UCRL 149
cy 3/D
G-1

UNCLASSIFIED

RESTRICTED

UNIVERSITY OF CALIFORNIA

Radiation Laboratory

FOR REFERENCE

NOT TO BE TAKEN FROM THIS ROOM

BERKELEY, CALIFORNIA

DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

UNIVERSITY OF CALIFORNIA
RADIATION LABORATORY

Cover Sheet
Do not remove

INDEX NO. UCRL-149
This document contains 39 pages
and 2 plates of figures.
This is copy 3 of 5. Series D

Issued to: Inf. Div.

UNCLASSIFIED

RESTRICTED

Classification

Each person who received this document must sign the cover sheet in the space below.

Route to	Noted by	Date	Route to	Noted by	Date

UNCLASSIFIED

UCRL-149

RESTRICTED

UNIVERSITY OF CALIFORNIA

Radiation Laboratory

Contract No. W-7405-eng-48

Classification changed to UNCLASSIFIED
by authority of R K Wakerling
on 4-14-65 B Forhoff
Date Person making change

SOME NUCLEAR AND CHEMICAL PROPERTIES OF AMERICIUM AND CURIUM

S. G. Thompson

July 15, 1948

Berkeley, California

UNCLASSIFIED

SOME NUCLEAR AND CHEMICAL PROPERTIES OF AMERICIUM AND CURIUM

RESTRICTED

S. G. Thompson

Radiation Laboratory, University of California
Berkeley, California

Abstract

Investigation of the chemical properties of elements 95 (americium, Am) and 96 (curium, Cm) by means of tracer techniques has led to the following conclusions. In aqueous solutions, both elements exist predominantly in the tripositive oxidation state and exhibit a high degree of similarity to the tripositive rare earth elements, particularly those in the range of atomic numbers 60-64. (By taking advantage of small differences in chemical properties, two methods for the separation of americium and curium from the rare earth elements have been devised.) Evidence for the oxidation and reduction of Am(III) is obtained only through the use of the most powerful oxidizing and reducing agents and even these are ineffective in the case of Cm(III). In general, the results of these studies support the view that americium and curium are members of an "actinide series" of elements related to actinium in the same sense that the rare earth elements are related to lanthanum.

Determination of the specific activity of Am^{241} which had been bombarded for a long period of time with neutrons in a Hanford pile showed that not more than 11% of other americium isotopes had been produced. The specific activity determination along with other considerations suggested that about 8% by weight of the long lived isomer of Am^{242} was present in

this material. The specific activity of unbombarded americium, determined at the same time for comparison, gave a value of 474 years for the half life of Am^{241}.

An isotope of highest known mass number, namely Cm^{243}, has been discovered as the result of the bombardment of Am^{241} with 40 Mev helium ions. This isotope decays by alpha emission with a half life estimated by yield considerations to be of the order of ten years. The energy of its alpha particles is 5.78 Mev as determined by differential pulse analyses.

SOME NUCLEAR AND CHEMICAL PROPERTIES OF AMERICIUM AND CURIUM

S. G. Thompson

Radiation Laboratory, University of California
Berkeley, California

Introduction

The search for transuranium elements has resulted in the discovery of four elements, neptunium, plutonium, americium and curium[1]. These discoveries, particularly that of plutonium, were not only of considerable scientific interest but they were of very great practical importance and as such have had a very great effect on the whole of science. It was logical, therefore, to continue the search for transuranium elements - that is, to search for elements 97 and 98.

The search for transcurium elements was begun in 1945 by S. G. Thompson, B. B. Cunningham, A. Ghiorso and G. T. Seaborg. The experimental difficulties associated with this problem were soon found to be formidable even though the primary approaches which could be taken were obvious and straightforward. Nevertheless, the efforts to solve this problem, while unsuccessful, did result in the accumulation of some information concerning the chemical properties of americium and curium and in the determination of some of the nuclear properties of the heaviest isotopes. Some of the results of this work will be included here.

In introducing the subject of the chemistry of americium and curium it seems worthwhile to begin with the discovery of these elements. The discovery of americium[2] and

curium[3] was aided by the hypothesis that these elements are members of an "actinide series" in which the trivalent oxidation states are chemically similar to the trivalent rare earth elements. According to this hypothesis, the relation of actinium to the actinide series is somewhat analogous to that of lanthanum and the succeeding fourteen rare earth elements[4]. Thus, for illustration the first 5f electron might appear in thorium, just as the first 4f electron appears in cerium. This, however, is not required by the hypothesis; the essential point is that curium should possess seven 5f electrons as gadolinium possesses seven 4f electrons. Thus, as atomic number increases beyond actinium it is not necessary that the added electrons always enter the 5f shell; differences between the energies of 5f and 6d electrons in the early members of the series might be small. The added electrons might go into 6d orbits, or the structure might vary depending on the compound. However, the tendency to attain the very stable $5f^7$ configuration should be increasingly evident as the seventh member of the series (starting with thorium) is approached and electrons should be in lower energy states when they enter the 5f shell as this configuration is approached. Thus, curium, the seventh member of the series, should possess a stable $5f^7$ configuration in analogy to gadolinium, the seventh member of the rare earth series with its $4f^7$ structure. If this hypothesis is assumed to be correct, americium and curium should be predominantly trivalent in aqueous solutions. Both elements

were discovered in the rare earth fractions from the bombardments in which they were produced.

The work of Seaborg and co-workers in connection with the discovery of americium and curium was sufficient to show that these two new elements were, in fact, markedly similar to the rare earths[5]. These investigations, as well as those which followed, showed that the similarity exists both in the properties of the (III) state and in the stability of this oxidation state.

These investigations of the properties of americium and curium were continued, with one very important objective in mind--that of finding methods for the separation of americium and curium from each other and from the rare earth elements. Such investigations should lead not only to a better understanding of the chemistry of the actinide elements and the relationship of this series to the lanthanide or rare earth series but also should provide methods of separation, particularly rapid ones which could be applied to the study of the heavy isotopes and aid the determination of their nuclear properties. Furthermore, as mentioned before, the results of such investigations were important in the search for transcurium elements which depended on them and proceeded hand in hand with them.

It should be clear that a major part of this work depended on the use of tracer methods, the preparation of samples for alpha counting, and on the instrumentation which is common to the measurement of radioactivity. The reliability of the tracer method in establishing many of the

chemical properties had to be considered. The validity of this method, however, is hardly to be doubted in view of the success which was obtained in its application to the chemistry of plutonium. The tracer techniques in the cases to be mentioned here are those used for alpha emitters, or rather mixtures of alpha emitters as was always the case when comparing the properties of americium and curium in a single experiment; the alpha emitters Am^{241} and Cm^{242} were the only isotopes used for the tracer studies of these elements.

