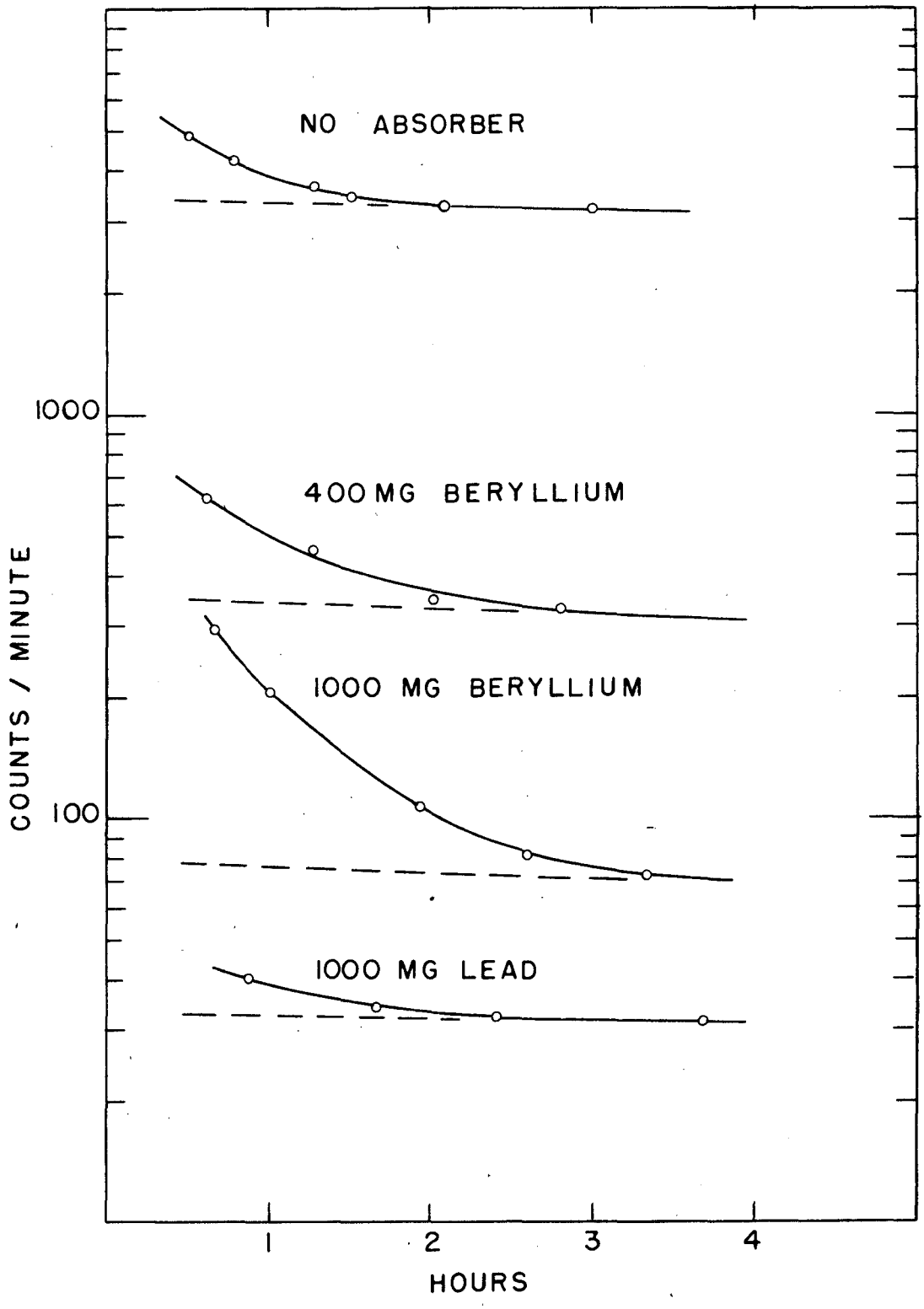

Fig. 4 Decay of 35 min. activity (Np^{233}) measured through various absorbers. Zero time is 65 min. after end of 45 min., 45 Mev deuteron bombardment of U^{233}.

evident from the counting rates through the beryllium absorbers. Absorption data with lead absorbers indicated roughly that the energies of the electromagnetic radiations ranged from 10-120 kev as expected for the uranium K and L x-radiations resulting from an electron capture process in a neptunium isotope.

Many absorption and decay measurements of the neptunium Geiger activities of half-lives greater than 50 minutes showed that all radiations observed could be accounted for on the basis of the known isotopes with mass numbers greater than 233. The U^{233} and U^{235} used in the bombardments contained of the order of 5% U^{238} so the heavier neptuniums were always formed.

A preliminary assignment of the 35-minute activity was made on the basis of four assumptions. The first was that the activity was a new isotope and not an isomer of a known one. The second was that the activity was either Np^{232} or Np^{233}, later confirmed by bombardments at lower energy. The third and fourth assumptions required that one L x-ray with a counting efficiency of 2% be emitted per disintegration. The uranium daughter was carefully milked from a large sample of the 35-minute activity after complete decay. If the parent were Np^{232}, ca. 3 alpha counts/minute of U^{232} should have been found; whereas, if the parent were Np^{233}, no counts would be detectable because of the long half-life of U^{233}. A limit of less than one count $minute^{-1}$ of U^{232} was established by this determination, so the 35-minute activity is assigned to Np^{233}.

The 35-minute activity was formed in larger yield by bombardment of U^{233} with 15 Mev deuterons in the 60-inch cyclotron. At

this energy the alpha particles of Np^{231} were not observed, so the (d,4n) reaction does not occur, in accord with the behavior[10] of U^{238}. To provide additional chemical proof that the 35 minute activity is a neptunium isotope, a different isolation procedure was used, consisting of the zirconium phosphate, ether extraction, and resin column separations(cf. section V). To characterize better the 35-minute radiations, many decay and absorption measurements were taken. Figure 5 indicates the large amount of electromagnetic radiation in the x-ray energy region. The upper curve shows the decay in counting rate of the radiations penetrating 1.5 gram/cm^2 of beryllium, while the lower curve shows the counting rate of the same sample through 1.5 gram/cm^2 of beryllium plus 155 mg/cm^2 of lead. The beryllium absorber alone stops all electrons, about half the L x-rays (10-20 kev) of uranium and very little of the more energetic electromagnetic radiation. The beryllium plus lead combination stops all the L x-rays and about half the K x-rays so the difference between the beryllium and beryllium plus lead counting rates is a measure of the amount of x-ray activity. The gap in data after 1-1/2 hours was caused by two successive Geiger counter failures so the long -lived tails were measured with a different counter but with identical geometrical arrangement. The possible difference in counting efficiency introduces an uncertainty in half-life resolution but the curves indicate at least one short period of ca. 35 minutes.

The decay in counting rate of the same sample through 1.5 gm/cm^2 of beryllium plus 1 gm/cm^2 of lead is given in figure 6. The activity measured in this case, principally electromagnetic radiation

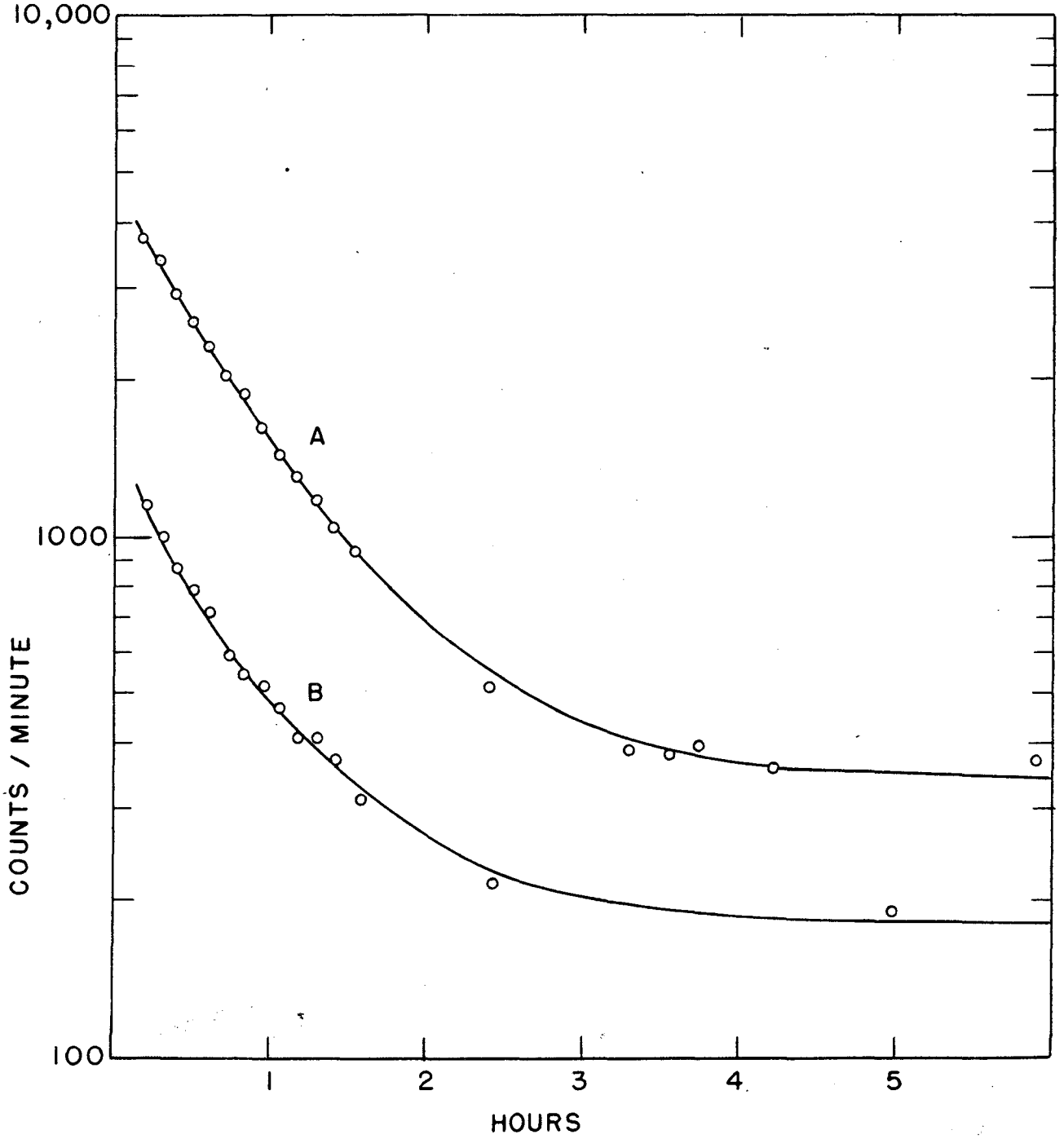

Fig. 5 Decay of short lived electromagnetic radiation. Curve A with 1.483 gm/cm^2 beryllium absorber. Curve B with 1.483 gm/cm^2 beryllium plus 155 mg/cm^2 lead. Zero time is 60 min. after end of 30 min., 15 Mev deuteron bombardment of U^{233}.

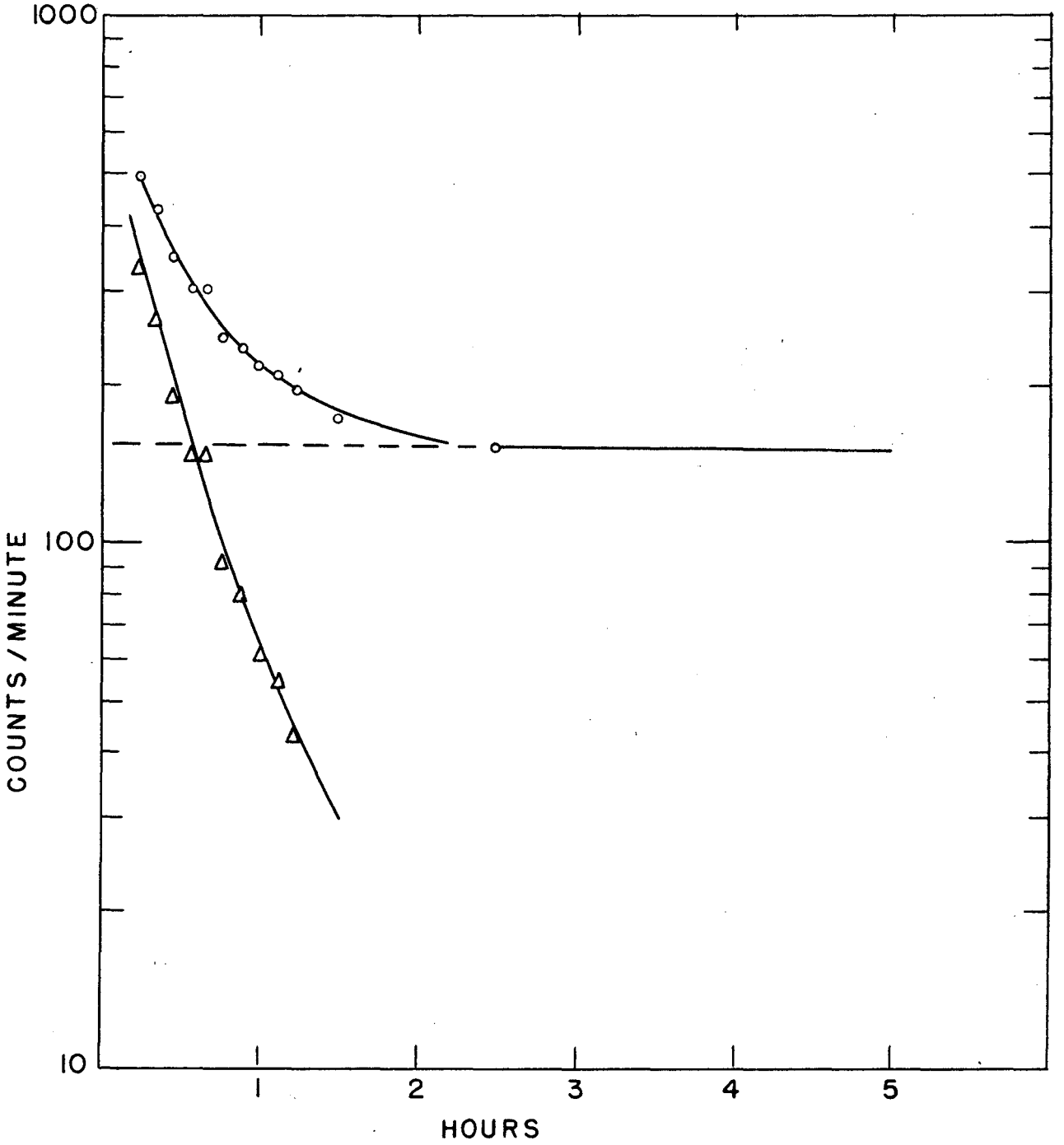

Fig. 6 Short-lived neptunium gamma radiation. 1.483 gm/cm^2 beryllium plus 1 gm/cm^2 lead. Same time scale as Fig. 5.

of energy greater than 200 kev, decays in large part with a half-life much shorter than 35 minutes. This gamma decay suggested the presence of Np^{232} with a shorter half-life than that of Np^{233}. The data are not precise enough for resolution of two short periods.

