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### Title

THE FIRST ISOLATION OF AMERICIUM IN THE FORM OF PURE COMPOUNDS - THE SPECIFIC ALPHA-ACTIVITY AND HALF-LIFE OF Am241

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THE FIRST ISOLATION OF AMERICIUM IN THE FORM OF PURE COMPOUNDS

THE SPECIFIC ALPHA-ACTIVITY AND HALF-LIFE OF Am<sup>241</sup>

B. B. Cunningham and L. B. Asprey

July 20, 1950

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THE FIRST ISOLATION OF AMERICIUM IN THE FORM OF PURE COMPOUNDS  
THE SPECIFIC ALPHA-ACTIVITY AND HALF-LIFE OF Am<sup>241</sup>

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ABSTRACT

The microgram scale isolation and preparation of pure compounds of americium is described. Data are presented to show that the alpha-half-life of the isotope Am<sup>241</sup> is  $490 \pm 14$  years. The absorption spectrum of Am(III) in 1M nitric acid in the range 3500-8000 m $\mu$  is given. The wave lengths of 10 of the most prominent lines in the copper spark emission spectrum of americium are given to the nearest 0.01 Å. Evidence is presented to show that the potential for the Am(III)-Am(IV) couple in acid solution is more negative than -2v and that the potential for the Am(II)-Am(III) couple is more positive than +0.9v.

THE FIRST ISOLATION OF AMERICIUM IN THE FORM OF PURE COMPOUNDS  
THE SPECIFIC ALPHA-ACTIVITY AND HALF-LIFE OF  $\text{Am}^{241}$ \*

B. B. Cunningham and L. B. Asprey\*\*  
Department of Chemistry and Radiation Laboratory  
University of California, Berkeley, California

July 20, 1950

Americium<sup>1</sup> was discovered in November, 1944 by Seaborg, James, and Morgan<sup>2</sup>

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(1) G. T. Seaborg, Chem. Eng. News, 24, 1193 (1946).

(2) G. T. Seaborg, R. A. James, and L. O. Morgan, National Nuclear Energy Series, Plutonium Project Record, Vol. 14B, "The Transuranium Elements: Research Papers," Paper No. 22.1 (McGraw-Hill Book Co., Inc., New York, 1949).

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who showed that an alpha-particle-emitting isotope of element 95 was obtained from the beta-decay of the plutonium isotope of mass 241. Early investigations of the chemistry of americium were carried out by its discoverers and others, using trace concentrations of the element. The results of this work have been published by Thompson, James, Morgan, and Perlman.<sup>3</sup>

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(3) S. G. Thompson, L. O. Morgan, R. A. James, and I. Perlman, ibid., Paper No. 19.1.

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Trace concentration studies established the fact that the chemical properties of americium in aqueous solution were closely similar to those of the tripositive rare earths. Attempts to obtain definite evidence for a higher or lower oxidation state of americium in aqueous solution were not successful.

At the time the work described in this paper was done the half-life of the isotope  $\text{Am}^{241}$  was not known. Decay measurements by James<sup>4</sup> suggested a

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(4) R. A. James, unpublished work.

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value  $\geq$  50 years.

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\* This work was carried out in part at the wartime Metallurgical Laboratory (now the Argonne National Laboratory) at the University of Chicago.

\*\* Present address: Los Alamos Scientific Laboratory, P. O. Box 1663, Los Alamos, New Mexico.



By June, 1945 sufficient Pu<sup>241</sup>, made by successive (n,γ) reactions<sup>5</sup> on Pu<sup>239</sup>,

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(5) G. T. Seaborg, Phys. Rev., 78, 472 (1950).

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was available to suggest that fractional microgram amounts of americium could be obtained for isolation and study of americium in the form of pure compounds, using the apparatus and techniques previously developed for the isolation of microgram amounts of plutonium and neptunium.<sup>6,7,8</sup>

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(6) B. B. Cunningham and L. B. Werner, J. Am. Chem. Soc., 71, 1521 (1949).

(7) L. B. Magnusson and T. J. LaChapelle, J. Am. Chem. Soc., 70, 3534 (1948).

(8) B. B. Cunningham, Nucleonics 5, no. 5, 62 (1949).