Continuation of the tracer investigations, some of which will be mentioned here, revealed several methods by which americium and curium could be separated from each other and from the rare earths. These methods for separating the (III) states were, however, with one exception, methods of the type which were used for the separation of the individual rare earths; in fact, americium(III) and curium(III) nearly always fell within the rare earth group as a whole and they resembled most closely the rare earths of atomic numbers 60 to 64[5]. This relationship is clearly shown in adsorption-elution studies with commercial resins such as Dowex 50 cation exchange resin. Other tracer experiments indicated that americium possesses oxidation states both higher and lower than III. There were also some experiments comparing the distribution ratios of americium and the rare earths between aqueous and organic solvent phases. Other experiments revealed differences between americium(III) or curium(III) and rare earths in fluoride solutions in which partial precipita-

tion of rare earths was made. Accurate control of the fluoride concentration was generally accomplished by the addition of fluosilicate.

The development of chemical procedures was only one of several factors of interest in the search for transcurium elements. Obviously, the properties of higher mass isotopes of americium were also important as stepping stones to higher elements. L. O. Morgan (thesis)[6] investigated two isomers of Am^{242}, which are characterized by their decay as follows:

$$(1)\quad Am^{242} \xrightarrow[16\ hr.]{\beta^-} Cm^{242}$$

$$(2)\quad Am^{242} \xrightarrow[\sim 600\ y.]{\beta^-} Cm^{242}$$

$$Am^{242} \xrightarrow[\sim 3 \times 10^5\ y.]{} Np^{238}$$

These isomers of Am^{242} are produced whem Am^{241} is subjected to neutron bombardment thus:

$$Am^{241}(n,\gamma)\ Am^{242}$$

The half lives based on several assumptions were estimated by Morgan[6]. As the long lived isomer of Am^{242} should be a good starting material for the production of other high mass isotopes, it was of interest to measure how much of it had been formed in americium which had been subjected to intensive neutron bombardment. An upper limit for the amount was obtained by a measurement of the specific activity of americium that had been subjected to a long bombardment with neutrons in a Hanford pile. The details of this work are discussed in Section II.

Another isotope of interest for similar reasons is a curium isotope which decays by the emission of alpha particles of energy 5.78 Mev. This isotope has been assigned tentatively as Am^{243}. The specific activity of curium produced by pile bombardment by the reaction $Am^{241}(n,\gamma)Cm^{242}$ has been measured by L. B. Werner[7]. This work, however, did not show that curium isotopes other than Cm^{242} were present. Likewise, Chiorso[8], by examination of the alpha radiations of this same curium in a differential pulse analyzer, was not able to detect alpha disintegrations due to anything but Cm^{242}. Finally, R. A. James[9] failed to detect in this same curium any Geiger radiations other than those arising from Cm^{242}. It appeared that there might be two possibilities for the decay of Cm^{243}. It might decay either by orbital electron capture or more probably by the emission of alpha particles. It should also be produced directly by the bombardment of Am^{241} with 40 Mev He^{++} in the 60-inch Berkeley cyclotron thus:

$$Am^{241}(\alpha,pn)Cm^{243}.$$

If Cm^{243} were an alpha emitter, it might be possible to detect it in the presence of Cm^{242}, which would be produced along with it if the alpha activities were examined in a sufficiently sensitive alpha pulse analyzer. This method was used successfully after extensive chemical separations in the detection of this new isotope and the details of this work are discussed in Section III.

General Experimental Methods

The tracer experiments on the chemistry of americium and curium generally involved the use of a mixture of Am^{241} and Cm^{242} tracers with approximately equal amounts of alpha activity from each isotope. It was usually convenient to perform an experiment with a solution containing a few thousand disintegrations per minute of each activity. The ratio of the two alpha activities at the beginning of the experiment and at the end in the various fractions resulting from chemical separations was usually determined by means of a multichannel pulse analyzer.[10] With this instrument a thin sample is placed in an ionization chamber in which the total ionization of an alpha particle can be measured as a voltage pulse. Individual pulses are sorted electronically and recorded on a number of fast mechanical registers in such a way as to separate the individual alpha particle energies in a mixture of alpha emitters.

In order to obtain accurate measurements and good resolution in identification of alpha particles, it was necessary to prepare thin, uniformly spread samples. Such samples were usually prepared by precipitating a rare earth fluoride in a solution of the americium or curium tracer, and transferring the washed precipitate as a slurry onto a platinum disc or by evaporating similarly a solution of low solid content. The moisture was evaporated and the disc dried by using an infrared heat lamp. The plates were always ignited in the flame of a burner or by means of an induction heater to remove the last traces of moisture or other volatile

material. In order to facilitate the preparation of thin samples it was common to employ a semi-micro technique where solution volumes of the order of 1 ml and weights of carrier precipitate of the order of 20 to 100 micrograms were used. The precipitates were always separated by centrifugation, and lusteroid centrifuge cones were used for solutions containing HF.

The health hazard associated with the handling of large amounts of alpha radioactivity was provided for by the use of a great many protective devices which need not be described in detail here. Examples of the more ordinary type of equipment were fume hoods, dust masks, rubber gloves, and dry boxes. Such equipment was a particular requirement in the case of bombardments of appreciable amounts of americium and in the measurement of the specific activity of americium. The tracer experiments usually did not require any special equipment. In the preparation of americium targets, special equipment was required to minimize the spread of activity in the cyclotron and the surroundings. The samples as solutions of americium nitrate were transferred to a grooved platinum dish of 0.1 cm^2 area. The water was removed under a heat lamp and the residue ignited to a black oxide of americium. The targets were then placed in a special box containing thin dural windows through which passed the 40 Mev helium ions from the 60-inch Berkeley cyclotron. The target assembly was usually arranged so that the position of the americium target could be adjusted in the particle beam so as to obtain the maximum intensity of bombardment. In some cases

the intensity of the bombardments were measured. After bombardment the targets were removed and the americium oxide dissolved in nitric acid. The chemical operation during the early stages were performed in a dry box.

The neutron irradiation of the americium sample was made in a uranium-graphite chain reacting pile at the Hanford Engineer Works. After bombardment, the container was opened in a hot laboratory behind about four inches of lead shielding. The slug was cut open, the sample dissolved in nitric acid and the primary chemical separations made by remote control inside this hot laboratory. The americium-curium separation was made by adsorption of the mixture on columns of Dowex 50 resin, followed by elution with ammonium citrate solution[11]. A series of such separations on columns varying from 10 to 50 cm in length finally gave an americium fraction which was free of activity arising from curium isotopes. The americium was then concentrated by the precipitation of an americium compound and chemical purification was performed on this material. The microchemical techniques were employed for these final stages of purification, weighings being made on a quartz fiber microbalance[12] after ignition of the americium to the oxide in a small tared platinum boat. Some pure americium which had not been subjected to neutron bombardment was carried through the same steps for comparison. The weighed samples were dissolved in nitric acid, the boat reweighed, the solution diluted to a known volume, and an aliquot evaporated on platinum. These fractions were then counted in a low geometry alpha counter, employing argon in

the ionization chamber. The geometry of the chamber had been accurately determined.

