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# A REVIEW OF METHODOLOGIES FOR DETERMINING THE AGE AND HISTORY OF NUCLEAR MATERIALS OF INTEREST IN THE NUCLEAR SAFEGUARDS, ARMS CONTROL, AND NONPROLIFERATION REGIMES

Walter R. Kane, Edward Kaplan, Garman Harbottle, Seymour Katcoff, and Anant R. Moorthy,
Brookhaven National Laboratory

Bldg 197C, P.O. Box 5000, Upton, NY 11973-5000 USA 516/344-3841 FAX 516/344-7533

## Abstract

In the nuclear safeguards, arms control, and nonproliferation regimes there is a compelling need for analytical methods which will provide information on the age of various materials since chemical separation, and to the extent possible, their history, i.e., methods of production, and exposure to a neutron flux or other environments which influence their properties. Where possible, a unique signature for an individual item can be of great value. While analytical methods for investigating these materials utilizing chemical separation and mass spectrometry are well-developed, alternative methods have, in general, not been as fully exploited. The feasibility, sensitivity, and achievable accuracy of alternate methodologies, including high resolution gamma-ray spectrometry with both HPGe semiconductor detectors and crystal diffraction, fission track detection, and ICP mass spectrometry will be discussed. In certain instances these approaches afford advantages in terms of cost, elapsed time for receipt of results, and field deployability. Methods for analyzing samples of plutonium, uranium, including uranium in the form of $UF_6$, neptunium, and thorium are reviewed.

## INTRODUCTION

The nuclear materials of interest in the nuclear safeguards, arms control, and nonproliferation regimes decay through a chain of descendants with greatly varying half-lives, each with a characteristic spectrum of emitted radiation. In addition, many of these materials contain minor, impurity isotopes with their own characteristic half-lives and spectra. In most instances these properties can be utilized, through high-resolution gamma-ray spectrometry (HRGS) or other means, to establish the elapsed time that a given item has existed in its current state, i.e., since chemical processing, vaporization, etc.. In certain instances, it may also be possible to obtain additional information on the history of the material, such as methods of production or exposure to certain types of radiation, from these measurements.

### Plutonium

**$^{241}$Pu:** A well-known and straightforward example of a parent-daughter isotope relationship which provides information on the age of a given item of nuclear material is that of the decay of $^{241}$Pu (14.35 yr.) to $^{241}$Am (432.7 yr.) and $^{237}$Np ($2.14 \times 10^6$ yr.). The half-life of $^{241}$Pu is sufficiently short that the ratio of the Am and Pu isotopes, which can be determined by a measurement of the gamma rays emitted from the item, should change significantly in a comparatively short time, typically 2 to 5 years. For very long elapsed times, where the $^{241}$Pu will have essentially decayed away and the $^{241}$Am attained a nearly steady value, the growth of

$^{237}$Np provides an additional measure of the time the item has existed since it was last subject to chemical purification. The growth and decay of these isotopes is illustrated in Fig. 1.

**$^{238}$Pu:** Although the residence time of a quantity of $^{238}$Pu (87.74 yr.) in an item can in principle be determined from the accumulation of its daughter $^{234}$U ($2.45 \times 10^5$ yr.), the long half-life of the daughter renders this determination difficult without resorting to a destructive analysis technique. A more feasible approach is to utilize the decay of the isotope $^{236}$Pu (2.87 yr.) which, typically, is present as a minor impurity in $^{238}$Pu samples. The relative amounts of these two isotopes at any time can be determined by measuring relatively strong gamma rays at 165 and 153 keV, respectively, emitted after their alpha decay. The decay of $^{236}$Pu leads to $^{232}$U (68.9 yr.), which in turn decays to $^{228}$Th (1.913 yr.). A number of strong gamma rays are emitted from short-lived descendants of $^{228}$Th, the most prominent at 238, 583, and 2614 keV. These provide a measure of the $^{228}$Th content of the item, and thus, the residence time of the plutonium isotopes. The time dependence of the content of $^{228}$Th in a $^{236}$Pu sample is shown in Fig. 2. It is seen that up to a residence time of about 15 years, when the $^{228}$Th reaches secular equilibrium with its $^{232}$U parent, it provides an accurate measure of the residence time of the sample.