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Work on this project was initiated in July, 1945. Two preliminary runs, designed to test the chemical procedures and techniques employed, were carried through during July and August. The first run yielded an americium fraction of 1.03 micrograms weight which had a specific alpha-activity corresponding to a half-life of 850 years. This work was then repeated using more elaborate measures to exclude impurities (especially rare earth impurities) from all reagents and apparatus used. An americium fraction of 1.3 micrograms weight, having a specific alpha-activity corresponding to a half-life of 550 years was obtained.

The chemical procedures used in these separations did not differ in principle from the procedures described below, which were used to effect the isolation of ten micrograms of pure americium oxide in September, 1945.

## EXPERIMENTAL

### Apparatus and Technique

The apparatus and general techniques for conducting chemical operations in aqueous solutions on a microgram scale have been described by Cunningham and Werner,<sup>6</sup> Magnusson and LaChapelle,<sup>7</sup> and Cunningham.<sup>8</sup> No new apparatus was

required for the isolation of americium, although a simple modification of the 0.2 ml. microcone described by Cunningham and Werner<sup>6</sup> was found to be superior to the unmodified cone for conducting precipitation reactions from 1-5  $\mu$ l. of solution. The design of the modified cone is shown in Fig. 1.

The final operations in the chemical purification of the americium were conducted in cones of this type.

#### Isolation of Americium

The source of americium for the work described in this paper was a quantity of plutonium which had been purified from rare earth and other impurities by repeated precipitation with hydrogen peroxide from 1M nitric acid solution.<sup>9</sup>

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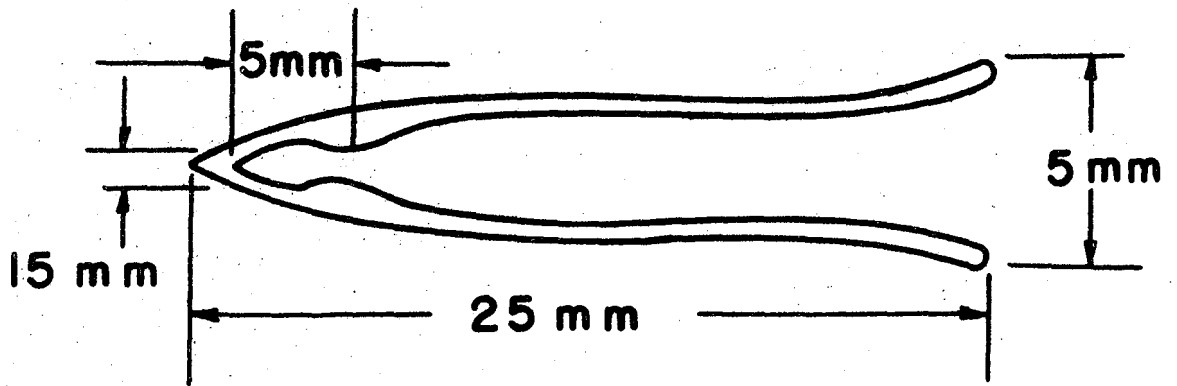
(9) An extremely high degree of purification from rare earth impurities was essential for the success of the subsequent work. At the time this work was done no method of efficient quantitative separation of americium from rare earth impurities was known. The starting material contained substantial amounts of rare earths. Experiments in which trace amounts of La<sup>140</sup> had been used showed that separation factors from rare earth impurities of ca. 50 could be obtained consistently in successive peroxide precipitations.

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The Am<sup>241</sup> daughter was separated from the bulk of the plutonium by precipitating the latter as the peroxide. Upon addition of an excess of ammonia to the separated supernatant solution, the plutonium which had not precipitated as the peroxide then precipitated as the "hydroxide," carrying the americium with it. (Under the experimental conditions described the solubilities of the plutonium peroxide and "hydroxide" were about 100 mg./l. and 1 mg/l., respectively.)

These very simple chemical operations proved to be remarkably efficient for the quantitative separation of americium from plutonium and the concentration of the americium fraction.

Less than two percent of the americium precipitated with the plutonium peroxide, while more than 98% precipitated with plutonium "hydroxide."



MU 550

Fig. 1

Modified Microcone

The precipitated "hydroxides" were dissolved in a small volume of 1M acid and the peroxide-hydroxide cycle repeated on a smaller scale.

Four cycles, with progressive reduction in the scale of operations yielded an americium concentrate containing about 60  $\mu\text{g}$ . of plutonium in 60  $\mu\text{l}$ . of 1M nitric acid.