Discussion of Results

I. The Experiments on the Chemistry of Americium and Curium.

A. Use of Fluoride in the Separation of Americium and Curium from the Rare Earth Elements. Lanthanum (or rare earth) fluoride carriers for Am(III) and Cm(III) tracers have often been employed successfully in glass equipment when the time of contact with HF solutions is short. However, after overnight contact between glass and 6 M HF, it was found that CeF_3 failed to carry Am(III) and Cm(III) tracers completely. Further study showed similarly poor carrying of Am(III) and Cm(III) using "Lusteroid" or other plastic containers when H_2SiF_6 was added to precipitate the rare earth carrier. Other experiments led to the use of fluosilicate alone and an increase in the amount of rare earth carrier in order to give better separations of americium or curium from rare earths.

Using this procedure, americium and curium were separated effectively from yttrium, lanthanum, praseodymium, neodymium, element 61 and europium as well as from cerium by a separation factor of 10^8. The work of S. Petersen[13] has shown that the behavior of Ac(III) toward H_2SiF_6 is similar to that of Am(III). Thus the use of H_2SiF_6 provides a group separation of tripositive rare earth elements from Am(III) and Cm(III). While other methods provide more satisfactory separations from lanthanum or from single rare earth elements, these methods do not permit a sharp group separation.

The optimum procedure for the use of this fluosilicate method as determined by a large number of individual experiments in which conditions were studied is as follows. To a 5 M HNO_3 solution containing Am(III) and/or Cm(III) tracer, add (in the form of a concentrated solution) 5-10 mg Ce(III)/ml of the 5 M HNO_3 solution. Heat to 35-40°C and add 30% H_2SiF_6 solution slowly and with stirring over a period of 0.5 to 1 hour until the total volume is 1 2/3 times the volume of the original 5 M HNO_3 solution (i.e., a final H_2SiF_6 concentration of ca. 1 M). Digest at 35-40° for an additional 0.5 to 1 hour.

After application of this procedure followed by separation of the rare earth precipitate, the solution is usually found to contain about 70-85% of the americium and/or cerium and about 8-10% of the rare earths. Americium and curium may then be removed from solution by making the fluosilicate solution 5 M in HF, whereupon residual rare earths in the solution (0.5-1 mg/ml) precipitate as fluorides and carry ca. 97% of the remaining americium and curium. If necessary, Ce(III) carrier may be added (0.5 mg ce(III)/ml of fluosilicate solution) if the solution does not contain a sufficient concentration of rare earth elements to act as the carrier. If further separation of americium and curium from the rare earths is desired, additional fluosilicate cycles may be used. The rare earth fluoride precipitate (containing the americium and curium) is converted to hydroxide by agitation and digestion with hot concentrated KOH solution for several minutes. Following centrifugation,

the clear supernatant solution is withdrawn, more KOH solution is added, and the above treatment repeated. Finally, the hydroxide precipitate is separated, washed with water, dissolved in HNO_3, and the resulting solution is used in another fluosilicate cycle.

In a typical fluosilicate cycle, the completeness of precipitation of rare earth elements increases with increase in time of digestion but increased time also reduces the proportion of americium and curium remaining in the solution. This relationship is shown in Fig. 1. After digestion for two hours, about 75% of the americium and 4% of the cerium remains in solution. The rate of precipitation of both americium and rare earths increases with increase in temperature or decrease in the concentration of HNO_3. Decrease in the concentration of H_2SiF_6 leads to poorer separation of americium and curium from rare earths but the separation is not improved by making the H_2SiF_6 concentration greater than 1 M, and effective separation is favored by slow rate of addition of H_2SiF_6. La(III), Y(III) and Ce(III) are equally good carriers and the rare earth carrier precipitates serve to separate small amounts of Th(IV) and Pu(IV) rather completely. Precipitation of the rare earth fraction is inhibited by Zr(IV) but is not significantly influenced by the presence of Fe(III).

The experiments using fluosilicate solutions to separate actinide and lanthanide elements suggest that rare earth fluorides may be more insoluble than the fluorides of Am(III) and Cm(III) although the differences may not be very

large. It may also be true that complex fluorides of the type AmF_2^+ are involved in which a difference in the stability of actinides and lanthanides exists. It should be emphasized that the fluoride system is one of very few where significant differences between actinides and rare earths exists.

James[14] has extended this work by experiments showing that exactly the same sort of precipitation curve is obtained by controlled addition of dilute fluoride solutions as is obtained with fluosilicate in the separation of a mixture of element 61 and americium tracers using lanthanum as the rare earth carrier. In fact, the points on the curve in which the fraction of element 61 precipitated is plotted against the fraction of the americium precipitated are essentially identical for fluoride as compared with fluosilicate. James also found that similar separations could be made by using fluoboric acid. The conclusion appears to be justified that it is only the relative solubilities of the actinide and rare earth fluorides that are important in this separation. The use of fluosilicate is only to provide fluoride in the optimum concentration and in sufficient amounts by hydrolysis. It may be taken for granted that the strength of the fluoride bond is greater for rare earths than for actinides. It might also be expected that the greatest differences in properties between the two series would appear in reactions with a small negative ion such as fluoride.

B. <u>Attempted Oxidation of Am(III) and Cm(III) in Aqueous Media</u>. Demonstration of the existence of oxidation states

other than three for americium and curium is of interest not only in relation to possible methods of separation but also because of its importance in connection with the actinide hypothesis. Since americium and curium would be analogous to europium and gadolinium, respectively, americium would be expected to be more readily convertible to other oxidation states than curium. Because americium is preceded by actinide elements which exhibit oxidation states higher than are encountered among the corresponding rare earth elements, the probability of oxidation states higher than three should be greater for americium than for europium. Such speculations, however, should recognize the possibility of a marked trend toward stabilization of the (III) state.

These expectations are indeed borne out by the results of tracer experiments. There is evidence that Am(III) may be reduced in aqueous solutions and that a higher oxidation state exists, but these changes may be brought about only through the use of the most powerful oxidizing and reducing agents. Similar experiments involving Cm(III) provided no evidence whatever of either oxidation or reduction. These results provide strong evidence in support of the actinide hypothesis.

Attempts have been made to oxidize Am(III) and Cm(III) through the use of the strongest oxidizing agents under a variety of conditions. The best possibility seemed to involve the use of oxidizing agents such as peroxide and hypochlorite in basic solutions and several experiments employing these reagents have been performed. In basic solutions, however,

there are few if any carriers which may be used to distinguish between Am(III) or Cm(III) and their oxidation products. If the hydroxides of higher oxidation states are insoluble (as might be expected by analogy with neptunium and protactinium) these as well as the (III) state would most likely be carried by any insoluble hydroxide carrier. Thus the identification of higher oxidation states of americium or curium would probably require the use of a selective complexing agent which would exhibit stability in strongly basic media. The latter requirement is unlikely to be satisfied, particularly by organic complexing agents.