**$^{242}$Pu:** While the isotope $^{242}$Pu (373,300 yr.) is present only in very small amounts in weapons grade plutonium, it may attain concentrations of several per cent in the high-burnup plutonium produced in electric power reactors. Since it has a high spontaneous fission rate, its concentration must be known when the plutonium content of an item is determined by neutron correlation counting. Because the decay of $^{242}$Pu does not produce any gamma rays in an energy range that are detectable under usual conditions, the concentration is customarily arrived at from the systematics of the other plutonium isotopes. While this approach is useful for low-burnup material, it is not applicable for high-burnup material containing several per cent $^{242}$Pu. An alternative approach, developed at Brookhaven several years ago, utilizes the capture of neutrons in an extremely strong neutron resonance at 2.67 eV (72,000b), with the detection of gamma rays emitted subsequent to this process.[1] At that time this approach was taken to the "proof of principle" stage with the fabrication of a neutron moderating geometry which was designed to maximize the flux from a $^{252}$Cf source in the region of 2.67 eV while eliminating neutrons of lower energies which would cause fission in the odd-mass plutonium isotopes. Measurements with this system demonstrated that a substantial number of neutron capture events could be realized in a small sample of $^{242}$Pu. This approach is applicable evidently, only to items within a certain range of masses, configurations, and matrix materials.

**Uranium**

**$^{233}$U:** Although the isotope $^{233}$U (159,200 yr.) is not encountered often in nuclear fuel cycles, it nevertheless possesses considerable potential importance, as it is equivalent to plutonium as a fissile material and can be produced more easily than plutonium by irradiation of thorium in a reactor. $^{233}$U (159,200 yr.) decays to $^{229Th}$ (7340 yr.); characteristic gamma rays are emitted in the decays of both these nuclides. Measurements of these gamma rays thus provide a direct value for the elapsed time since chemical purification. Because of the long half-life of $^{229}$Th, its concentration in the uranium will increase essentially linearly over times of practical concern.

An independent approach exists for investigating the history of an item containing $^{233}U$. During the reactor irradiation of thorium to produce this isotope by thermal neutron capture, other processes lead inevitably to the production of a certain quantity of the isotope $^{232}U$. The relative concentration of the two uranium isotopes will depend on the irradiation history (neutron energy spectrum, etc.). As discussed previously, $^{232}U$ (68.9 yr.) decays to $^{228}Th$ (1.913 yr.), which will grow in over a period of about 15 years until it is in secular equilibrium with its parent isotope. If the original concentration of $^{232}U$ is known, this then provides a value for the elapsed time the material has existed in situ; conversely, if the elapsed time is known, the original concentration of $^{232}U$ will be known. This may be characteristic of a given production process. It may also, in principle, provide a means for tracking and identifying an individual item. Because of the emission of the strong 2614 keV gamma ray, and other gamma rays of lower energy in the decay of the $^{228}Th$ chain, this is a straightforward process.

In connection with the measurement of gamma rays from various nuclear materials, it is worth noting that because of the wide energy range of these gamma rays, from 238 to 2614 keV, for example, for $^{228}Th$, and the emission of gamma rays with other energies from other materials, combined with the strong energy dependence for gamma-ray absorption in these materials, the spectrum observed will be highly dependent upon the mass, density, and geometrical configuration of the material as well as the presence of any intervening material which also absorbs gamma rays ("gamma-ray fingerprint principle"). Thus the spectrum observed will be a signature of an individual class of items, for example, a metal button or part will not have the same spectrum as a can of the oxide of the same material. Evidently, the template obtained in this manner is a powerful means for tracking and identifying individual classes of items, and establishing that they are what they purport to be.