The decay in gross activity, measured with no absorber other than the counter window, is plotted in figure 7. The sample counting rates have been normalized to the same neptunium content as the sample used for figures 5 and 6. The precision again is not high enough for resolution.

Absorption data for short-lived activity was obtained with both argon - and xenon-filled Geiger tubes. During the decay two complete sets of beryllium absorption points were measured with the xenon counter over the range 0 - 1.5 gm/cm^2. The short-lived activity measured through each absorber was determined in the usual manner by determining the decay slope of the long-lived activity and making the appropriate subtractions. In attempts to correct all absorption points for decay to an arbitrarily chosen mid-point, it was found that the assumption of a single short-lived activity did not fit the data. Figure 8 shows the two sets of beryllium absorption points after subtraction of long-lived activity. The decay measured with no absorber, 12.6, and 42.6 mg/cm^2 is more rapid than that with heavier absorbers. The data may be fitted by the assumption of two electron-capturing, short-lived activities with somewhat different particulate radiations. The shorter-lived evidently has a larger number of detectable conversion electrons. Resolution of correct absorption points from these data is therefore entirely dependent on accurate

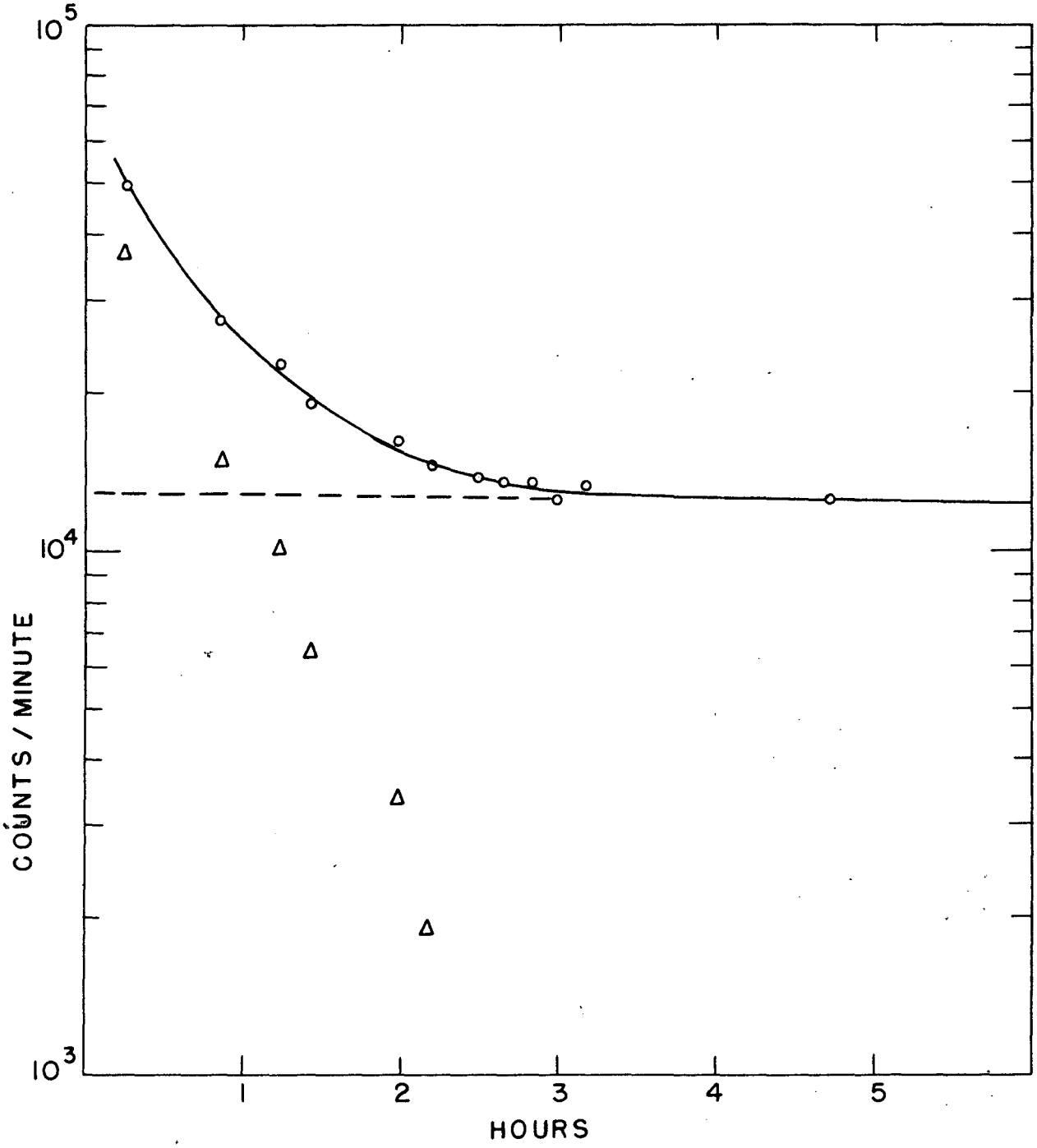

Fig. 7 Short-lived neptunium measured with no absorber. Same time scale as Fig. 5.

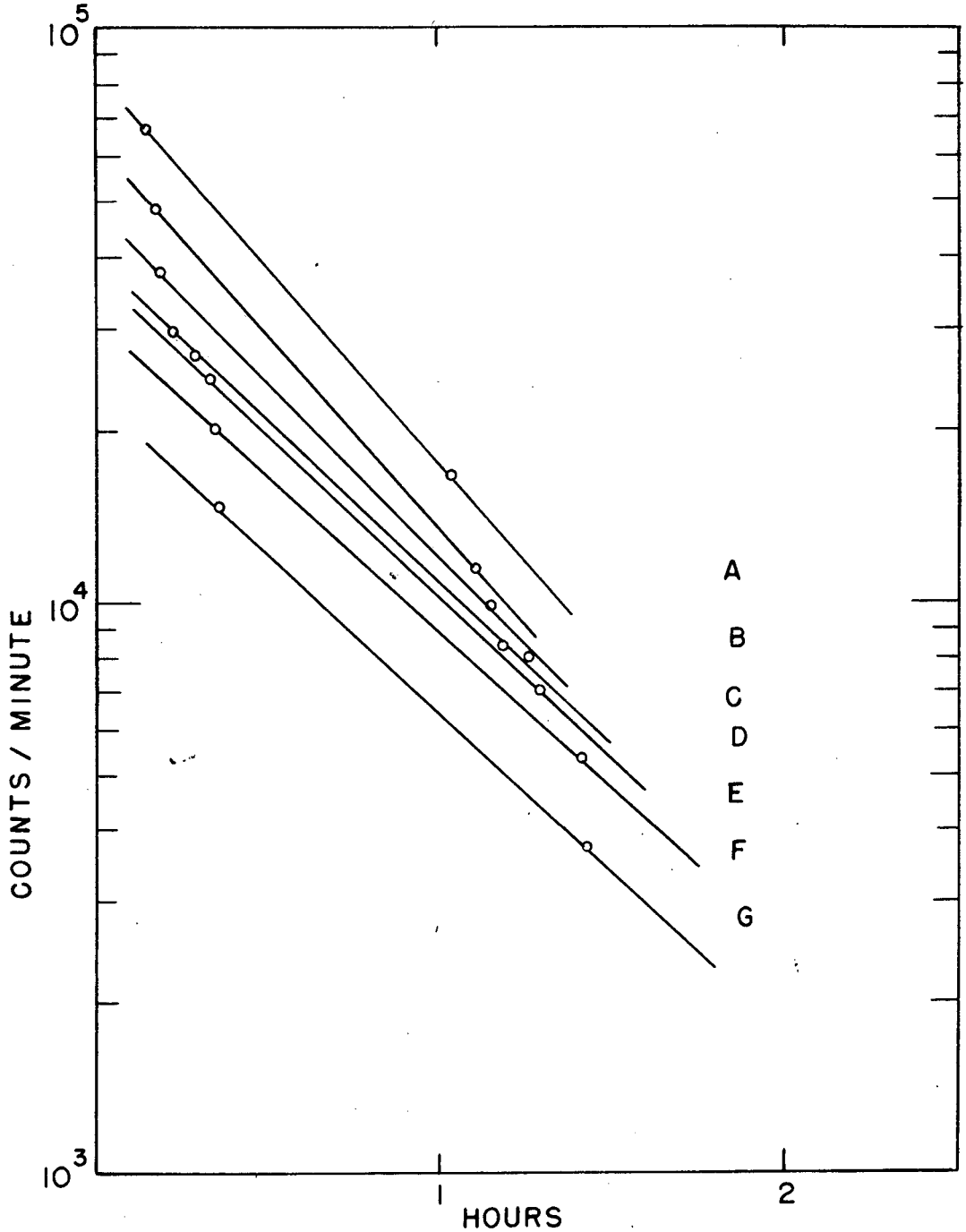

Fig. 8 Decay measured through beryllium absorbers (mg/cm^2) with xenon counter tube. Long-lived activity has been subtracted. Same time scale as Fig. 5.

A No absorber
B 12.6
C 42.6
D 99 or 196 (not distinguishable)
E 402
F 804
G 1483

knowledge of the half-lives and relative abundance of the two activities. From two decay points for a mixture of two activities of known half-lives, one may of course calculate the separate counting rates for each activity, but the precision of the data and the accuracies of the half-lives do not justify the calculations. On the assumption that the short-lived activity was essentially dead, the absorption points read from the lines in fig. 8 at one hour on the time scale were taken to be close approximations to those for Np^{233} and are plotted in fig. 9.

Beryllium absorption measured with an argon Geiger tube was less adequate because of the lower counting rates. Figure 10 shows these points after subtraction of long-lived activity. Only four of the absorber points were repeated. The slopes of the others have simply been drawn in from comparisons with the xenon data and the other argon slopes. The counting rates at one hour on the time scale were again taken as approximations to those for Np^{233} and are plotted in figure 9. The argon and xenon data, taken on different aliquots, were normalized to the same neptunium content.