The first attempts involved the use of K_2CO_3 as the complexing agent and peroxide as the oxidizing agent. It was anticipated that an insoluble peroxide of Am($>$ III) might be produced and might coprecipitate with perceric hydroxide ($CeO_3 \cdot 2H_2O$) or thorium peroxide precipitated from the same medium. At the same time it was expected that Am(III) and the rare earth elements would remain complexed in the carbonate solution and consequently would not coprecipitate with the carrier unless oxidation occurred. Treatment with 5% H_2O_2 by weight in 20% K_2CO_3 solution over various periods of time at various temperatures gave complete precipitation of cerium as $CeO_3 \cdot H_2O$ or of thorium as thorium peroxide but these precipitates carried only a small fraction, usually less than 2% of the americium. Thus it appears that an oxidizing agent more powerful than alkaline peroxide is required to oxidize Am in solutions of K_2CO_3.

Evidence for the conversion of americium to oxidation states greater than III was obtained first by Cunningham[15] in ultramicrochemical experiments. He observed that a darkening of the color of $Am(OH)_3$ in alkaline suspension occurred when it was mixed with NaOCl or peroxide. Cunningham also prepared some americium oxide ignited in air at 800°C which x-ray analysis showed to be AmO_2. The use of hypochlorite to oxidize americium in K_2CO_3 solutions has been investigated by Werner and I. Perlman[16]. Their first experiments involved the use of weighable amounts of americium. They found under these circumstances that americium was oxidized presumably to the +5 state, and that its solubility in the K_2CO_3 solutions was low. The compound which precipitates appears to be $KAmO_3$. Attempts to carry tracer amounts of americium from such solutions, however, has met with slight success. Plutonium carrier gave erratic results and there are only a few elements which are able to precipitate from concentrated K_2CO_3 solutions under such conditions.

Attempts to convert Am(III) to higher oxidation states in acid solutions has been subject to much investigation. A wide variety of the most powerful oxidizing agents and solution conditions failed to give evidence for such oxidation with one exception. This was the case of $KBrO_3$ used in concentrated nitric acid solutions. Ceric iodate precipitated from such solutions carried a high fraction of americium but the results were erratic and might be explained in other ways.

C. <u>Oxidation of Am(III) and Cm(III) by Fusion with</u>

Sodium Nitrate. Rare earth separations which depend upon the production of higher oxidation states of certain rare earth elements other than cerium (e.g., praseodymium and terbium) have been reported in the literature. One such method[17] involved oxidation by fusion with $NaNO_3$ followed by dissolution in an acetate-buffered solution, which leaves the higher oxides undissolved. Thus a reasonably good separation of lanthanum from praseodymium may be accomplished. According to the actinide hypothesis, one might expect americium to follow praseodymium while curium would follow lanthanum in such a separation. A separation of americium from curium was obtained by this method. The undissolved oxide fraction contained a higher proportion of americium than of curium, while the aqueous leachings contained a higher proportion of curium than of americium. The change in the americium/curium ratio, however, was not great enough to provide a satisfactory separation of the two elements.

In three separate experiments, each using a different rare earth carrier, the maximum change in the americium/curium ratio was obtained using terbium as carrier. Initially, the americium/curium tracer ratio was 1.14. After fusion for 1.5 hours at 460°C followed by leaching, the ratio in the TbO_2 was 2.0. With PrO_2 and CeO_2, the ratios were 1.5 and 1.3 respectively. In all of these experiments, lanthanum equivalent to the oxidizable rare earth carrier was present.

D. Reduction of Am(III) and Cm(III) in Aqueous Media.

1. Use of Sodium Amalgam. Morgan[18] had found that

Am(III) is not reduced by Zn amalgam. In subsequent efforts to reduce Am(III), sodium amalgam was used as the reducing agent in a method similar to that employed by J. K. Marsh[19] in the separation of certain of the rare earth elements. A sulfuric acid solution containing La(III), Sm(III) and Eu(III) together with Am(III) and Cm(III) tracers was shaken with sodium amalgam. The resulting precipitate of $EuSO_4$ and $SmSO_4$ was separated and leached rapidly with cold dilute nitric acid. (According to Marsh, this treatment dissolves $SmSO_4$ and leaves most of the $EuSO_4$ undissolved.) About 40% of the americium tracer and 20% of the curium tracer were found in the soluble fraction. The increase in the americium/curium ratio in the samarium fraction suggests that Am(III) may have been partially reduced to Am(II).

2. Use of Barium. The results obtained by the use of sodium amalgam suggested other experiments which might not only confirm the existence of Am(II) but also provide a method for the separation of americium and curium based on differences in oxidation state. In the separation of americium and curium following reduction with sodium amalgam, the carrying of Am(II) by the mixture of $EuSO_4$ and $SmSO_4$ might not be particularly selective in comparison with the carrying of Am(III). A better separation might be accomplished by the use of a more selective carrier such as barium chloride. Barium metal and concentrated HCl containing americium and curium tracers were employed and a precipitate of $BaCl_2$ formed as the barium dissolved slowly over a period of about

five minutes. The americium/curium ratio in the original HCl solution was 0.9 while that found in the $BaCl_2$ precipitate was 1.4. That such enrichment occurs, however, is not proof that reduction of americium occurred. Recent experiments by K. Street using concentrated HCl for elution of americium and curium from columns of Dowex 50 resin indicate that in concentrated HCl significant differences exist in the properties of the two elements in their (III) states.

E. Separations Using Cation Exchange Resins. A method for the separation of rare earth elements by adsorption on an Amberlite IR-1 resin followed by selective elution with ammonium citrate has been devised by W. Cohn and his associates[20]. Further development of the method by Cohn, F. H. Spedding[21] and their co-workers has led to the efficient separation of many of the rare earth elements by this method. In view of the similarity between americium and the rare earth elements in other systems, it was obviously worthwhile to study their behavior in the IR-1-citrate system from the standpoint of possible separations.

Preliminary experiments employed a 12-inch column of 1 cm I. D. packed with 40-60 mesh IR-1 resin. The resin was washed with 0.1 M HCl and the excess acid was removed by washing with water. A mixture of Am(III) and, for example, Y(III) tracers was adsorbed on the column from a 0.1 M HCl solution. After displacement of the residual acid with water, 5% ammonium citrate solution (pH = 2.75) was passed through the column and the elutrient was collected in a number of small fractions. These were analyzed separately for both americium and yttrium activities.

From this and similar experiments involving comparison of americium with other elements, the decreasing order of rate of elution was found to be: Y > 61 > Am > Ce > La. Americium falls between element 61 and element 58 (cerium) and was more similar to element 61 in this system.

Other experiments designed to separate americium from several of the rare earth elements employed a 6 foot column. Some separation was accomplished, and rare earth elements in the region of element 61 were separated by a factor of approximately 2.

Peterson's work[22] on the adsorption and elution of actinium has shown that it is more slowly eluted from IR-1 with citrate than is lanthanum. Thus the decreasing order of rate of elution of actinium in comparison with members of the actinide and lanthanide series elements is as follows: Y > 61 > Am > Ce > La > Ac. Hence it appears that the behavior of the elements of the actinide series (with respect to adsorption and elution) is similar to that of the rare earths. Differences between individual members of each series must be of about the same magnitude and in the same direction with increase in atomic number.