**$^{235}U$:** Several years ago Moorthy and Kato[2] developed and reported on a methodology for determining the age of a sample of high enriched uranium (HEU) which utilized the chemical separation of thorium and protoactinium daughters of $^{234}U$ and $^{235}U$ and the subsequent measurement of the alpha particle spectra of $^{230}Th$ and $^{231}Pa$. While this method is straightforward and reliable, it does require the sampling and analysis of material from the item in question.

Just as in the case of the production of $^{233}U$ by reactor irradiation of thorium, the exposure of a quantity of $^{235}U$ to a neutron flux will, over time, produce a certain amount of $^{232}U$. This occurs via a number of pathways, the most important being the capture of thermal neutrons on the $^{231}Pa$ daughter of $^{235}U$. In past decades, in both the United States and Russia, substantial quantities of uranium that had resided in reactors were reprocessed and then utilized as feed for gaseous diffusion enrichment plants. Since a significant fraction of the uranium fed to a diffusion plant remains in the equipment as holdup, this led to a significant, long-term contamination of these plants by the $^{232}U$ isotope. In the enrichment process, the $^{232}U$ is concentrated in the high end of the enrichment cascade; this concentration increases rapidly with the uranium enrichment.[3] For HEU produced in the United States, the concentration of $^{232}U$ is, typically, in the range of several hundred parts per trillion. Available evidence indicates that HEU produced in Russia has a $^{232}U$ concentration two or three times higher. It is expected, by comparison, that uranium enriched in gas centrifuges will have little or no $^{232}U$ contamination. As a consequence of this process, all items containing HEU produced in gaseous diffusion plants will emit gamma rays from the $^{228}Th$

decay chain, of these, the 2614 keV gamma ray will be the most useful, since it is very penetrating, still detectable, for example, through 3 cm. of uranium metal. This provides an essential signature for high enriched uranium. It should be noted that while these gamma rays are also emitted from ordinary thorium, in this case additional gamma rays with energies of 911 and 968 keV are also emitted, so that the two materials can be distinguished one from the other. Just as in the example of $^{233}U$, if the initial concentration of $^{232}U$ is known, the age of the item can be determined from the $^{228}Th$ concentration, and conversely, if the age is known the original $^{232}U$ concentration can be determined.

**$UF_6$:** In the case of uranium in the form of uranium hexafluoride, an additional opportunity exists for determining the elapsed time that the material has existed as a solid (and probably also in the liquid phase.) High enriched uranium contains, typically, about 1 per cent $^{234}U$. This isotope is responsible for practically all of the production of neutrons from the $^{19}F(\alpha,n)^{22}Na$ reaction, with a yield of 580 n/sec per gram of $^{234}U$. This reaction thus constitutes a source of the isotope $^{22}Na$ (2.609 yr.), which will grow in at a uniform rate, eventually reaching secular equilibrium with the rate of production. The sodium atoms produced will lodge in the solid uranium hexafluoride matrix, they will remain behind if the material is transferred in the vapor phase, and will probably be entrained as NaF molecules when the material is transferred as a liquid. These assumptions can readily be verified by experiments on existing samples whose history is known.

At secular equilibrium in $UF_6$ containing HEU (1 % $^{234}U$) the $^{22}Na$ will decay at a rate of about 20 events/$cm^3$-s. Ordinarily the gamma rays from a source of this strength would be very difficult to measure in the presence of the strong background of gamma rays from the uranium isotopes. The decay of $^{22}Na$, however, takes place through the emission of a positron which then annihilates with an electron, producing two 511 keV gamma rays emitted in opposite directions. In addition, this process is accompanied by the emission of a 1274 keV gamma ray from the $^{22}Ne$ daughter nucleus. Thus each event is characterized by the emission of three gamma rays, two of which are directionally correlated. The detection of all three of these gamma rays in coincidence provides the possibility to obtain a very high level of discrimination against the background of individual gamma rays from the uranium isotopes, and at the same time, acquire reasonable statistical precision on the determination of the $^{22}Na$ concentration.