A number of aluminum and lead absorption points were taken with 1.5 gm/cm^2 of beryllium next to the window of the xenon tube but only two of the aluminum points were repeated. These two aluminum points and the lead absorptions of figures 7 and 8 were used as approximate guides for correction to a reference time corresponding to 30 minutes on the time scale. Since the shorter-lived activity contributes most of the harder electromagnetic radiation and sufficient data was not obtained to show the extent of contribution at each absorber, the

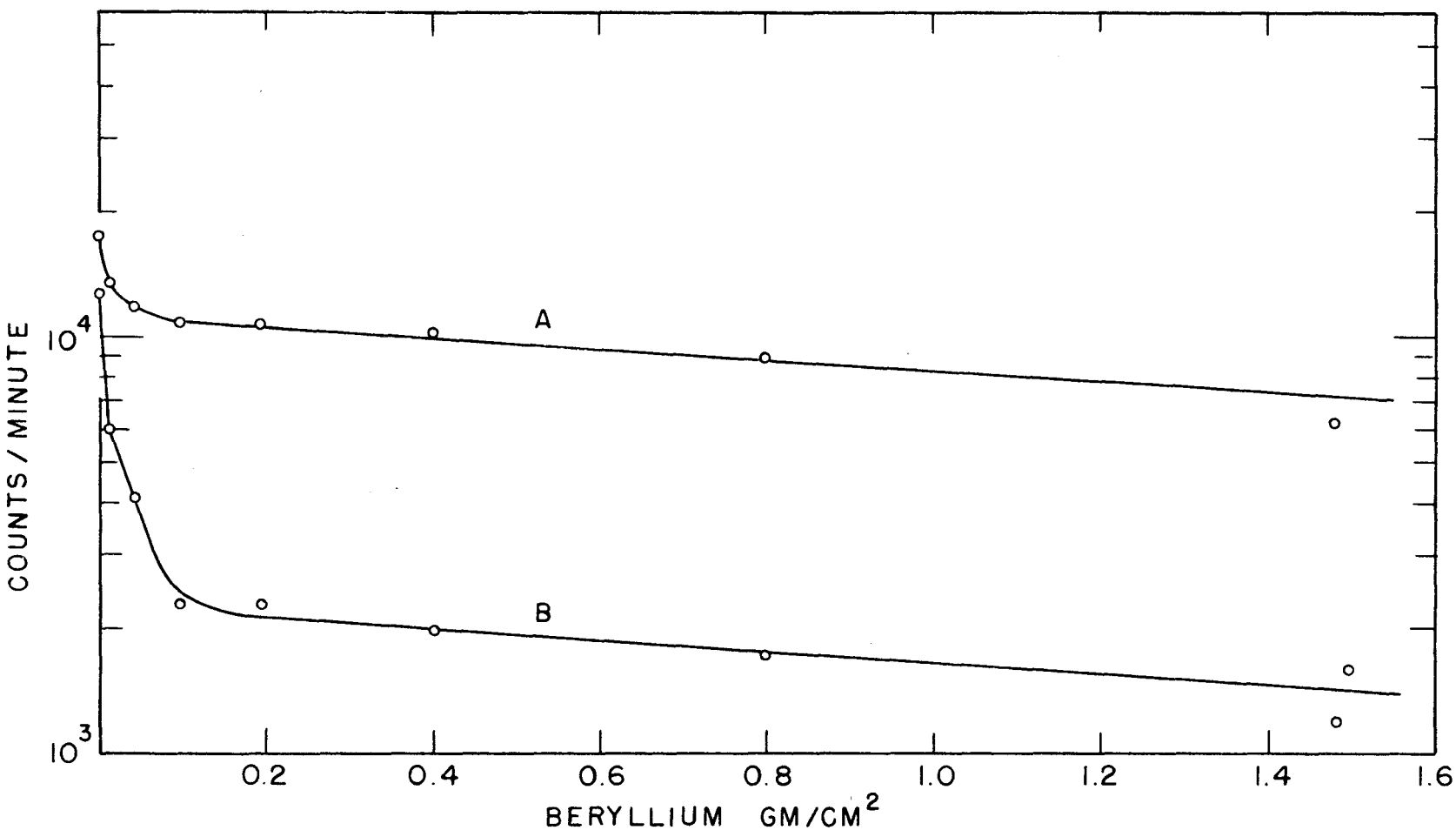

Fig. 9 Beryllium Absorption of Np^{233}.
A Xenon tube
B Argon tube

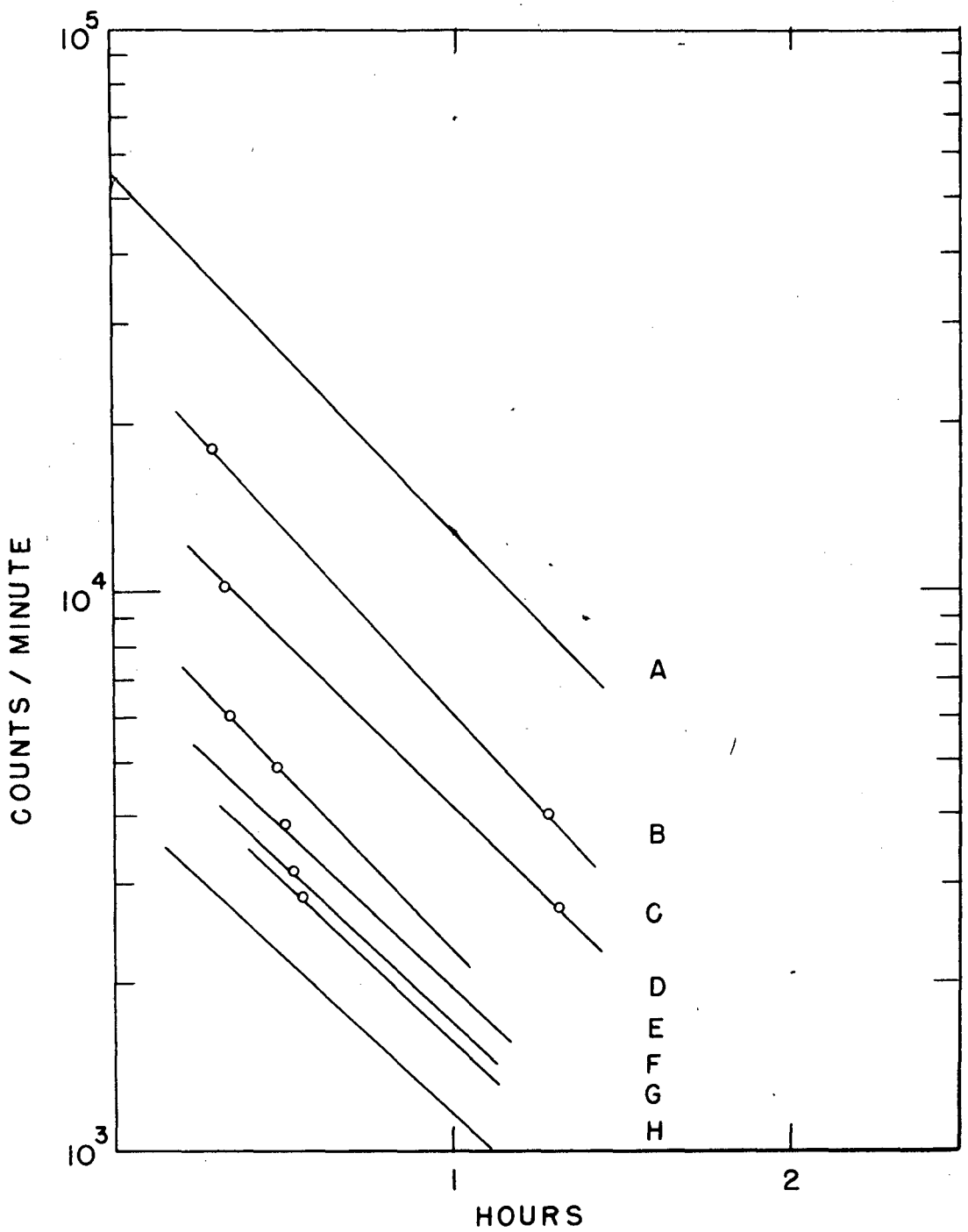

Fig. 10 Decay measured through beryllium absorbers with argon counter tube. Long-lived activity has been subtracted. Same time scale as Fig. 5.

A No absorber (from Fig. 7)
B 12.6 mg/cm^2
C 42.6 mg/cm^2
D 99 or 196 mg/cm^2 (not distinguishable)
E 402 mg/cm^2
F 804 mg/cm^2
G 1494 mg/cm^2
H 1483 mg/cm^2 (from Fig. 5)

lead and aluminum points in figure 11 are upper limits for the Np^{233} radiation. All the aluminum points and the lead points out to 200 mg/cm^2, however, should be close approximations. Fig. 12 gives the aluminum and lead absorption corrected to the same time with an argon counter. The counting efficiency of the L x-rays is larger by a factor of ca. 5.0 and that of the K x-rays plus gamma rays is larger by a factor of ca. 2.5 in the xenon tube.

The qualitative absorption characteristics of the radiations are little affected by the uncertainties in half-lives and abundance. From the well-established fact that such electromagnetic radiations cause ionization much more abundantly in xenon than in argon and hence are counted more efficiently, it is evident that the absorption data reveal the x-radiation characteristic of isotopes decaying by electron capture. Comparison of the argon and xenon beryllium curves (fig.9) shows soft electrons (maximum energy 300 kev) which are absorbed by 100 mg/cm^2 of beryllium. The apparent component of 2 gm/cm^2 beryllium half-thickness is a composite of the K and L x-rays plus more energetic electromagnetic radiation. The composite electromagnetic radiation counted more efficiently in the xenon tube by a factor of five. The deviations of the points are attributable mainly to varying degrees of purity of the beryllium (cf. section VI). The aluminum and lead points prove the electromagnetic nature of the radiations and indicate roughly the range and relative abundance of energies (10 - 20 kev for L x-rays and 100 - 120 kev for K x-rays from uranium). From all evidence, including that discussed in the section on Np^{232}, the best choice for the half-life of Np^{233} is 35 minutes.

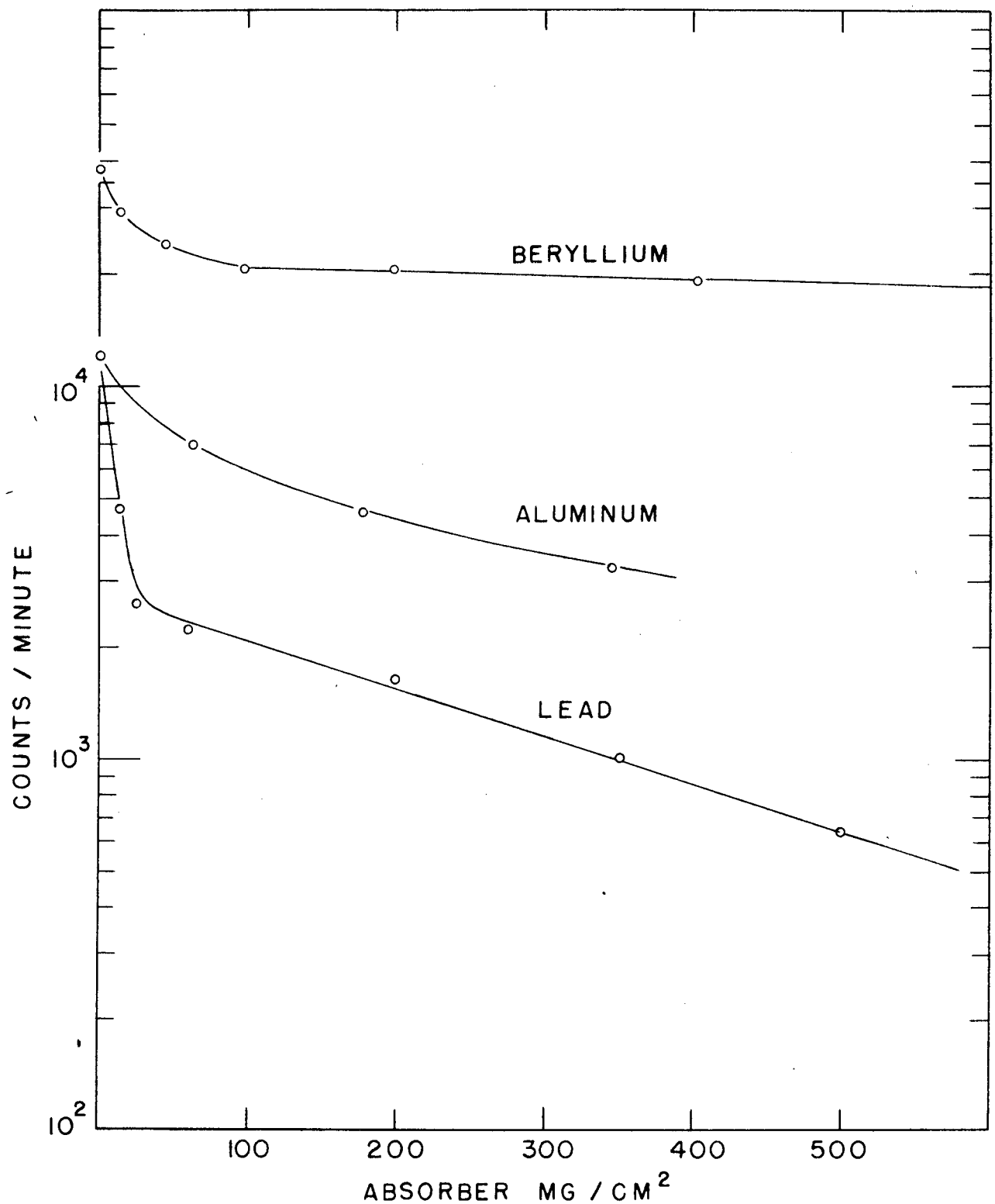

Fig. 11 Absorption of short-lived electromagnetic radiation. Points have been corrected to time = 1/2 hour. (Cf. decay plots in Figs. 5, 6, 8, 10). Xenon tube.