The difference in behavior of actinide and lanthanide elements in fluosilicate solutions suggested an experiment in which a mixture of Am(III) and La(III) were adsorbed on IR-1 resin and were eluted with fluosilicate. In this case the two were removed from the column at approximately the same rate.

Since this work was done improved methods have resulted

from the use of Dowex 50 resin, as shown by the results of E. R. Tompkins, Cunningham, Street, James and Thompson[23,24,25]. However, the order of elution and relative positions of actinide and lanthanide elements are the same as those given above.

F. Solvent Extraction Methods for the Separation of Americium and Curium from Each Other and from Other Elements. Separations based upon extraction of inorganic compounds from aqueous solutions into organic solvents are known to be advantageous from the standpoint of both rate and efficiency of separation. Such methods may depend upon the formation of a complex between the ion to be extracted and molecules of the organic solvent into which the complexed component of the aqueous solution is extracted. Efficient separations of other elements have been made through the use of extraction columns employing countercurrent flow.

In the earliest work on the separation of americium and curium by solvent extraction, aqueous solutions containing hydroxamic acids (general formula, $R - \overset{O}{\overset{\|}{C}} - NHOH$) were used. At Iowa State College, F. J. Wolters and H. D. Brown[26] have used these compounds successfully in connection with the extraction of other actinide elements into benzene. On the basis of Brown's work and in view of the actinide hypothesis, it was anticipated that Am(III) and Cm(III) would be extracted similarly. Experimentally, such was found to be the case and a fairly good separation of Am(III) from La(III) was demonstrated. However, rare earth elements (particularly those in the region of element 61) were not separated to any

significant extent and development of the method was temporarily abandoned.

The extraction of americium into $CHCl_3$ in comparison with actinium and the rare earth elements has been investigated in experiments in which benzohydroxamic acid was used. The procedure was as follows: To an acid solution containing the tracer activities to be separated, potassium benzohydroxamate (5 mg/ml) was added and the pH was then adjusted to 5-6 by addition of sodium acetate. The mixture was shaken and allowed to stand for about two hours at room temperature. The aqueous solution was then shaken with an equal volume of chloroform, the two liquid phases were separated and each was analyzed for the activities in question. Although most of the Am(III) was extracted into the $CHCl_3$, the results varied considerably. These variations may have been due to failure to duplicate conditions exactly and to establish optimum conditions for this extraction. As judged from separate experiments which were not necessarily conducted under identical conditions, the approximate extent of extraction was found to be as follows: Am(75%), element 61 (65%), Y (50%), La(40%), Ac(8%). The experimental values for element 61, yttrium, lanthanum and actinium were converted to values corresponding to 75% extraction of americium.

Although less satisfactory than certain other methods, the foregoing experiments show that americium may be separated effectively from some elements and serve to demonstrate again the similarity between the lanthanide and actinide elements.

II. The Isotope Am^{242}

By a comparison of the specific activity of americium which had been subjected to neutron bombardment with that of unbombarded Am^{241}, it seemed possible that the amount of longer lived isotopes in the bombarded material could be determined. If an isotope such as Am^{242} were present in sufficient amounts, the bombardment of such material with helium ions might produce detectable amounts of transcurium isotopes. The following experiments were done with this objective in mind.

A small sample of pure Am^{241} was subjected to a long bombardment with neutrons in a Hanford pile. Complete separation of curium radioactivities from the americium was made by adsorption on Dowex 50 resin and elution with ammonium citrate solution and by repeating these steps a number of times. The americium was precipitated as AmF_3, dried, and ignited in a platinum dish. The resulting black americium oxide was dissolved in nitric acid and evaporated to dryness. The residue was dissolved in water and further purified. Some pure Am^{241} which had not been bombarded with neutrons was now obtained in a solution of the same characteristics as above. The following primary steps of purification were carried out on the two solutions:

(1) By passage of H_2S into the solutions all sulfide insoluble impurities were separated.

(2) Precipitation of $Am(OH)_3$ was performed by the addition of NH_3 gas.

(3) Removal of Fe(III) was accomplished by extraction with ether from a solution of the Am(III) in 6 N HCl.

(4) $Am(OH)_3$ was then precipitated with NH_3 gas and was dissolved in dilute HNO_3.

Each solution was divided into three parts, the first being used for spectrographic analysis to determine purity, the second being used for specific activity determination, and the third part held for further purification if necessary.

The following main operations were performed on the two americium samples in order to determine the specific activities:

(1) Part of the dilute nitric acid solution of Am(III) was transferred to a weighed Pt boat, the water was removed by evaporation under a heat lamp, and the precipitate was ignited to the black oxide of americium.

(2) The boat and sample were weighed on a calibrated quartz fiber microbalance.

(3) The americium oxide was then dissolved from the boat by heating with several portions of dilute nitric acid. The solutions and washings were transferred to a volumetric flask and made to volume with water. After mixing known aliquots were taken for counting.

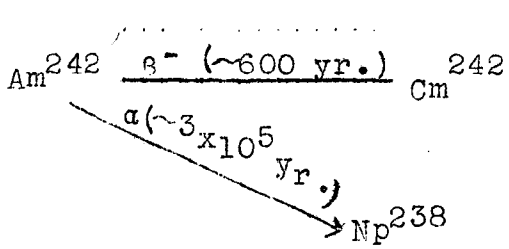
(4) The aliquot was evaporated on a platinum plate, ignited and counted in a low geometry counter. The geometry factor had been accurately determined

as 1677 to give alpha counts per minute at 52% geometry.

Several small samples of both the neutron bombarded americium and the unbombarded americium were carried through essentially the same steps as mentioned above. In some cases the purification was more rigorous than described above and in some cases there was a final precipitation of the americium as fluoride. In such cases a slurry of the AmF_3 was transferred to the platinum weighing boat.

In only one case was the neutron bombarded americium very pure as shown by the spectrographic analyses, and this sample was reported as containing about 3% of aluminum as the only detectable impurity. The unbombarded americium contained no detectable impurities. It should be noted that 3% of aluminum would account for about 6% of the weight of the ignited oxide.

There is another correction to be made in the measurement of the specific activity of the neutron bombarded americium which is due to the growth of Cm^{242} and its alpha radioactivity. As mentioned previously the long lived isomer of Am^{242} decays as follows:



Even though the americium had once been completely free of Cm^{242} alpha a ctivity, differential pulse analysis showed, at the time of specific activity determination, that 1.2%

of the alpha disintegrations in the sample were due to Cm^{242}.

Neglecting the presence of the aluminum impurity which is believed to be doubtful and correcting for the presence of Cm^{242} the specific activities of the two americium samples were as follows:

	Specific Activity (counts per minute per microgram at 52% geometry)
Neutron bombarded americium	3.30×10^6 *
Unbombarded americium	3.61×10^6

The presence of aluminum in one of the samples and not in the other is difficult to understand since the same steps of purification were performed on both. The aluminum content of the bombarded sample eluted from Dowex 50 resin with ammonium citrate, and precipitated as fluoride should be very low since aluminum should not follow either step. Therefore it seems more reasonable to assume that the aluminum was introduced in some way during the analysis or preparation for analysis, when the two samples were not handled in the same way.