As an example we consider the measurement of the $^{22}Na$ concentration in a 1S cylinder (1.5 in. diam.) of $UF_6$. The experimental arrangement is shown in Fig. 3. The mean free path of a 511 keV gamma ray in $UF_6$ is 6 mm., so that most of the gamma rays detected will originate in the outer 1 cm. of the material. The cylinder is surrounded by a symmetrical arrangement of four 3 in. x 3 in. NaI gamma-ray detectors; a valid detection event consists of a 5ll-5ll keV coincidence between two oppositely situated detectors coincident with the detection of a 1274 keV gamma ray in any of the four detectors. For $^{22}Na$ in secular equilibrium, the counting rate for such events will be about 10/sec, so that a measurement with satisfactory statistical precision can be performed in 10 or 15 minutes.

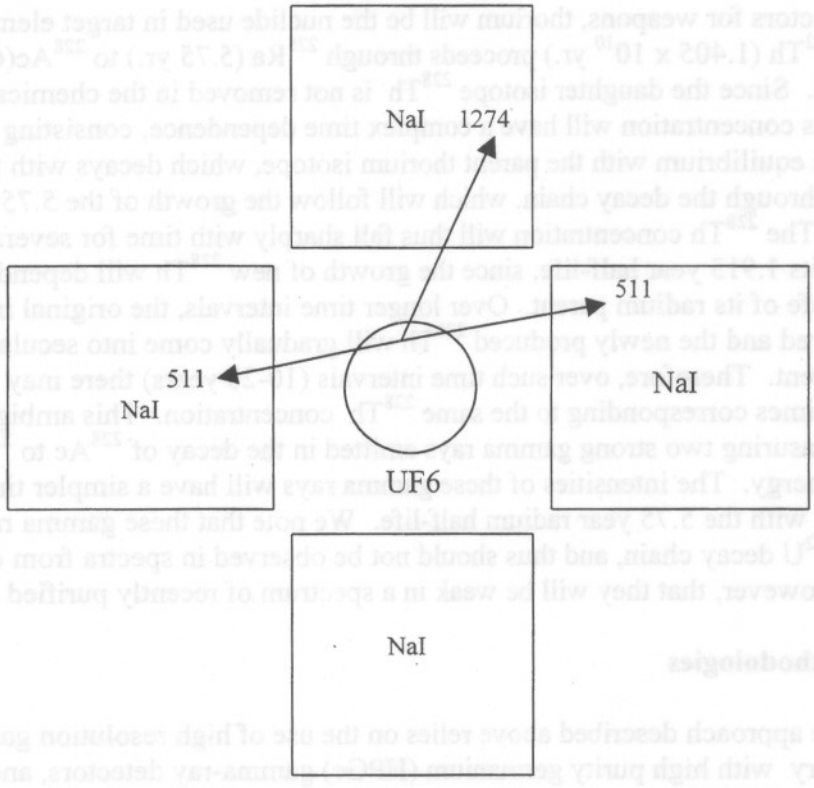


Figure 3. Triple coincidence arrangement for detecting $^{22}Na$ in $UF_6$.

**Neptunium**

**$^{237}$Np:** The isotope $^{237}Np$ ($2.14 \times 10^6$ yr.) decays to the relatively short-lived $^{233}Pa$ (26.97 d.), which in turn decays to $^{233}U$(159,200 yr.). For elapsed times up to the order of a year, a measurement of the gamma rays associated with these decays provides a measure of the age in situ of the neptunium sample. For longer times, the protoactinium activity will be in equilibrium with the neptunium, and the best measure of the elapsed time will be the growth of the $^{233}U$ in the item. Because of the long half-life of $^{233}U$, however, its activity will be weak in comparison with that of the parent isotopes, and hence, difficult to determine by means of gamma-ray spectrometry. A preferable alternative approach, since $^{233}U$ undergoes fission by thermal neutrons, may be chemical separation and fission track analysis (see below).