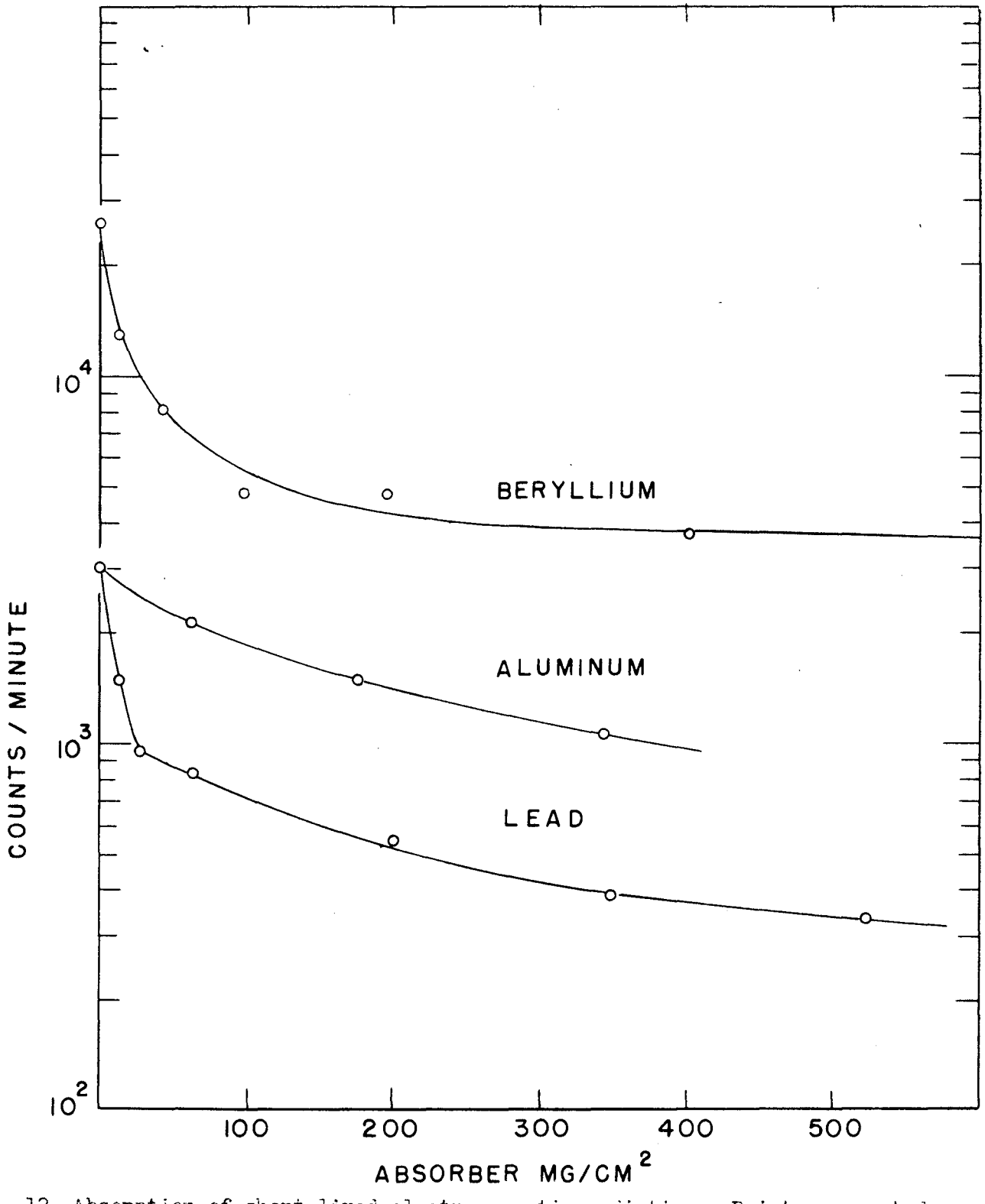

Fig. 12 Absorption of short-lived electromagnetic radiation. Points corrected to time = 1/2 hr. Argon tube.

B. Alpha particles from Np^{233}.

The absence of Np^{231} alpha particles in the pure neptunium fraction from the low energy deuteron bombardment permitted a sensitive detection of other short-lived neptunium alpha activity. Figure 13 is a series of three of the alpha pulse analyses. A small short-lived peak at 5.55 Mev was present with a possible still smaller peak from an activity of shorter half-life at ca. 5.8 Mev. The decay of the 5.55 Mev peak was followed by summing the counting rates recorded over the channel range 13-20. The decay of counts/minute recorded on these channels is given in figure 14. Subtraction of background yielded a half-life of ca. 35 minutes. No other short-lived alpha activity of this energy is known, so, together with the correspondence in half-life with the Geiger radiations, the alpha particles are assigned to Np^{233}. The ratio of alpha disintegrations/minute to Geiger counts/minute (argon tube, 1.5 gm/cm^2 Be absorber as in fig. 5) for Np^{233} was 1.8 (10^{-2}). By making assumptions discussed in the section on yields as to counting efficiency and decay scheme the half-life of Np^{233} for alpha particle emission is calculated to be ca. 3 years.

III. The Isotope Np^{232}.

A. Production, half-life, and radiations.

The data discussed in the previous section indicated strongly that the radiations of Np^{232} had been detected. A better ratio of Np^{232} to Np^{233} was sought by omitting some of the chemical purification in another short bombardment of U^{233} in the 60-inch cyclotron at slightly higher energy (17 Mev). The first count of the neptunium

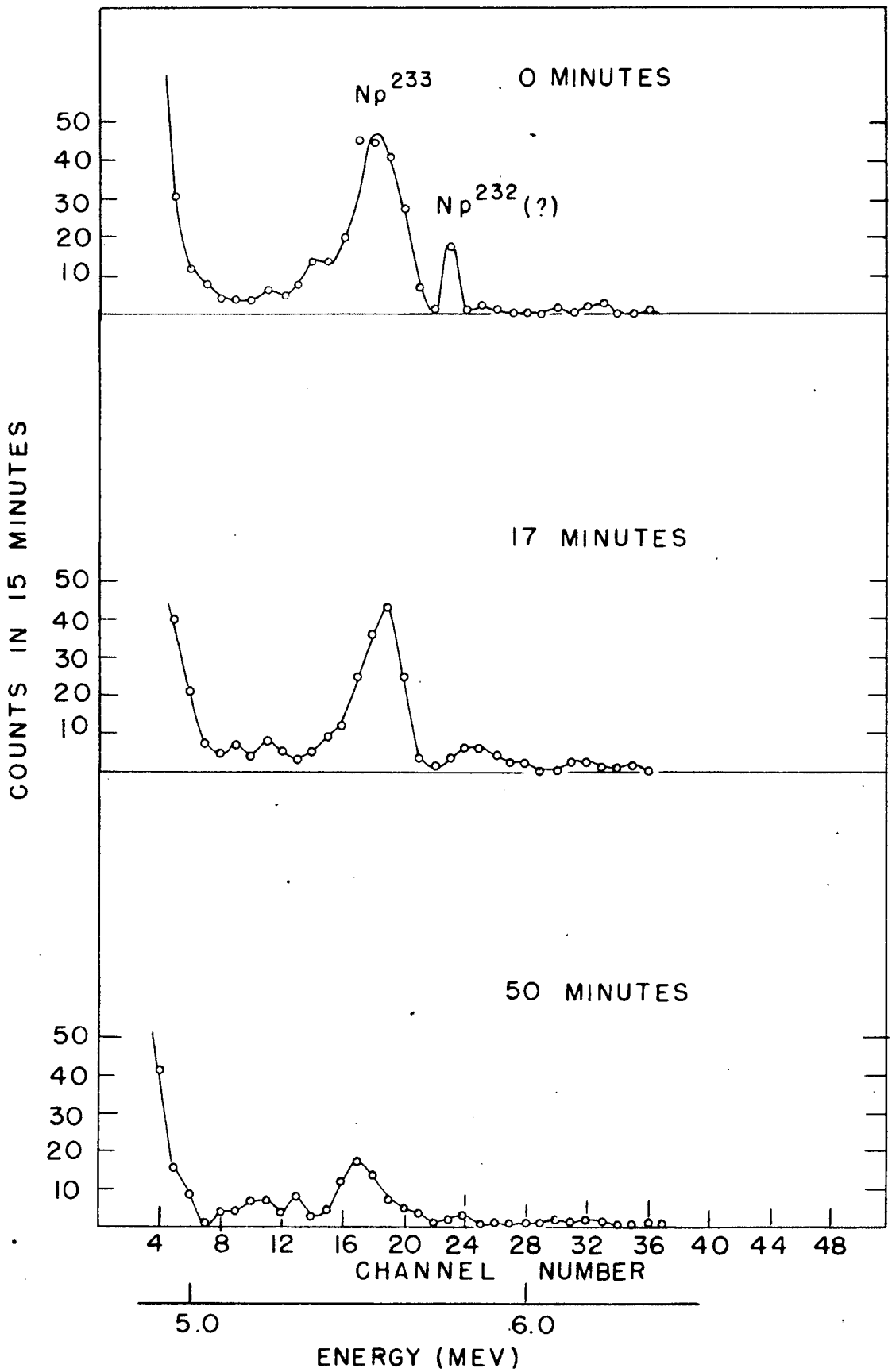

Fig. 13 Alpha particles from Np^{233}. First reading begun at 4 min. on time scale (Fig. 5).

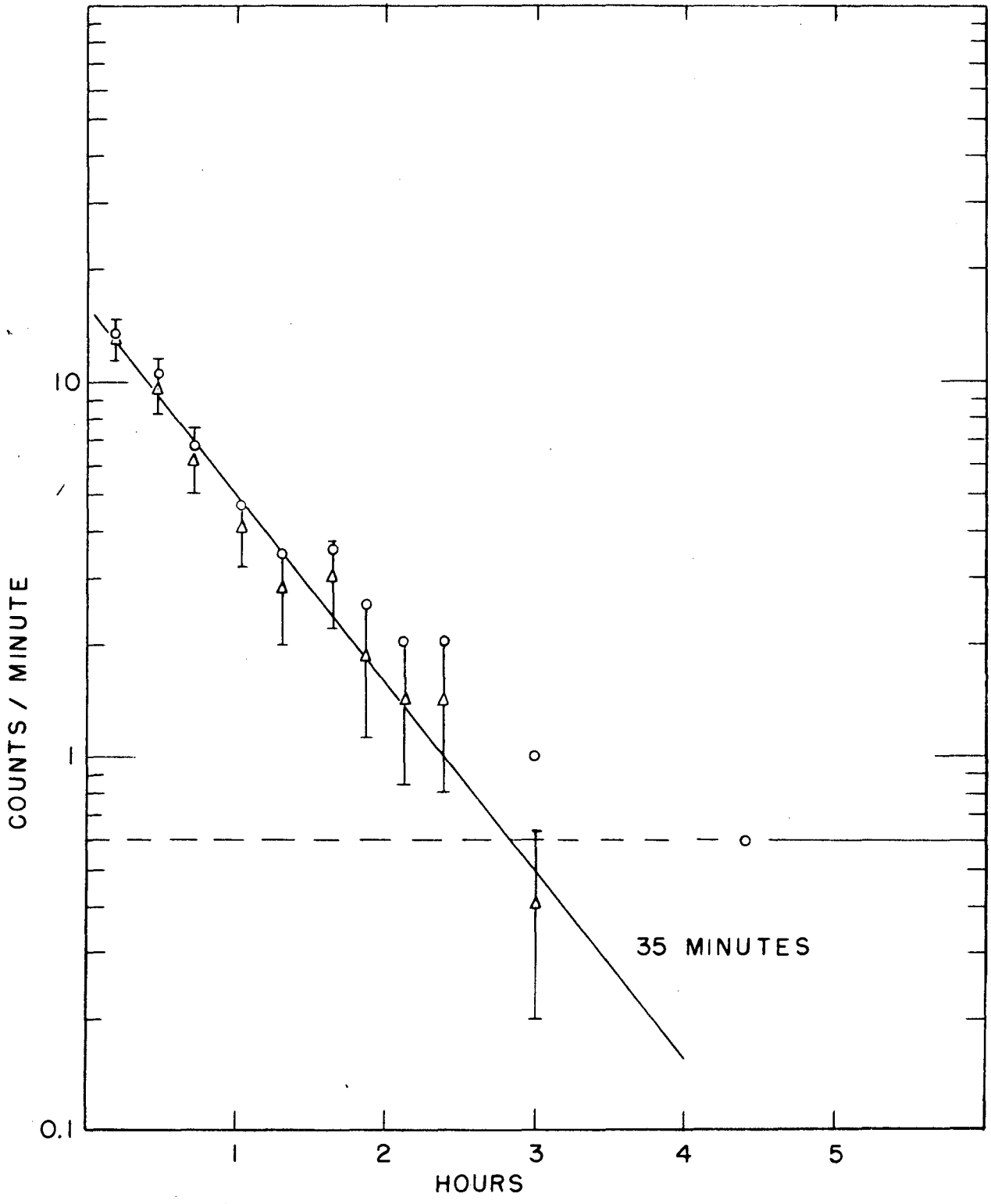

Fig. 14 Decay of Np^{233} alpha activity. Sums of counting rates over pulse analyzer channels 13-20. Same time scale as Fig. 5.

fraction was taken 45 minutes after cyclotron shutdown. The x-ray activity was accentuated by following decay with a xenon Geiger tube through 1.5 gm/cm^2 of beryllium and 1.5 gm/cm^2 beryllium plus 155 mg/cm^2 of lead(figures 15 and 16). The x-ray decay can be resolved only on the basis of two short-lived activities and the half-life values 35 minutes and 13 minutes seem to give the best fit to the data.

The decay of hard electromagnetic radiation was followed with a xenon tube using alternate absorbers, 1 gm/cm^2 and 11 gm/cm^2 of lead, in the top shelf. Most of this gamma radiation (fig. 17) seems to be associated with the 13 minute activity although an unequivocal resolution of the data was not possible. The difference in counting rate between the two absorbers places the average gamma energy at ca. 0.6 Mev.

The neptunium fraction isolated from this bombardment was not entirely pure. The gross decay with no absorber was followed with an argon counter to measure the amount of electron activity. After the decay of the short-lived neptunium isotopes, about five hours after the end of the bombardment, beryllium absorption counts showed the presence of hard beta activity, not attributable to neptunium. This contamination could not be identified but the gross decay indicated a half-life of the order of five - six hours. Superimposition of the decay of this unknown contamination on the already complicated decay of the mixture of Np^{233}, Np^{234}, Np^{238}, and Np^{239} yields an unresolvable curve, although it appeared that the electron to x-ray ratio for the 14 minute activity was greater than that for Np^{233}, perhaps by a factor of two.