The ratio of the specific activities is as follows:

$$\frac{\text{Specific activity of bombarded Am}}{\text{Specific activity of unbombarded Am}} = 0.914$$

The limits of error in the spectrographic determination of aluminum content of the small sample submitted for analysis is about 50%. Strictly speaking, therefore, as much as 9% of the weight of the AmO_2 could be due to Al_2O_3 and within

---

* Average of four determinations of 0.5% maximum difference - different samples, two weighings.

the limits of the other errors of the experiment (~2%) it is possible that the change in specific activity was negligible. It is also possible to establish a maximum value of 11% for the change in specific activity, if we assume that all of the impurity was introduced at some time after the specific activity determination, and if, at the same time a maximum error of 2% is allowed. Nevertheless, for the reasons mentioned previously, it is believed that the most probable value for the actual change in specific activity of the americium is about 8%. The decrease is believed to be due to the presence of Am^{242} in the amount of 8% by weight which is produced by the following reaction:

$$Am^{241}\ (n,\gamma)\ Am^{242}\ \text{(long lived isomer)}$$

The maximum error of the experimental determination of the specific activity aside from error due to purity is about 2%. In calculating this maximum error, the following factors have been taken into account:

(1) Statistical fluctuations in counting (0.1%).

(2) Geometry of low geometry counter (0.5%).

(3) Calibration of quartz fibre microbalance (0.3%).

(4) Volumetric equipment (0.5%).

(5) Actual weighing (1.0%).

However, since the same equipment was used for both samples, most of these errors cancel out in calculation of the ratio and the main errors are those arising from errors in technique which are more difficult to evaluate.

From the specific activities of two chemically pure americium samples, it is not difficult to deduce that the

difference is due to the presence of Am^{242} in one and not the other. In bombarding Am^{241} with neutrons, the following possible reactions may occur:

(1) $Am^{241}(n,\gamma)\ Am^{242} \xrightarrow[16\ hr.]{\beta^-} Cm^{242}$

(2) $Am^{241}(n,\gamma)\ Am^{242}$ (long lived isomer)

(3) Am^{242} (long) $(n,\gamma)\ Am^{243}$

(4) $Am^{241}\ (n,2n)\ Am^{240}$

Although adjacent isotopes might emit alpha particles of range so near to those of Am^{241} that their presence would not be detectable in the chemically pure americium, an examination of the daughters in equilibrium with this americium fraction essentially rules out this possibility. Otherwise, the specific activity might be increased by the presence of one of these inactive isotopes and an erroneous value for the weight of isotopes other than Am^{241} might be obtained. The chemical separations of Cm from Am were made after the 17 hr. beta emitting Am^{242} had decayed, thus eliminating interference from this species. It is known that the long lived Am^{242} isomer is present in the americium, and that it decays both by alpha and beta emission. The daughter of the alpha decay is the well known beta emitting Np^{238} of 2.0 day half life. The alpha decay of Am^{243} and of Am^{240} would similarly give well known beta emitting daughters. Morgan (thesis) has examined these daughters, and found that they consist mainly of Np^{238} which is produced by the decay of Am^{242}. Morgan and Street[27] found further that at equilibrium the ratio of the number of beta disintegrations due to neptunium isotopes to that of the americium alpha disinte-

grations in the americium used above for specific activity was one part in 10^4. Therefore it may be calculated that less than .01% of the alpha disintegrations in the americium fraction are due to isotopes other than Am^{241} and the Am^{242} content of chemically pure americium should be calculable from the specific activity as compared with that of pure Am^{241}.

The value for the specific activity of Am^{241} given above allows a direct calculation of its half life and gives a value of 474 years. The value reported originally by Cunningham[28] is 510 $\pm$20 years. The two values, however, may approach agreement within the experimental error of the determination. Allowing a 2.5% maximum error for the value of 474 years gives an upper limit at 486 years, while Cunningham's lower limit should be 490 years. It might then appear that a half life of about 490 years is a better value than either of the others. Part of the differences might be accounted for by the assumptions made as to the composition of the ignited black oxide of americium. In all specific activity measurements made to date the assumption is made that its composition is AmO_2. It is likely, however, that this oxide is a mixture containing americium in at least two oxidation states and the composition could vary considerably depending on the conditions of ignition.

III. The Isotope Cm^{243}

The isotope Cm^{243} was found as a result of the bombardment of Am^{241} with 40 Mev helium ions. The total bombardment was about 1 microampere hour on a target of 0.1 cm^2 area.

The americium oxide was dissolved in nitric acid. The hydroxide was precipitated by the addition of NH_3 and was dissolved in 45% K_2CO_3. The americium was precipitated by the addition of NaOCl and by heating the solution to give the insoluble americium(V) compound which presumably is $KAmO_3$. Curium is not oxidized to a higher oxidation state and is not carried by this compound. The americium and curium remaining in the solution were then separated as hydroxides by the addition of concentrated KOH, and the above cycle was repeated. These two steps separated the americium from the curium by a factor of ~2000. Further separation of the americium from curium was made by adsorption of the mixture on a 15 cm column packed with Dowex 50 resin and elution with ammonium citrate solution. The fractions taken every 15 minutes were counted for alpha activity and the elution peaks for curium and americium were determined. Differential pulse analysis of the alpha radioactivities in the curium peak revealed that most of the activity was that of Cm^{242} of energy 6.08 Mev corresponding to a disintegration energy of 6.18 Mev. There was, however, a small percentage (~5%) of alpha radioactivity of energy 5.78 Mev as shown in Fig. 2.

That the isotope in question is a curium isotope is essentially proved by the fact that it was removed from the resin in the curium peak. It is, however, barely possible that element 97 could be removed in this same position. It is not difficult to deduce the mass assignment of such a curium isotope. The production of Cm^{243} should occur by both of the following mechanisms:

$Am^{241}(\alpha,2n)\ 97^{243} \xrightarrow{K\ capt.} Cm^{243}$

$Am^{241}(\alpha,pn)\ Cm^{243}$

According to James (thesis)[29], Cm^{240} decays by the emission of alpha particles of energy 6.26 Mev, and Cm^{241} probably decays by orbital electron capture. In the bombardment of Am^{241} with 40 Mev helium ions, the production of significant amounts of isotopes of mass number less than 240 is improbable. Of the two remaining possibilities in the curium isotopes, Cm^{243} and Cm^{244}, the Cm^{243} is the best possibility since the yield of reactions involving the emission of 2 or 3 particles from the compound nucleus as above are higher than those involving the emission of only one particle such as the α,p and α,n reactions. Strictly speaking, however, the possibility cannot be ruled out that the isotope discovered above is Cm^{244} or even the lesser possibility that it is an isotope of element 97. From a consideration of alpha particle energy as a function of mass numbers[30] for isotopes in the heavy region an alpha energy of about 5.8 Mev would be predicted for Cm^{243} and of course this is what was found above, although the irregularities are such that it is not out of the question that this energy would correspond to Cm^{244}.