**Thorium**

**$^{232}$Th:** While thorium, as a common source material, does not rank in importance with the fissile materials, there still may be instances in which it would be useful to have information on its provenance. The thorium fuel cycle may be adopted as a source of electrical energy by one or

more countries, in which case the fissile isotope $^{233}U$ will engender the same proliferation concerns as plutonium in the uranium-based fuel cycle. In the case of clandestine production of $^{233}U$ in reactors for weapons, thorium will be the nuclide used in target elements. The decay chain of $^{232}Th$ ($1.405 \times 10^{10}$ yr.) proceeds through $^{228}Ra$ (5.75 yr.) to $^{228}Ac$(6.15 hr.) to $^{228Th}$ (1.913 yr.). Since the daughter isotope $^{228}Th$ is not removed in the chemical purification of the thorium, its concentration will have a complex time dependence, consisting of the original quantity in equilibrium with the parent thorium isotope, which decays with time, and that newly produced through the decay chain, which will follow the growth of the 5.75-year radium daughter. The $^{228}Th$ concentration will thus fall sharply with time for several years, closely following its 1.913 year half-life, since the growth of new $^{228}Th$ will depend on the longer 5.75 year half-life of its radium parent. Over longer time intervals, the original inventory of $^{228}Th$ will have decayed and the newly produced $^{228}Th$ will gradually come into secular equilibrium with its radium parent. Therefore, over such time intervals (10-20 years) there may be two different residence times corresponding to the same $^{228}Th$ concentration. This ambiguity can be resolved by also measuring two strong gamma rays emitted in the decay of $^{228}Ac$ to $^{228}Th$ with 911 and 968 keV energy. The intensities of these gamma rays will have a simpler time dependence, growing in with the 5.75 year radium half-life. We note that these gamma rays are not emitted from the $^{232}U$ decay chain, and thus should not be observed in spectra from either $^{236}Pu$ or HEU. We note, however, that they will be weak in a spectrum of recently purified thorium.

**Other Methodologies**

The approach described above relies on the use of high resolution gamma-ray spectrometry with high purity germanium (HPGe) gamma-ray detectors, and is suitable for macroscopic (1-1000g) samples of the materials measured. It has the advantages of equipment portability, rapid turnaround, and non-destructive measurements on the items in question. It is worthwhile also to consider other methodologies which may be applicable in other situations.

**Crystal Diffraction:** In situations in which certain gamma rays must be measured in the presence of a very high background of other gamma rays, HPGe detectors may not be applicable, since there will be a very high background of compton events at the energies of interest. This may apply, for example, if it is desired to determine the intensities of certain gamma rays from isotopes in spent reactor fuel or dissolver solution. A possible alternative is the utilization of the Bragg reflection of the gamma rays of interest from a crystal, or suitable array of crystals. In this case the reflecting crystals function as very narrow "band pass filters," reflecting only gamma rays in a narrow energy region around the gamma ray of interest, and at the same time, accepting only gamma rays in a narrow range of incident angles. This approach appears to be feasible in assaying the remaining concentration of $^{235}U$ in spent research reactor fuel elements.

**Compton Suppression HPGe Well Counter:** The measurement of the gamma rays from small samples of radionuclides is usually limited by the ambient gamma-ray background and the continuum from compton scattering events in the detector. An approach to this problem has been followed at Brookhaven[4] with the use of a HPGe well counter situated in a sodium iodide (NaI) anticoincidence shield. The HPGe detector has a volume of about 125 $cm^3$; the central well is 1 cm in diameter. When the NaI shield is employed to veto any events associated with the detection of a gamma ray in the shield, which can arise either from ambient background or

from the compton scattering of a gamma ray from the inner, well counter, background is suppressed by more than an order of magnitude. For $^{235}U$, the minimum detectable quantity is 50 nanograms.

**Fission Track Detection and ICP Mass Spectrometry:** Ultra-sensitive technologies for detecting plutonium and other nuclides have been developed at Brookhaven. These include fission track analysis[5], and more recently, the use of an inductively coupled mass spectrometer[6]. Each of these approaches possesses a detection sensitivity of 1-2 femtograms ($10^{-15}$ g) for $^{239}Pu$.

## CONCLUSIONS

High resolution gamma-ray spectrometry provides a powerful and practical technique for determining the age, and in some instances, the history of most materials of interest in the nuclear safeguards, arms control, and nonproliferation areas. Ultra-sensitive techniques also exist for investigating extremely small samples of these nuclides.