In carrying out the preceding work, precautions had been taken to use the purest reagents available. Nevertheless, it was anticipated that relatively large amounts of common impurities would concentrate with the americium.

Accordingly, one percent of the americium concentrate was taken for spectrographic analysis. This aliquot was found to contain 0.1  $\mu\text{g}$ . of iron and 0.2  $\mu\text{g}$ . of lead, in addition to the plutonium known to be present.

The main americium fraction was saturated with hydrogen sulfide and allowed to stand for an hour. A small amount of sulfide precipitate was obtained. The supernatant solution was separated from the precipitate after vigorous centrifugation in a high speed air driven centrifuge.

The americium and plutonium were then precipitated as "hydroxides" by the addition of excess ammonia. The "hydroxides," colored black by the sulfides of iron and lead, were washed with a few microliters of dilute ammonia solution and then dissolved in 50  $\mu\text{l}$ . of 1M nitric acid. Sufficient 6M sulfuric acid was added to make the solution 1M in sulfuric acid, and 20 minutes were allowed for the precipitation of lead sulfate. Following vigorous centrifugation, the supernatant solution was separated from the precipitate by means of a micro-pipet and transferred to a new microcone which had been coated with a thin film of paraffin. To this solution was added 10  $\mu\text{l}$ . of 27M hydrofluoric acid. Twenty minutes were allowed for precipitation of the fluorides. Radiometric assay of an aliquot of the supernatant solution showed that only about one-half of the alpha-activity originally present in the solution had precipitated.

Accordingly, two 10  $\mu\text{g}$ . portions of plutonium (as plutonium (IV) nitrate) were added to provide a "carrier" for the unprecipitated americium. Recentrifugation yielded a supernatant solution containing less than 2% of the total alpha-activity. This fraction was removed and set aside. The precipitate was slurried with 50  $\mu\text{l}$  of 18M sulfuric acid, transferred to a small platinum dish and heated to dryness.

The residue was dissolved in 15  $\mu\text{l}$ . of 1M nitric acid. The solution was transferred to a new microcone and 5  $\mu\text{l}$ . of 30% hydrogen peroxide were added. Twenty minutes were allowed for precipitation of the plutonium peroxide, after which the solution was centrifuged and the supernatant solution removed. Calculation, using known values for the solubility of plutonium peroxide,<sup>10</sup> indicated

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(10) D. G. Pye, G. Watt, and F. R. Yett, unpublished.

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that all but about 2  $\mu\text{g}$ . of plutonium would precipitate under these conditions.

Radiometric analysis of the solution showed a total alpha-activity of  $8 \times 10^7$  alpha-disintegrations per minute in the whole americium fraction.

The results of a spectrographic analysis<sup>11</sup> of 10% of this fraction are

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(11) The analysis was carried out by Drs. Mark Fred and Frank Tompkins.

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shown in Table I.

The only impurities detected were La (0.01  $\mu\text{g}$ .) and Fe (0.01  $\mu\text{g}$ .) A similar amount of iron was found in the hydrochloric acid solution used to dilute the sample preparatory to analysis. Nine lines which could not be attributed to any previously known element, were assigned to the americium spectrum.

When the remaining americium fraction was made alkaline with ammonia gas, a bright reddish-brown precipitate formed. This precipitate was centrifuged to the bottom of the microcone and allowed to stand for some time. It was

Table I

Spectrographic Analysis of 1/10 of Fraction No. 24 of  
Americium Concentrate, Prepared September 13, 1945

Element Analyzed For	Amount Found ( $\mu\text{g}$ )	Limit of Detection ( $\mu\text{g}$ )
Ca	None	0.1
Ce	None	0.05
Dy	None	0.05
Er	None	0.05
Eu	None	0.005
Fe	0.01-0.02*	0.01
Ga	None	0.05
La	0.01-0.02	0.01
Nd	None	0.02
Pb	None	0.005
Pr	None	0.02
Sc	None	0.0005
Sm	None	0.05
Th	None	0.05
Tm	None	0.005
U	None	0.1
V	None	0.02
Y	None	0.001
Zr	None	0.01

\*A similar amount of iron was found in the HCl solution used to dilute the americium preparatory to putting it on the copper electrode.

observed that after some hours of standing, the color of the precipitate had faded to light salmon pink.