It is possible to make an estimate of the half life of the Cm^{243} so assigned, from a consideration of the yields of nuclear reactions in the heavy region. In this region the sum of the cross sections for the α,2n and the α,pn reactions for bombardments of the type in question, is generally of the

same order of magnitude as the sum of the α,3n and α,p2n reactions and is generally of the order of .01 barn. Since there was about 5% as much alpha activity from Cm^{243} as from Cm^{242} and the number of atoms produced should be about the same, the half life of Cm^{243} should be 20 times as long as that of Cm^{242} or about eight years. Prediction of the half life from the extension of a modified J. Schintlmeister[31] plot for isotopes in the heavy region gives a value of about 10 years.

From these considerations, we believe it is reasonable to tentatively assign the new curium isotope to Cm^{243}.

Summary

Investigation of the chemical properties of elements 95 (americium, Am) and 96 (curium, Cm) by means of tracer techniques has led to the following conclusions. In aqueous solutions, both elements exist predominantly in the tripositive oxidation state and exhibit a high degree of similarity to the tripositive rare earth elements, particularly those in the range of atomic numbers 60-64. (By taking advantage of small differences in chemical properties, two methods for the separation of americium and curium from the rare earth elements have been devised.) Evidence for the oxidation and reduction of Am(III) is obtained only through the use of the most powerful oxidizing and reducing agents and even these are ineffective in the case of Cm(III). In general, the results of these studies support the view that americium and curium are members of an "actinide series"

of elements related to actinium in the same sense that the rare earth elements are related to lanthanum.

Determination of the specific activity of Am^{241} which had been bombarded for a long period of time with neutrons in a Hanford pile showed that not more than 11% of other americium isotopes had been produced. The specific activity determination along with other considerations suggested that about 8% by weight of the long lived isomer of Am^{242} was present in this material. The specific activity of unbombarded americium, determined at the same time for comparison, gave a value of 474 years for the half life of Am^{241}.

An isotope of highest known mass number, namely Cm^{243}, has been discovered as the result of the bombardment of Am^{241} with 40 Mev helium ions. This isotope decays by alpha emission with a half life estimated by yield considerations to be of the order of ten years. The energy of its alpha particles is 5.78 Mev as determined by differential pulse analyses.

Acknowledgement

The work described in this dissertation was performed under the direction of Professor G. T. Seaborg. Dr. B. B. Cunningham, Mr. Albert Ghiorso and Mr. H. H. Hopkins participated in many of the experiments. The health hazard associated with the handling of large amounts of radioactivity, particularly alpha radioactivity, was eliminated by the use of excellent protective equipment provided by Dr. Nelson Garden and his Health Chemistry group. We wish to thank Dr. Garden and the members of his group, particularly John

Gifford and Carroll Gordon who designed and constructed much of the equipment. We wish to thank Dr. John Conway for spectrographic analyses of the americium samples.

We wish also to thank Professor J. G. Hamilton, Mr. T. M. Putnam, Mr. B. Rossi for their cooperation in operating the 60-inch cyclotron, and the operating crew of the uranium graphite pile at the Hanford Engineer Works for their aid in the neutron irradiation of the americium sample. These researches were carried out under the auspices of the Manhattan District, Corps of Engineers, United States Army, and later under Contract No. W-7405-eng-48 with the Atomic Energy Commission in connection with the Radiation Laboratory, University of California.

References

1. Seaborg, G. T., American Scientist 36, 361 (1948).

2. Seaborg, G. T., R. A. James and L. O. Morgan, Plutonium Project Record 14B, No. 22.1, to be published.

3. Seaborg, G. T., R. A. James and A. Ghiorso, Plutonium Project Record, 14B, No. 22.2, to be published.

4. Seaborg, G. T., Chem. and Eng. News 23, 2190 (1945); Seaborg, G. T., Science 104, 379 (1946).

5. Thompson, S. G., L. O. Morgan, R. A. James, and I. Perlman, Plutonium Project Record, 14B, No. 19.1, to be published.

6. Morgan, L. O., thesis, reference 2.

7. Werner, L. B., and I. Perlman, unpublished work.

8. Ghiorso, A., private communication (1947).

9. James, R. A., private communication (1947).

10. Ghiorso, A., H. H. Jaffey, H. Robinson and B. Weissbourd, Plutonium Project Record 14B, No. 16.8 (1946), to be published.

11. Reference 5, pp. 19-22.

12. Kirk, P. L., R. Craig, R. O. Boyer and J. T. Gullberg, Anal. Chem. 19, 427 (1947).

13. Petersen, S., private communication (1945).

14. James, R. A., private communication (1948).

15. Cunningham, B. B., Plutonium Project Record 14B, No. 19.2, to be published.

16. Werner, L. B., and I. Perlman, unpublished work (1946).

17. Noyes, A. A., and W. C. Bray, "A System of Qualitative Analysis for the Rare Elements", The MacMillan Company, New York, 1927, pp. 215-218.