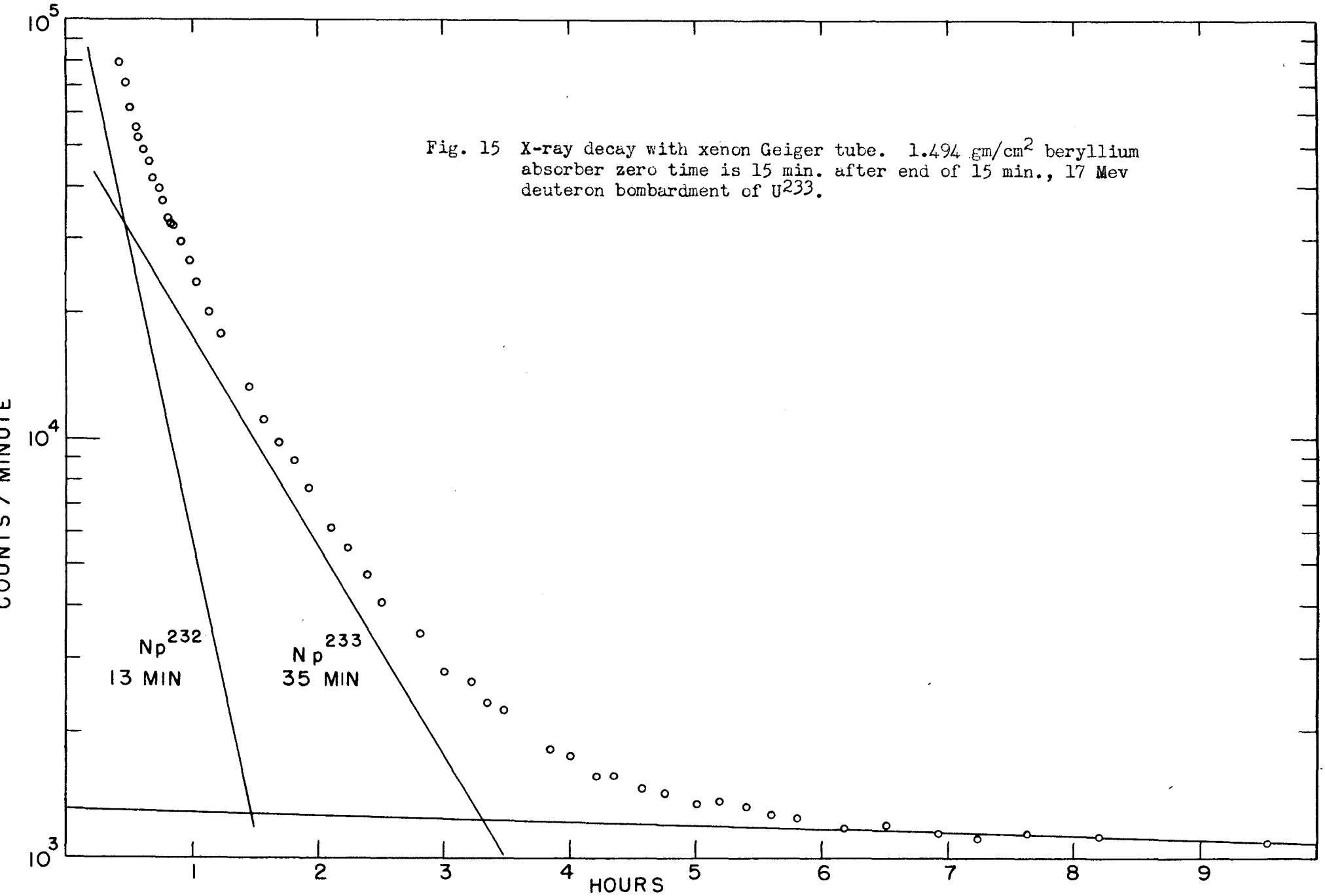

Fig. 15 X-ray decay with xenon Geiger tube. 1.494 gm/cm^2 beryllium absorber zero time is 15 min. after end of 15 min., 17 Mev deuteron bombardment of U^{233}.

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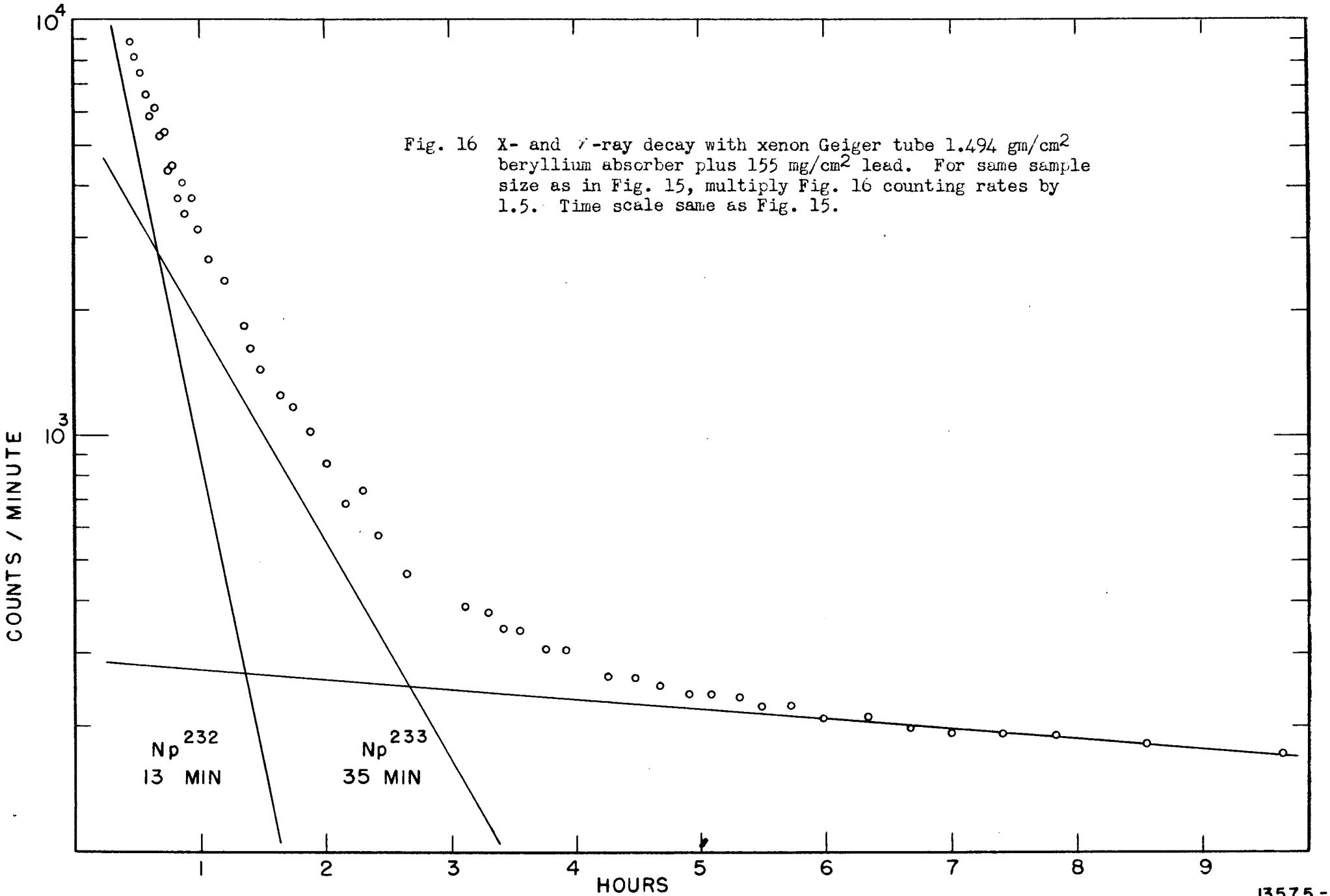

Fig. 16 X- and γ-ray decay with xenon Geiger tube 1.494 gm/cm^2 beryllium absorber plus 155 mg/cm^2 lead. For same sample size as in Fig. 15, multiply Fig. 16 counting rates by 1.5. Time scale same as Fig. 15.

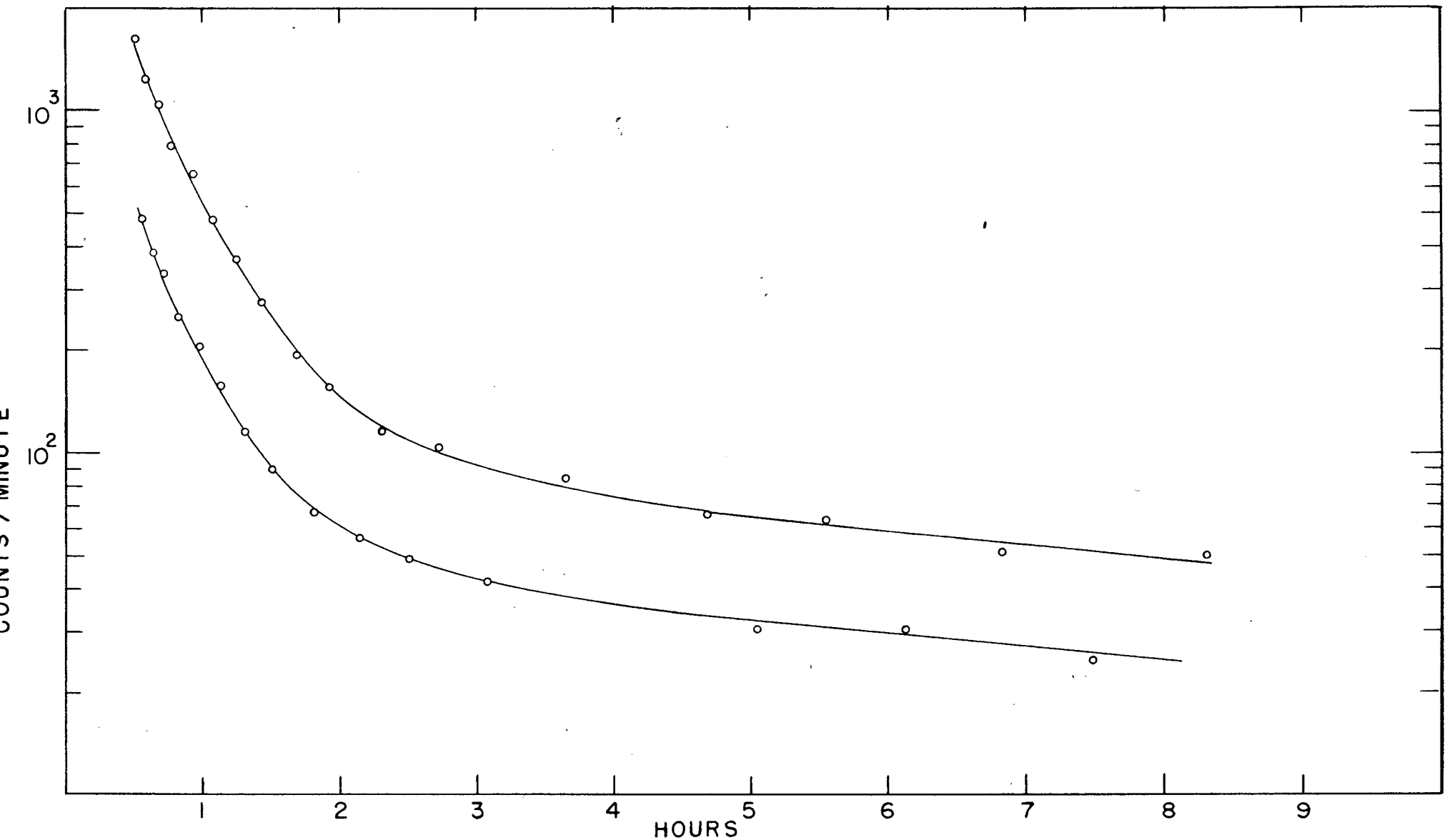

Fig. 17 Short-lived neptunium gamma radiation (xenon Geiger tube). For same sample size as in Fig. 15, multiply counting rates by 3.3. Time scale is same as Fig. 15.

B. Alpha particles from Np^{232}.

The alpha particles from Np^{232} were not detected in this bombardment. Pulse analysis showed that the neptunium fraction was contaminated with Th^{228} and daughters to an extent which would obscure any Np^{232} alpha activity. The very small peak seen in the preceding bombardment is the only evidence for Np^{232} alpha particles.

With new bombardment apparatus now in design, it should be possible to produce enough Np^{232} to measure the alpha particles accurately and to identify the daughter by electron capture, U^{232}.

V. Chemical Methods

A. General

The chemical properties of neptunium are not discussed here. All the information available at the time of this research may be found in the Plutonium Project Record and in the references given in the Introduction. The essential need in this research was for a neptunium isolation process much more rapid than any devised hitherto, since the objective was the discovery of isotopes believed to be short-lived. This need was fulfilled by modification of the mechanics of previously known processes rather than by discovery of any fundamentally new process. The most rapid isolations from the target, required only forty-five minutes, but serious sacrifices in purity resulted. The methods to be described required on the average from an hour to an hour and a half. For short-lived studies of neptunium the need still remains for very rapid, efficient processes and as fundamental physical and chemical studies of the element progress

these processes will undoubtedly be developed. Only the general outlines of the methods will be given since the details varied with the bombardment. Conditions, such as concentrations, were in general not critical.

B. Targets.

The targets in every case were uranium. One of the most time consuming steps was the dissolution of the target material. Np^{231} was first found in bombardments of natural uranium metal. The metal strip, 10-20 mil thick and 0.5-1 gram in weight usually, was clamped edgewise to the deuteron beam for maximum beam exposure. Dissolution of the metal in the desired time, not more than ten minutes, was difficult. Hot, strong nitric acid required 20-30 minutes to dissolve a gram of 20 mil metal. Much thinner metal, not available, would probably dissolve rapidly enough. A new method, used to some extent, was to drop the metal strip into a molten bath at about 600° C. of sodium and potassium nitrates in a Pyrex tube. The metal and melt react completely in a few seconds. After two or three minutes cooling the solidified mass can be dissolved in dilute acid. Precipitation of LaF_3 from these solutions, however, often produced precipitates of material corroded from the Pyrex tube.