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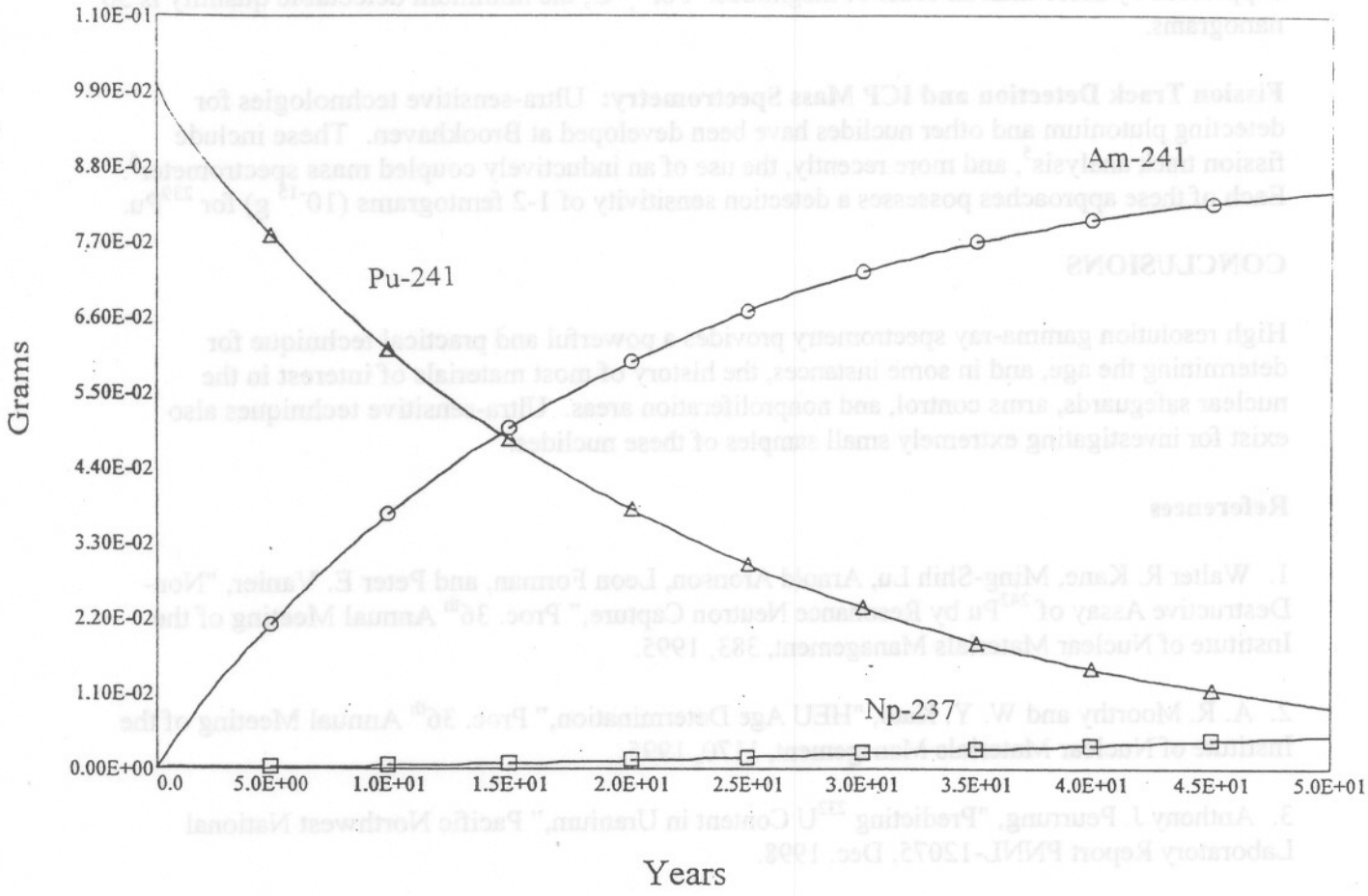