18. Reference 5, p. 16.

19. Marsh, J. K., J. Chem. Soc. 398 (1942); 531 (1943).

20. Cohn, W., et al, Plutonium Project work (June, 1945).

21. Spedding, F. H., et al, Plutonium Project work (May, 1945); J. Am. Chem. Soc. 69, 2777 (1947).

22. Petersen, S., Plutonium Project Record 14B, 19.3 (1946).

23. Tompkins, E. R., B. B. Cunningham and S. G. Thompson, unpublished work.

24. Street, K., and R. A. James, unpublished work.

25. Reference 5, pp. 18-22.

26. Wolters, F. J., and H. D. Brown, Plutonium Project work (June, 1945).

27. Street, K., private communication.

28. Cunningham, B. B., reference 14.

29. James, R. A., thesis, reference 3.

30. Ghiorso, A., and G. T. Seaborg, unpublished work (1948).

31. Schintlmeister, J., Oesterr. Chem. Ltg. 41, 315 (1938).

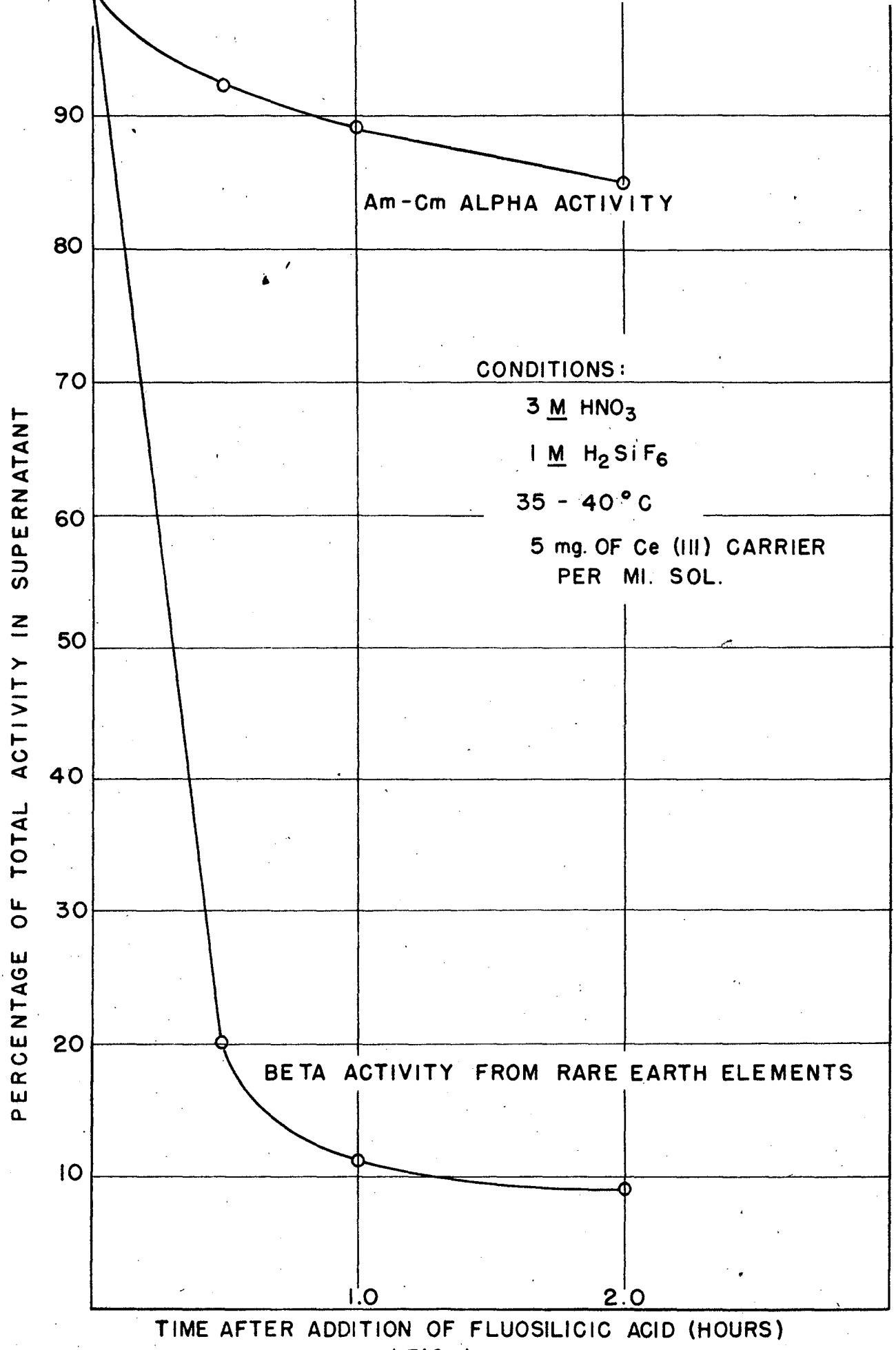


FIG. 1

COMPARISON OF PRECIPITATION OF Am, Cm, & RARE EARTH ELEMENTS AS A FUNCTION OF TIME FROM FLUOSILICATE SOLUTIONS USING CERIUM(III) CARRIER.

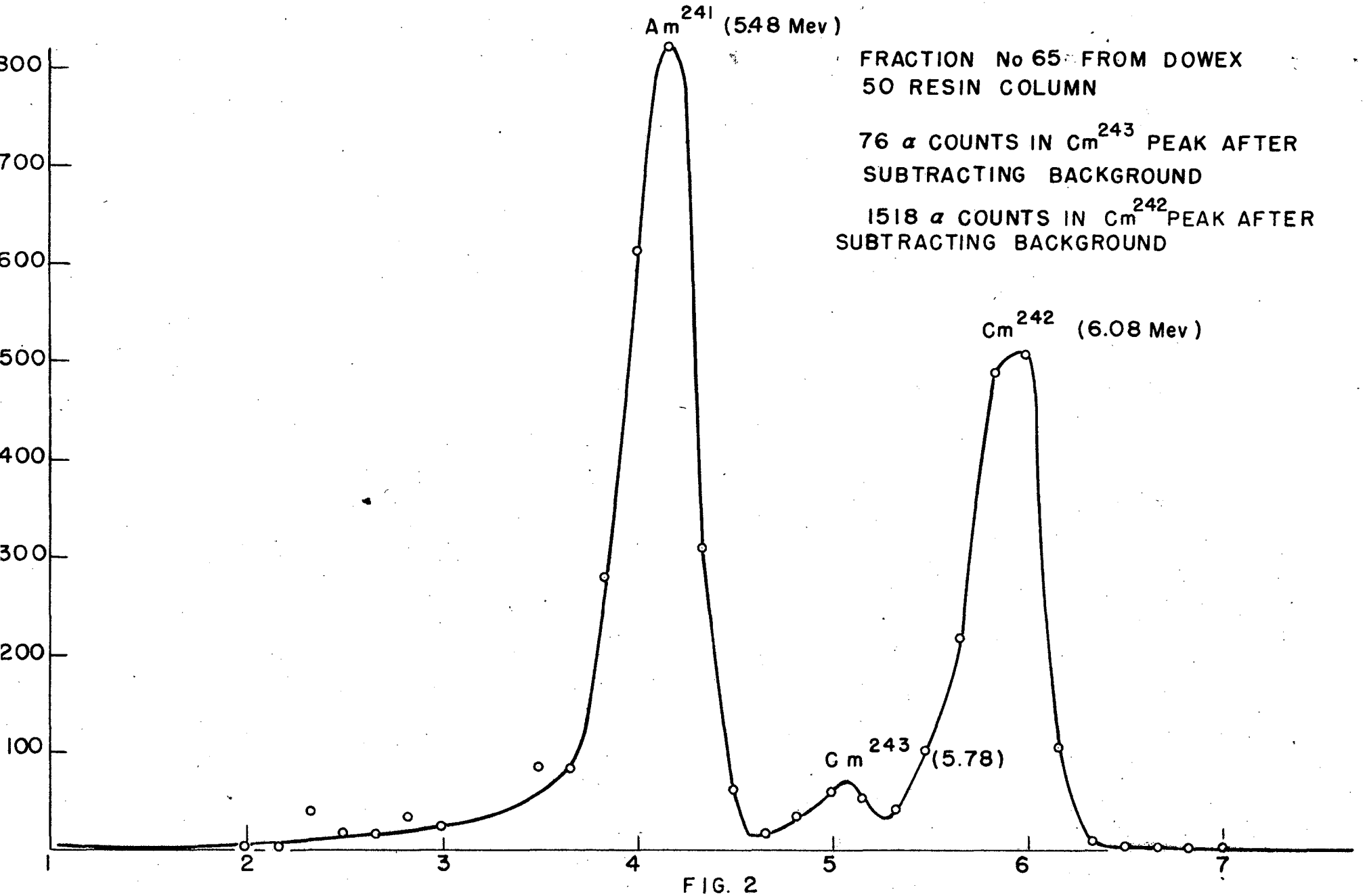


FIG. 2

DIFFERENTIAL PULSE ANALYSIS OF CURIUM FRACTION FROM BOMBARDMENT OF Am^{241} WITH 40 Mev He^{++}