The precipitate was washed once with two  $\mu$ l of water, and was then dissolved in 0.5  $\mu$ l of 4M nitric acid. The resulting solution was diluted to 2.0  $\mu$ l with water. The diluted solution was clear pink in color, closely similar in shade to that of dilute solutions of manganous chloride.

The possibility that the color of the solution might actually be due to manganous manganese was checked by reprecipitation of the hydroxide, which showed no evidence of rapid darkening in the alkaline solution, such as would have occurred had the precipitate been  $Mn(OH)_2$ .

Moreover, re-examination of the spectrographic plate obtained in the analysis of 10% of the americium fraction revealed no lines which could be attributed to manganese (limit of detection 0.05  $\mu$ g). It was concluded that the color of solution was due to the hydrated ion of Am(III).

The solution was again saturated with hydrogen sulfide, allowed to stand for 16 hours and subjected to high speed centrifugation. A small amount of grayish-yellow precipitate, barely visible when the tip of the cone was examined under 30x magnification, had collected. The color of the precipitate suggested that it was composed mainly of free sulfur.

It was estimated that not more than about 0.02  $\mu$ g of lead could have remained in the supernatant solution.

The supernatant solution was carefully removed from the precipitate, transferred to a clean microcone, warmed to expel excess hydrogen sulfide and then treated with 0.15  $\mu$ l of 30% hydrogen peroxide. Sixteen hours were then allowed for precipitation of the plutonium as peroxide, after which the solution was centrifuged and the supernatant liquid transferred to a new microcone, which had been thoroughly cleaned and subjected to careful microscopic examination

for the presence of any traces of dust or other impurities. It was calculated that the quantity of plutonium remaining in the solution could not exceed 0.2  $\mu\text{g}$ .

A careful consideration of the chemical purification scheme together with the results of the spectrographic analysis made it appear highly improbable that more than fractional microgram amounts of any impurity could be present in the americium fraction.

Addition of an excess of ammonia again caused the precipitation of a dark reddish-brown material, which was collected in the tip of the cone by centrifugation. The volume of the precipitate was estimated by using a microscope and filar micrometer. Previous experience in judging the mass of a heavy element hydroxide precipitate from the volume obtained on centrifuging suggested that the mass of heavy element present was about 10  $\mu\text{g}$ . This estimate, together with the known amount of alpha-activity associated with the sample, indicated that the half-life of  $\text{Am}^{241}$  was of the order of 500, rather than 50 years.

#### Determination of the Specific Activity and Half-Life of $\text{Am}^{241}$

The supernatant solution from the precipitation with ammonia was removed with a micropipet and the precipitate was dissolved in 2  $\mu\text{l}$ . of 1M nitric acid. The solution of americium activity was transferred by means of a micropipet onto a shallow platinum dish of 1 cm. diameter and 0.01 mm. thickness, which had been thoroughly cleaned and ignited to constant weight at 800°C. The transfer of the americium activity onto the platinum dish was carried out under 30X magnification, using a pair of simple micromanipulators to hold the pan and syringe, as described by Cunningham and Werner.<sup>6</sup>

The solution of americium was evaporated to dryness under an infrared lamp and the pan transferred to a small closed platinum vessel, which was heated slowly to 800°C., held at this temperature for about one minute, and allowed to cool. On inspection of the weighing dish with a microscope, it was



observed that the ignition residue was black except at the very thin edges of the deposit, where it appeared brown. The color suggested that this material consisted principally of a higher oxide of americium (cf. "Pr<sub>6</sub>O<sub>11</sub>", "Tb<sub>4</sub>O<sub>7</sub>") rather than the sesquioxide. This residue was weighed on a quartz fiber micro-balance, similar to that described by Kirk, Craig, Gullberg, and Boyer.<sup>12</sup>

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

The weighing data are summarized in Table II.