The best solvent for uranium metal targets was hot 10 M hydrochloric acid containing a trace of Fe(III). The resulting U(IV) solution was oxidized to U(VI) with an excess of liquid bromine.

The targets for the bombardments of U^{235} in the 184-inch cyclotron were UO_2 sealed in thin-walled Pyrex tubes. After bombardment the tube was dropped into a centrifuge tube containing solvent and

crushed with a glass rod. Hot 8 M nitric acid with a trace of Fe(III) was a rapid solvent for the uranium oxide. A known amount of Np^{237} tracer was always added to the target solvent for later measurement of the chemical yield. The 45 Mev bombardments of U^{238} and U^{233} were also on material held in Pyrex tubes. The U^{238} was bombarded as UO_2 and the U^{233} as the dried precipitate from a uranyl nitrate solution made alkaline with NH_3.

The bombardments of U^{233} in the 60-inch cyclotron were on UO_3 prepared by drying uranyl nitrate solution in platinum interceptor boats.

C. Neptunium separations.

Neptunium was isolated from all other radioactive species by well-known co-precipitation and solvent extraction techniques. The procedures may be classified and outlined as follows:

1. Lanthanum flouride.

a. Precipitation of a few mg. of MnO_2 from the uranyl nitrate solution, diluted to 1M HNO_3, by adding $KMnO_4$ solution followed by enough $NaNO_2$ solution to reduce all premanganate. The $KMnO_4$ ensured that all uranium was U(VI) and the MnO_2 was an effective decontaminant, particularly for protactinium, always formed in large yield.

b. Precipitation of LaF_3 with HF, carrying neptunium. Nitrite reduces Np(VI) to Np(V). On addition of HF, Np is carried by LaF_3. Whether the Np(V) is carried or whether Np(V) first reduces to Np(IV) which then is coprecipitated with the LaF_3 is not known. The uranium remains in the supernatant solution.

c. Metathesis of the LaF_3 to $La(OH)_3$ with strong NaOH or KOH by heating and stirring.

d. Bromate oxidation cycle. The $La(OH)_3$ is dissolved in HNO_3 and diluted with H_2SO_4 to give a solution about 1 M H_2SO_4, 1 M HNO_3. $NaBrO_3$ solution is added to about 0.1 M and and LaF_3 precipitated from 0.1 M HF. The solution is diluted by a factor of five with the addition of excess SO_2 solution to reduce all bromate to bromide. More La(III) is added and precipitated as LaF_3 carrying the neptunium from 1-3 M HF.

2. Ether extraction

a. The LaF_3 is dissolved by complexing fluoride with hot, saturated $Al(NO_3)_3$, the solution is diluted to 1M HNO_3 and 0.1 M $NaBrO_3$ and heated 2-3 minutes to oxidize the neptunium.

b. Solid NH_4NO_3 is added to 10 molar and the neptunium extracted from the solution with twice its volume of ether.(The ether used for this extraction must be free from reducing impurities, e.g.alcohols and aldehydes. Effective purification is attained by treatment with $K_2Cr_2O_7$-1M H_2SO_4 solution).

c. The ether extract of neptunium is washed once with 10 M NH_4NO_3 solution, and may then be poured or pipetted onto platinum counting plates.

This procedure, which could be carried out within an hour, yielded a neptunium fraction pure with respect to alpha activity and usually sufficiently pure for Geiger measurements. As confirmation of the

purity it was customary to put the neptunium through a thenoyl trifluoroacetone (TTA) extraction.

3. Thenoyl trifluoroacetone(TTA)

a. The neptunium is extracted from its ether solution into water containing a little $NaNO_2$ and La(III) which is precipitated as $La(OH)_3$ carrying the neptunium to separate from nitrate.

b. The $La(OH)_3$ is dissolved in 5 M HCl, 0.1 M KI, and 0.05 M $N_2H_4 \cdot 2HCl$ solution, followed by heating 1-2 minutes at 90° C.

c. The solution is diluted to 0.5 M HCl and heated for a minute again to reduce free iodine. This reduction treatment produces Np(IV) which may be chelated and extracted by a benzene solution of thenyl trifluoroacetone.

d. The 0.5 M HCl solution of Np(IV) is agitated 20-30 minutes with a 0.3 M solution of TTA in benzene. The benzene solution is placed on platinum counting plates and dried.

The neptunium chelate is volatile and a large percentage is lost if the benzene solution is simply dried and heated strongly. It was found that a small amount of trichloroacetic acid placed on the plate before adding the benzene solution effectively prevented volatilization of the neptunium during drying and ignition. Inclusion of the TTA extraction requires an additional forty-five minutes.

4. Zirconium phosphate

Zirconium phosphate may be used as a carrier for Np(IV) in a procedure analogous in principle to the lanthanum fluo-

ride method.[15,16] The target solvent used for the $U^{233}O_3$ was 6 M HNO_3, 10^{-3} M Ce(IV), 0.02 M Zr(IV) with added Np^{237} tracer.

a. The target solution is made 0.02 M in $NaBrO_3$ and heated one minute to oxidize neptunium. H_3PO_4 is added to 0.3 M and the solution is heated a minute to coagulate the $Zr_3(PO_4)_4$ precipitate, which does not carry the Np(VI).

b. The supernatant solution containing Np(VI) is reduced with excess $N_2H_4 \cdot H_2SO_4$ to destroy bromate and then made 0.01 M in $N_2H_4 \cdot H_2SO_4$ and 0.005 M in Fe(II) to reduce neptunium to NP(IV). This reduction is instantaneous.

c. Zr(IV) is added to 0.01 M with heating and stirring. $Zr_3(PO_4)_4$ precipitates carrying Np(IV). The precipitate is washed with 3 M HNO_3-0.5 M H_3PO_4 solution. Uranium and assorted activities remain in the supernatant solution.

d. Conversion to LaF_3. About 0.1 mg La(III) in solution is slurried with the $Zr_3(PO_4)_4$ and the zirconium dissolved by complexing in a 1 M HF, 1 M HNO_3 solution. A precipitate of LaF_3 remains, bearing the neptunium. The LaF_3 is washed with 0.1 M HF and may then be plated or used for further purification, as in the ether extraction (procedure 2 above).

5. Resin column.

A Dowex 50 resin column separation of trace amounts of neptunium from uranium and plutonium has been used.[17] Np(V) is adsorbed

on a small amount of resin from low acid solution and placed at the top of a resin column containing 13 M HCl. The neptunium is eluted rapidly by passing 13 M HCl through the column. This method was used once to show that 35 minute Np^{233} followed Np^{237} tracer quantitatively. Study of the data showed that only uranium and neptunium were present in the activity adsorbed on the resin. A sharp separation from U(VI) was made in the column with the uranium eluting first. The elutriant was sampled dropwise directly on platinum counting plates.

VI. Radiometry.

Samples for radioactive assay were mounted on 2 mil platinum. A uniform geometrical arrangement was used for all Geiger activity measurements. Since the principal objective of this work was measurement of electromagnetic radiations, no lead housing was used around the Geiger tube and sample. In place of a lead housing as a shield against general room radiation, a small lead shield, just large enough to fit around the brass, bell-type Geiger tube, was used. The sample was supported on a flat aluminum holder in the second shelf of a lucite stand below the mica window of the tube. The sample to window distance was 2.1 cm. for all measurements. This arrangement was used to minimize spurious counting rates caused by the scattering of primary and secondary radiations around absorbers as will occur from the walls of a housing. Counter backgrounds were about 30 counts/minute, only a little above backgrounds common for tubes in lead housings . The Geiger tubes were not light sensitive. The mica windows of all tubes used were near 3 mg/cm^2.

An approximate value of 3.5% for the absolute geometry of the 2.1 cm. distance was obtained by counting the β particles from Pa^{234} (UX_2) in equilibrium with a known weight of U^{238} (as UO_2) mounted between cellophane sheets. The Th^{234}(UX_1) β particles were absorbed by a 30 mg/cm^2 Al absorber.

Variations and plateaus in the Geiger counters were checked frequently by a UX_2 standard. When appreciable variation in the counting rate of the standard was observed, the sample counting rates were corrected by multiplying by the ratio, observed standard rate/ adopted standard rate.

Beryllium absorbers were used extensively to determine relative amounts of electron and electromagnetic radiation. The absorbers were placed in the top shelf of the lucite stand, giving a distance of 0.4 cm. between the top surface of the absorber and the window. Aluminum and lead absorptions of electromagnetic radiations were measured in general with the aluminum or lead resting on the sample plate holder and a large beryllium absorber in the top shelf. The beryllium available in this laboratory is variable in purity. The absorbers have been calibrated for the absorption of 8 kev Cu x-rays. The half-thicknesses for the 8 kev radiation of the absorbers used in this research are given in table 1. No attempt has been made to correct observed counting rates for the beryllium purity since extrapolated relative abundance was of primary importance.

A number of determinations of the alpha disintegration rates of Np^{237} and Pu^{236} in the same sample were required for yield calculations. These rates were determined by pulse analyzing[18] the sample

Table 1

Beryllium Absorbers

Absorber (mg/cm^2)	Half-thickness for 8 kev Cu x-rays
12.6	500
42.6	700
99	610
196	610
402	441
602	449
804	449
1483	348
1494	630

to obtain the ratio of the two activities and by counting the gross alpha activity in a 50% geometry ionization chamber. The ratio is obtained by summing the counts registered for each activity. The counting rate for each activity was then calculated from the pulse analyzer ratio and the gross activity. These rates were in general 10-20% higher than the counting rate given by the pulse analyzer. The pulse analyzer counting rates for Np^{231} were similarly corrected by comparison of the pulse analyzer counting rate of the Np^{237} tracer at about the same time with the counting rate determined more accurately later by the ratio method.

VII. The Isotopes Np^{237} and Pa^{233}

The alpha particles of Np^{237} were used as tracer in all isolations as a measure of chemical yield and relative amount of neptunium on different assay plates. The presence of Np^{237} and its 27-day daughter, Pa^{233}, complicated the resolutions of decay curves. The isolation procedure of course separated Pa^{233} along with protactinium activity formed by bombardment, so the re-growth of Pa^{233} to equilibrium with Np^{237} was superimposed on the decay of neptunium activity produced by bombardment. Some time was therefore spent in measuring the radiations of Np^{237} (other than alpha particles), Pa^{233}, and the rate of growth of the latter, under the conditions adopted as standard (argon counter tube).

Samples of stock Np^{237} were separated from Pa^{233} by MnO_2 precipitation and ether extraction. The Np^{237} activity was plated on 2 mil platinum and counted with various absorbers. The initial rate of re-growth of Pa^{233} is rapid so growth data was obtained and the Np^{237}

counting rate determined by extrapolation back to zero time (time of separation). The growth curve with no absorber was followed out to near equilibrium for convenient data for correcting bombardment samples. Figure 18 shows experimental counting rates on the basis of 1.92×10^4 disintegrations/minute of Np^{237}. The curve of counting rates, R, was calculated from the growth equation

$$R = (1868-178) - e^{-\lambda t} + 7.43$$

where equilibrium rate = 1868 counts/minute

Np^{237} contribution = 178 counts/minute

$$\lambda = 0.0253 \text{ day}^{-1}$$

The Pa^{233} decay constant, 0.0253 day^{-1}, is from Grosse, Booth, and Dunning.[19] There seems to be a small deviation outside the experimental error in determining the parameters of the growth equation but the reason for the deviation was not determined.

Beryllium absorption curves, measured on the same sample (1.92×10^4 dis/min Np^{237}), for Np^{237} and Pa^{233} in equilibrium with the Np^{237} are shown in figure 19. The difference between the two curves gives the Pa^{233} contribution. A comparison of beryllium, aluminum, and lead absorption for the Np^{237} radiations are shown in figure 20, on the sample basis of 1.0×10^5 dis/min Np^{237}. The sample was in the second shelf and all absorbers in the first shelf. Soft electrons of energy less than 150 kev are evident as well as electromagnetic radiation of energy corresponding to K and L x-rays. There can be no gamma radiation of energy greater than 200 kev. If one assumes a counting efficiency of about 1% for the x-radiation the alpha/L x-ray/K x-ray ratio is ca. 1/1/0.2.