Fig. 1 Growth of Am-241 and Np.237 from Pu-241

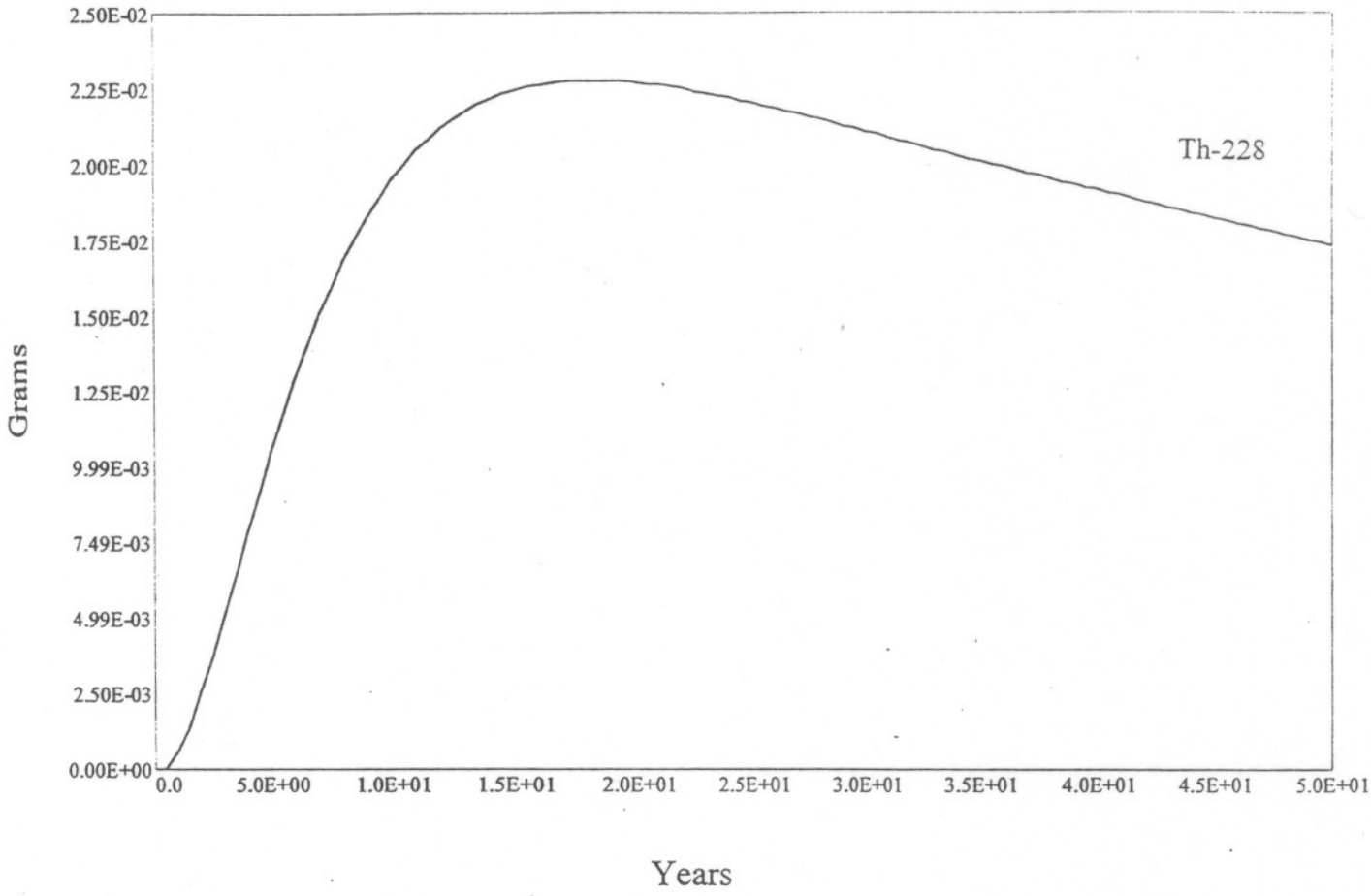


Fig. 2. Growth of Th-228 from Pu-236