Table II

Weighing Data on Americium Oxide Residue Obtained  
From A Solution of Americium Nitrate

Operation	Null Point Reading of Balance (Scale Divisions)*
Weighing pan cleaned, ignited to redness for 10 sec., cooled 5 min.	532.7
Rebalanced 15 min. after first weighing	532.5
Rebalanced 25 min. after first weighing	532.3
Rebalanced 40 min. after first weighing	532.3
Pan reignited to red heat for 10 sec., cooled 5 min.	532.1
Rebalanced 15 min. after second ignition	532.1
Rebalanced 25 min. after second ignition	532.1
Rebalanced 30 min. after second ignition	532.1
Americium soln. transferred to weighing pan. Dried at 70°C. Ignited to ~800°C. for 1 min. Cooled 5 min.	601.9
Pan and residue left on balance. Rebalanced 20 min. after first weighing of residue.	602.3

Weight of ignition residue =  $(602.1 \pm 0.2 - 532.1 \pm 0.1)$   
 $(0.1664 \pm 0.0004 = 11.65 \pm 0.06 \mu\text{g.})$

\*Calibration of the balance had shown each scale division to equal  
 $0.1664 \pm 0.0004 \mu\text{g.}$

The purity of the americium oxide preparation was calculated as follows. From the spectrographic analysis the weight of lanthanum as  $\text{La}_2\text{O}_3$  in 10% of Fraction No. 24 was equal to 0.016  $\mu\text{g}$ . As shown by a subsequent determination of the amount of alpha-activity on the weighing pan, 85% of the remaining americium was transferred to the weighing pan. Hence the ignition residue contained  $0.90 \times 0.85 \times 0.16 = 0.12 \mu\text{g}$  of  $\text{La}_2\text{O}_3$ . The amount of plutonium, as  $\text{PuO}_2$ , was estimated to be  $0.2 \times 0.85 \times 0.90 \times 271/239 = 0.17 \mu\text{g}$ . Hence the percent of americium oxide in the ignition residue was equal to:

$$\frac{11.65 - 0.12 - 0.17 \times 100}{11.65} = 97.5$$

The alpha-activity of the sample of americium oxide was determined without removing it from the weighing pan, in a low geometry alpha counter. Additional collimation was necessary in order to reduce the counting rate of the sample to within the range of reliable operation of the counting circuit. This was done by reducing the aperture of the window of the counting chamber by covering it with a mask of thin sheet aluminum through which a hole of  $1.27 \pm 0.025$  mm. diameter had been cut. The geometry factor of the counter was calculated as  $(2.18 \pm 0.06) \times 10^5$ .

The sample was introduced into the counting chamber and counted for 60 minutes. A total of 18,936 counts were recorded. The counting rate was calculated as  $= 315.6 \pm 2.3$  counts per minute. This was corrected for a coincidence loss of 0.8% per 1000 counts per minute to give the figure  $316.3 \pm 2.3$  c/m.

The sample was removed and the background of the counter was determined as  $8 \pm 1$  counts per minute.

The counting rate of the sample alone was equal to  $316.3 \pm 2.3 - 8 \pm 1 = 308.3 \pm 2.5$  counts per minute. This figure was converted to the number of alpha-disintegrations per minute for the sample by multiplying by the geometry factor.

$$\text{Alpha-disintegrations per minute} = (308.3 \pm 2.5) (2.8 \pm 0.06) \times 10^5 = 6.72 \pm 0.19 \times 10^7.$$

This number of disintegrations per minute were obtained from  $11.65 \pm 0.06$  microgram of americium oxide of 97.5% purity. The specific disintegration rate of the americium oxide was therefore equal to:

$$\frac{(6.72 \pm 0.19) \times 10^7}{(11.65 \pm 0.06)(0.975)} = (5.91 \pm 0.18) \times 10^6 \text{ alpha-disintegrations per minute per microgram.}$$

In order to calculate the specific alpha-activity of the isotope  $\text{Am}^{241}$ , it is necessary to know the formula of the oxide that was weighed. X-ray diffraction data, obtained by Dr. W. H. Zachariasen<sup>13</sup> on a sample of black oxide prepared in

(13) W. H. Zachariasen, Manhattan Project Metallurgical Laboratory Report MUC-FWHZ-156 (November, 1945).

October, 1945 showed this compound to be isomorphous with the fluorite-type dioxides of uranium, neptunium, and plutonium, and that the composition was approximately  $\text{AmO}_2$ . This formula leads to the value:  $(5.91 \pm 0.18) \times 10^6 \times 273/241 = (6.72 \pm 0.20) \times 10^6$  alpha-disintegrations per minute per microgram of  $\text{Am}^{241}$ .