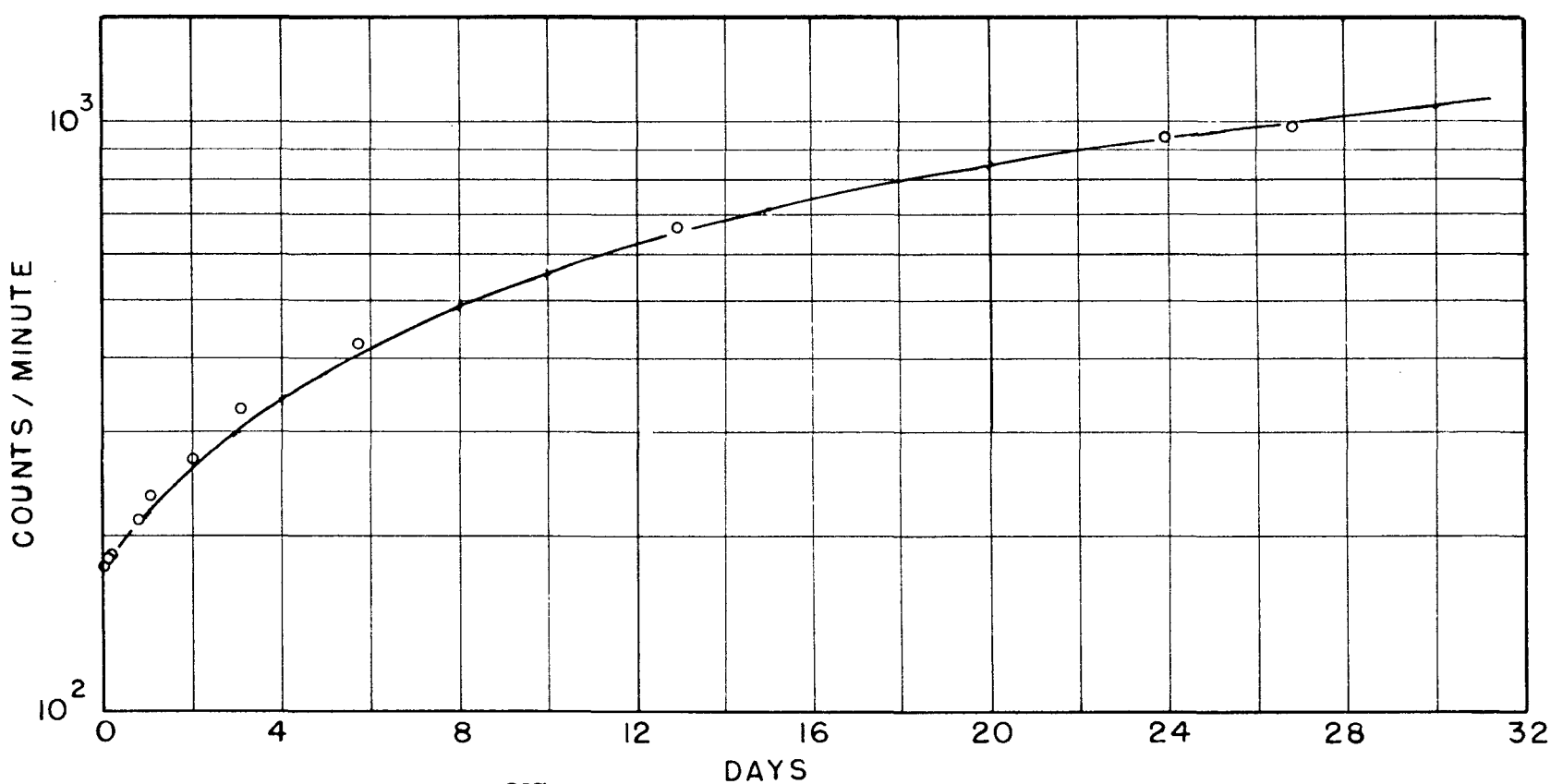

Fig. 18 Growth of Pa^{233} from Np^{237}. 10^4 alpha counts/minute Np^{237}. No absorber, standard conditions. Zero time is time of separation from protactinium. Equilibrium counting rate 1868 c/m from counts taken after several months.

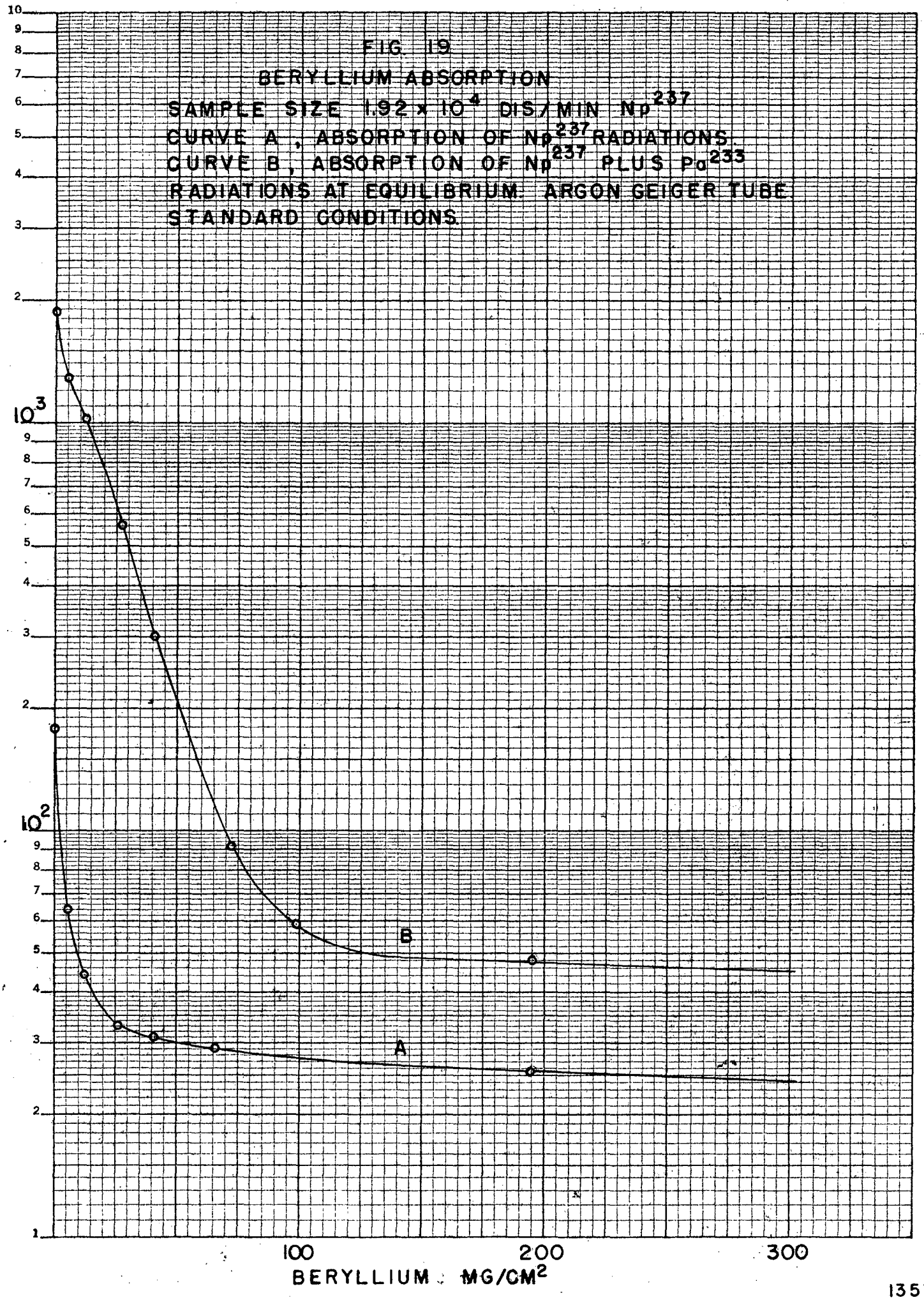
FIG. 19
BERYLLIUM ABSORPTION
SAMPLE SIZE 1.92 x 10^4 DIS/MIN Np^237
CURVE A, ABSORPTION OF Np^237 RADIATIONS.
CURVE B, ABSORPTION OF Np^237 PLUS Pa^233
RADIATIONS AT EQUILIBRIUM. ARGON GEIGER TUBE
STANDARD CONDITIONS.
10
9
8
7
6
5
4
3
2
10^3
10^2
1
A
B
100
200
300
BERYLLIUM MG/CM^2
KEUFFEL & ESSER CO. N. Y. NO. 359-71G
Semi-Logarithmic, 3 cycles X 10 to the inch, 5th lines accented.
MADE IN U.S.A.

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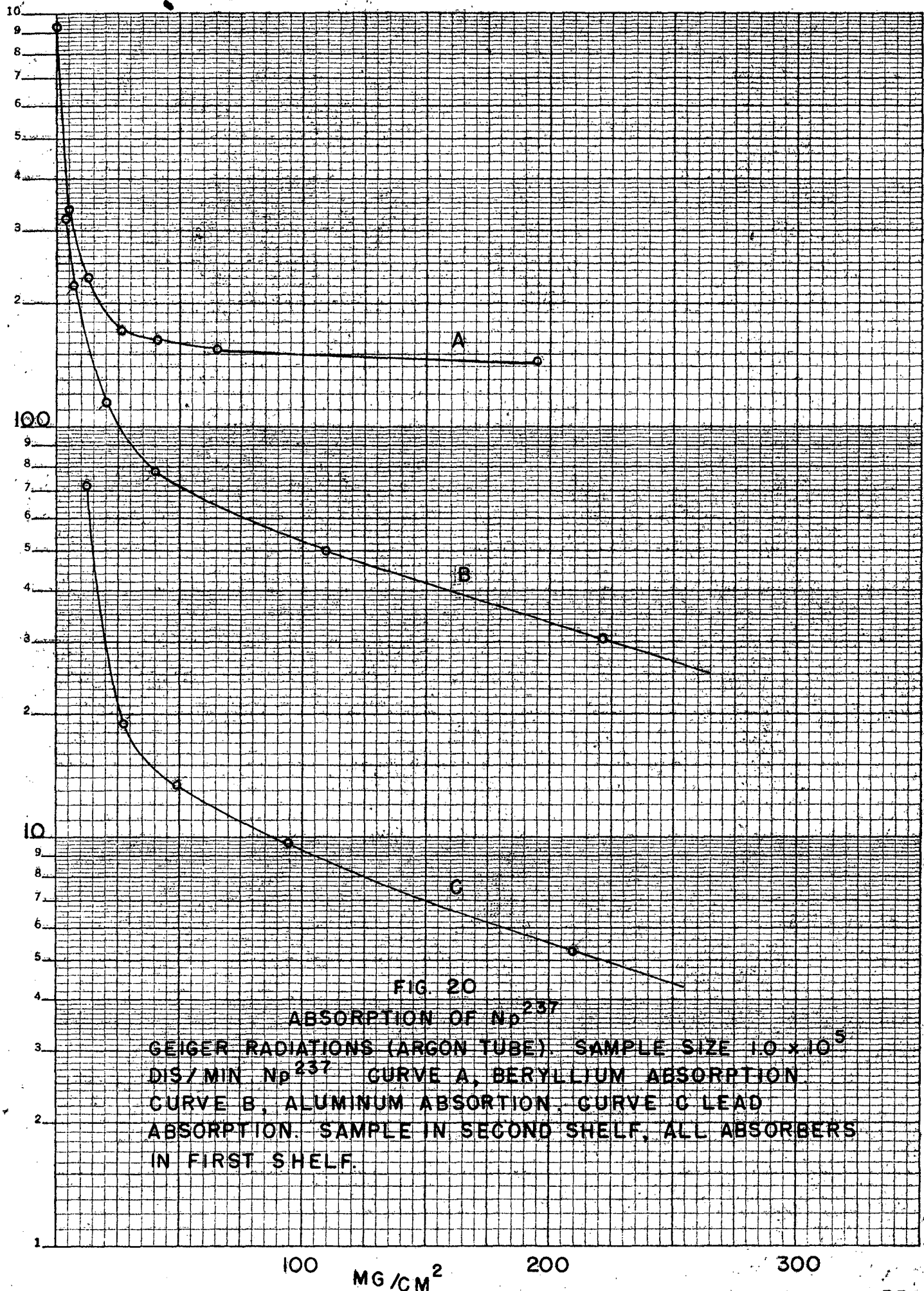

FIG. 20

ABSORPTION OF Np^{237}

GEIGER RADIATIONS (ARGON TUBE). SAMPLE SIZE 1.0×10^5 DIS/MIN. Np^{237} CURVE A, BERYLLIUM ABSORPTION. CURVE B, ALUMINUM ABSORTION. CURVE C LEAD ABSORPTION. SAMPLE IN SECOND SHELF, ALL ABSORBERS IN FIRST SHELF.

KEUFFEL & ESSER CO., N. Y. NO. 359-210
Semi-Logarithmic, 3 cycles X 10 to the inch, 5th lines accented.
MADE IN U. S. A.

VIII. Cross Sections

In the course of the search for radiations from light neptunium isotopes, measurements of the radiations of previously known isotopes were obtained. From these measurements and the times and intensities of bombardment one may calculate atom yields and cross sections for formation. It was believed possible, for a time, that Np^{232} and Np^{233} might have half-lives of the order of a day or two; consequently the decay of neptunium Geiger radiations, particularly x-ray, was carefully followed for each bombardment. All radiations from species with half-lives longer than an hour could be accounted for as coming from known isotopes of mass number greater than 233. The x-ray decay of neptunium from 45-100 Mev deuteron bombardments of U^{235}, for example, consisted of 22 hour and 4.4 day periods. The latter is Np^{234} and the 22 hour x-rays come from Np^{236}. A preliminary study not reported here of the radiations of Np^{236}(produced from deuterons on Np^{237}) has yielded an approximate electron/x-ray ratio which is the same as the electron/x-ray ratio of the 22 hour period from U^{235} bombardment. The expected amount of Pu^{236} alpha activity grew into the samples. A very small amount of ca. 2 day activity also appears which is Np^{238}. Neptunium fractions from U^{233} bombardment, contain no 22-hour x-ray period.

Only in the 60-inch cyclotron bombardments of U^{233} was the absolute beam intensity known to any accuracy. Cross sections were calculated for all the 184-inch cyclotron bombardments by assuming a deuteron beam of 1 microampere over a target area of 0.6 cm^2. This area corresponded roughly to that of the U^{233}, U^{235}, and U^{238} targets

in Pyrex tubes bombarded with 45, 70, and 100 Mev deuterons. Comparison of cross sections for formation of the same isotope calculated from two different bombardments probably has no significance within a factor of five. The relative cross sections for isotopes from the same bombardment, however, should be calculable as nearly as accurately as the decay schemes, half-lives, and counting efficiencies are known. The variations in relative cross sections for the same isotopes with bombardment energy do not depend on any assumptions but depend only on the accuracy of counting and decay resolution.

There are two large uncertainties in converting the experimental counting rates to numbers of atoms. They are a decay scheme factor (F, below) and counting efficiency(E) . The decay scheme factor involves the extrapolation of counting rates with absorbers and the ratio of counted events at 100% geometry to disintegrations. We will be interested in the counting efficiency of the x-rays from electron capturing isotopes. The number of L x-rays associated with each isotope was determined approximately and it was assumed that one L x-ray was emitted per disintegration.

Let c/m = counts/minute

d/m = disintegrations/minute

λ = decay constant

G = geometry factor

F = decay scheme factor

E = counting efficiency

N = number of atoms produced in bombardment

$$N_r = \frac{EN}{F}$$ relative number of atoms produced in bombardment

then $$N = \frac{d/m}{\lambda}$$

$$N = \frac{(c/m)F}{GE}$$

$$N_r = \frac{(c/m)}{G\lambda}$$

Values for N_r, corrected for decay and bombardment times, produced from U^{233}, U^{235}, and U^{238} at several energies are given in tables 2, 3, and 4. These values are given to permit later recalculation of yields as decay schemes and counting efficiencies become better known. All Geiger counts were made under the conditions described in Section VI. The counting conditions and methods for yield determination for each isotope are as follows:

Np^{239} Decay resolution of sample with no absorber. Np^{238} contribution subtracted.

Np^{238} Decay resolution of sample with 178 mg/cm^2 aluminum absorber. Counting rate through absorber converted to rate with no absorber by factor 9.2 for subtraction to get Np^{239} contribution and for calculation of N_r.

Np^{236} Alpha pulse analysis for daughter, Pu^{236}. N_r values calculated from Pu^{236} decay constant, 0.257 yr^{-1}.

Np^{235} Long-lived x-ray counts through 804 mg/cm^2 beryllium absorber with xenon Geiger tube. Approximate conversion to argon Geiger counting rate by factor 0.2.

Table 2

Relative numbers of atoms, N_r, from U^{233}

Deuteron(Mev)	15	17	50
Np^{234}	$3.2(10^8)$	- - -	$2.6(10^7)$
Np^{233}	$1.2(10^8)$	$1.5(10^6)$	$5.7(10^6)$
Np^{232}	- - -	$3.2(10^6)$	- - -
Np^{231}	0	0	$9.1(10^5)$

Table 3

Relative numbers of atoms, N_r, from U^{235}

Deuteron(Mev)	45	70	100	
Np^{236}	$7.6(10^9)$	$2.6(10^{10})$	$2.6(10^{10})$	$1.6(10^9)$
Np^{235}	$3.4(10^8)$	$8.5(10^8)$	$5\ (10^8)$	$3\ (10^7)$
Np^{234}	$3.3(10^8)$	$7.9(10^8)$	$9.7(10^8)$	- - -
Np^{233}	$9.9(10^7)$	- - -	- - -	$1.5(10^7)$
Np^{231}	$5.3(10^6)$	$2.0(10^7)$	$2.6(10^7)$	$1.9(10^6)$

Table 4

Relative numbers of atoms, N_r, from U^{238}

Deuteron(Mev)	45	120
Np^{239}	$8.7(10^{10})$	- - -
Np^{238}	$2.2(10^{10})$	- - -
Np^{236}	$1.8(10^{10})$	$1.5(10^{11})$
Np^{235}	$1.7(10^8)$	$1.7(10^9)$
Np^{234}	$3.4(10^8)$	- - -
Np^{233}	$1.4(10^7)$	- - -
Np^{231}	- - -	$2.9(10^6)$

Np^{234} Decay resolution with 804 mg/cm^2 beryllium absorber. F value estimated from unreported absorption data (this research).

Np^{233} Decay resolution with various beryllium absorbers. N_r values in tables 3, 4, and 5 on basis of 804 mg/cm^2 beryllium absorber.

Np^{232} Same as Np^{233}. F value assumed to be same as for Np^{233}.

Np^{231} Alpha pulse analysis. Upper limits for the cross section are calculated on assumption that electron capture/alpha emission ratio is 100.

The calculation of actual atom yields requires, particularly in the cases of electron capture, assumption of highly uncertain decay scheme factors and counting efficiencies. The assumed or known parameters are given in table 5. Cross sections may now be calculated from the equation

$$\sigma = N/nIT(10^{-24})$$

where σ = cross section in barns(10^{-24} cm^2/deuteron)

N = number of transmuted atoms

n = number of target atoms

It = total number of deuterons through 1 cm^2 of target area.

Tables 6, 7, and 8 list the cross section values derived from the N_r values, assumed parameters, target weights, and beam flux.

The large uncertainty factor in absolute beam, It, is apparent from the duplicate bombardments of U^{235} at 100 Mev. Np^{233} was not

Table 5

Conversion Factors

Isotope	λ	G	F	E	Ref.
Np^{239}	0.297 day^{-1}	0.085	0.74	1	(20)
Np^{238}	0.347 day^{-1}	0.085	1.7	1	(21)
Pu^{236}	0.257 yr^{-1}	0.52	1.0	1	(10)
Np^{235}	0.582 yr^{-1}	0.085	1.4	0.02	(10)
Np^{234}	0.158 yr^{-1}	0.085	0.7	0.02	
Np^{233}	0.0210 min^{-1}	0.085	1.0	0.02	
Np^{232}	0.0495 min^{-1}	0.085	1.0	0.02	
Np^{231}	0.0139 min^{-1}	0.52	100.	1	

Table 6

U^{233} Cross Sections (barns)

Deuteron(Mev)	15	17	50
Np^{234}	$3.4(10^{-3})$	- - -	$5\text{-}6(10^{-3}(?)$
Np^{233}	$1.8(10^{-3})$	$1.8(10^{-3})$	$1.9(10^{-3})$
Np^{232}	- - -	$3.8(10^{-3})$	- - -
Np^{231}	0	0	$<6.2(10^{-4})$

Table 7

U^{235} Cross Sections (barns)

Deuterons(Mev)	45	70	100	100
Np^{236}	$1.6(10^{-3})$	$1.8(10^{-3})$	$1.5(10^{-3})$	$4.5(10^{-4})$
Np^{235}	$4.9(10^{-3})$	$4.0(10^{-3})$	$2.1(10^{-3})$	$5.9(10^{-4})$
Np^{234}	$2.4(10^{-3})$	$1.9(10^{-3})$	$2.0(10^{-3})$	- - -
Np^{233}	$1.0(10^{-3})$	- - -	- - -	$2.1(10^{-4})$
Np^{231}	$<1.1(10^{-4})$	$<1.4(10^{-4})$	$<1.5(10^{-4})$	$<5.3(10^{-5})$

Table 8

U^{238} Cross Sections (barns)

Deuterons(Mev)	45	120
Np^{239}	$1.0(10^{-2})$	- - -
Np^{238}	$5.9(10^{-3})$	- - -
Np^{236}	$2.8(10^{-3})$	$6.0(10^{-3})$
Np^{235}	$1.9(10^{-3})$	$4.8(10^{-3})$
Np^{234}	$1.9(10^{-3})$	- - -
Np^{233}	$<(10^{-4})$	- - -
Np^{231}	- - -	$<1.2(10^{-5})$

observed in the 45 Mev bombardment of U^{238}, the table value is the limit of detection. Np^{231} was observed for all table entries; the limit values arise from the unknown decay by electron capture, as explained previously. The formation cross section of Np^{239} has little significance since a large but unknown fraction of the Np^{239} came from decay of U^{239}.

The fission reaction is predominant in the bombardment of uranium with high energy particles. The cross sections for formation of neptunium isotopes by (d,n), (d,2n), (d,3n), and (d,4n) reactions on uranium with 15 - 20 Mev deuterons were found in the earlier work to be small, of the order of 0.01 barn, compared to larger values for the same reactions on non-fissioning nuclei. The problem of producing lighter neptunium isotopes also raised the question as to whether the yields of (d,xn) reactions might be reduced by increased fission and other competing reactions induced by the greater excitation required to knock out more neutrons. At the higher energies used here, other reactions such as the (d,αxn), (d,2αxn), and (d,pxn) have been observed.

The data show that x may be at least as large as nine in the (d,xn) reaction on U^{238} with sufficient bombarding energy. The (d,5n) and (d,6n) reactions on U^{235} have thresholds between 20 and 45 Mev and the (d,7n) has a threshold greater than 45 Mev.

Despite lack of absolute beam data, a hypothetical discussion of the yield variations seems justified. The (d,n) reaction yield remains prominent even at 100 Mev. This reaction is interesting in that a proton mass must be captured. One might guess that a 100 Mev

deuteron would produce a compound nucleus much too excited to yield any (d,n) product, yet the yield is probably not down even by a factor of ten from that with 15 Mev deuterons. At least two mechanisms are at hand to account for the sustained yield. A stripping mechanism for high energy deuteron reactions has been proposed by Serber whereby the neutron-proton bond of the deuteron is broken without compound nucleus formation.[22] From a quantum mechanical model Serber calculates a wide spread in distribution of energy for the neutrons emerging from the collision. By conservation of energy the protons must have a similar distribution and one may postulate proton capture with small excitation. Peaslee has concluded that the stripping mechanism accounts for the major portion of the (d,n) cross section at all energies.[23]

As a second mechanism one may retain the compound nucleus model and postulate that the highly excited (d,n) product may still dissipate its energy entirely by gamma emission with a probability comparable to that for lower excitation. The sustained (d,n) yields, however, seem more probably to be evidence in favor of the stripping mechanism.

The relative yields of different isotopes for reactions which are energetically possible are remarkably similar, although a tendency to form the lighter isotopes in relatively greater yield with increasing energy seems clear. A consideration of the cross sections suggests that the total cross section for formation of neptunium isotopes does not change greatly over the energy range investigated (15-100 Mev); i.e., at energies well above the potential barrier to penetration of the nucleus by the proton. It would follow, therefore,

that increased excitation does not greatly increase fission and competing reactions at the expense of (d,xn) reaction yields. This conclusion with regard to fission would perhaps be predicted from theory since only a small excitation energy is required in general to raise a heavy element above the fission energy barrier. Increased excitation above that necessary to cross the barrier need not markedly increase the fission rate, particularly relative to the rates for dissipation of energy by neutron and gamma emission. The latter two processes are known to be very rapid and increase in rate with energy. The greatly increased (d,αxn) as well as other spallation type reactions, however, might be expected on first consideration to reduce the neptunium yields by large factors, but experimentally it is observed that they do not.

A sequence of events following the capture of a deuteron may now be postulated. The sequence is divided into a preliminary period of rapid events followed by a period of slower events. In the preliminary period following capture of a relatively low energy deuteron (15 Mev) or proton from the deuteron in the stripping mechanism emission of one or more neutrons up to the maximum energetically possible occurs. For higher energy deuterons(100 Mev) charged particle emission competes favorably with neutron and gamma emission. The compound nucleus(Np^{237})* , for example, may dissipate energy in the preliminary period through the following schematic reactions, where subscripts indicate decreasing degree of excitation:

$$(Np^{237})^* \longrightarrow (Np^{236})^*_1 + n$$
$$(Np^{236})^*_1 \longrightarrow (Np^{236})^*_2 + \gamma$$
$$\text{or } (Np^{236})^*_1 \longrightarrow (Pa^{232})^* + \alpha$$
$$\text{or } (Np^{236})^*_1 \longrightarrow (Np^{235})^*_1 + n$$
$$(Np^{235})^*_1 \longrightarrow (Np^{235})^*_2 + \gamma$$
$$\text{or } (Np^{235})^*_1 \longrightarrow (Np^{234})^* + n \quad \text{etc.}$$

The end of the preliminary, fast period is reached when the neutron and gamma emission rates become comparable to the fission rate, and the charged particle emission rate becomes negligible; i.e., the nuclei are still above the fission threshold. Further neutron emission may even be impossible. Most of the still excited nuclei fission and only those which successfully negotiate a cascade of gamma rays to the ground state survive as light neptunium isotopes. From this simple picture one would predict that fission products would be found from a wide range of fissioning nuclei, Np^A.

An explanation for the failure of other spallation reactions to reduce the neptunium yields by large factors may be derived from this kinetic picture. The spallation reactions with charged particle emission occur only from the highest levels of excitation and hence essentially at the expense of the fission reaction. The total spallation cross section at 100 Mev amounts perhaps to the order of 10% of the total cross section the remaining 90% being mainly the fission cross section. The total cross section for formation of neptunium isotopes is about 1% of the total reaction cross section. The occurrence of other spallation reactions means that, instead of 100

highly excited atoms each with a probability of 0.01 of settling down through neutron and gamma emission to the ground state of a neptunium nucleus, there are 90 highly excited atoms with about the same probability of going to neptunium isotopes. The gross neptunium yield, therefore, is not greatly effected, and the net effect of increased energy on neptunium yields is just to increase yields of the isotopes with lower mass numbers at the expense of the yields of the isotopes of higher mass numbers.

The relative cross sections further indicate that the very light neptuniums can not be produced with yields comparable to those for the heavier isotopes. Goeckerman and Street have observed significant effects attributable to the Bohr-Wheeler fission parameter, Z^2/A, on the fission of bismuth[25] and elements of high Z.[26] The rapid decrease in yield of the light neptunium isotopes may thus be attributable to increased fission of these isotopes relative to the heavier ones. The near constancy in total neptunium yield begins to break down when the excitation energy is sufficient to produce a large proportion of excited light nuclei.

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