The half-life for the alpha-particle decay of  $\text{Am}^{241}$  was calculated from the relation:  $T_{1/2} = 0.693.N/dN/dt$  where N is the number of atoms present and  $dN/dt$  the number of atoms disintegrating per unit time. In calculating N, the value of Avagadro's number<sup>14</sup> was taken as  $6.023 \times 10^{23}$ .

(14) S. Glasstone, "Textbook of Physical Chemistry," (D. Van Nostrand Company, Inc., New York, 1940), p. 13.

$$\text{Hence } T_{1/2} \text{ for } \text{Am}^{241} = \frac{0.693 \times 6.023 \times 10^{23} \frac{\text{atoms}}{\text{mole}} \times \frac{1}{241 \times 10^6} \frac{\text{moles}}{\text{microgram}}}{(6.72 \pm 0.20) \times 10^6 \text{ atoms/minute/microgram}} = (2.58 \pm 0.07) \times 10^8 \text{ minutes} = 2.58 \pm 0.07 \times 10^8 \text{ minutes} = 490 \pm 14 \text{ years.}$$

### The Emission Spectrum of Americium

After the specific alpha-activity of the americium oxide had been determined as described, the oxide was dissolved from the platinum pan by treatment with a few microliters of 1M HCl. Twenty percent of this sample was taken for spectrographic analysis, using the spark spectrum and copper electrodes.

A considerable amount (about 6% by weight) of platinum was found in this sample.<sup>15</sup>

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(15) As shown in a subsequent section of this paper, the  $\text{Am}^{+3}$ - $\text{Am}^{+4}$  potential is very negative, sufficiently so for  $\text{Am}^{+4}$  to oxidize  $\text{Cl}^-$  to  $\text{Cl}_2$ . Solution of some platinum metal on dissolving  $\text{AmO}_2$  deposited on platinum with hydrochloric acid solution will occur because of the localized formation of chlorine in the solution.

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No other impurities were detected. Fifty-one spectral lines, not attributable to any previously known element were found. The wave lengths of these lines were measured to the nearest  $0.01 \overset{\circ}{\text{A}}$  by Drs. Mark Fred and Frank Tompkins. The wave lengths of 10 of the most prominent of the lines, in the region  $2700\text{--}4000 \overset{\circ}{\text{A}}$  are given in Table III.

Table III

Most Prominent Lines in the Emission Spectrum of Americium  
in the Region  $2700\text{--}4000 \overset{\circ}{\text{A}}$  (Wave Lengths in Angstroms)

3926.24  
3696.43  
3161.88  
3038.39  
2972.57  
2969.29  
2966.71  
2920.61  
2756.55  
2755.78

It was found that the spectroscopic limit of detection of americium by the copper spark method was about  $0.01 \mu\text{g}$ , comparable to that of the most easily detected rare earths.

### The Absorption Spectrum of Americium

In February, 1946 about 10  $\mu\text{g}$ . of americium were isolated from a larger stock of plutonium which had become available. This material was used to determine the absorption spectrum of a dilute aqueous solution of americium (III) nitrate. The measurements were made with a Beckman Quartz Spectrophotometer, using micro absorption cells of 1 cm. path length.

The americium solution prepared for the spectrophotometric investigation consisted of 250  $\mu\text{l}$ . of a  $0.0117 \pm 0.007\text{M}$  solution of americium nitrate in 1M nitric acid. Complexing of the aqueous ion of Am (III) by nitrate ion was expected to be negligible in this solution.<sup>16</sup> The region investigated extended

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(16) J. C. Hindman and D. P. Ames, National Nuclear Energy Series, Plutonium Project Record, Vol. 14B, "The Transuranium Elements: Research Papers," Paper No. 4.2 (McGraw-Hill Book Co., Inc., New York, 1949).

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from 400 to 900  $\text{m}\mu$ . Optical density measurements were made at the following intervals: 2.5  $\text{m}\mu$  from 400-500  $\text{m}\mu$ ; 1.0  $\text{m}\mu$  from 500-515  $\text{m}\mu$ ; 2.5  $\text{m}\mu$  from 515 to 845  $\text{m}\mu$ ; and 5.0  $\text{m}\mu$  from 845 - 900  $\text{m}\mu$ . The absorption of the americium solution was measured against that of a 1M solution of nitric acid contained in a reference cell of the same design as that used to hold the sample. The optical densities measured in this way were plotted against wave length. These points were used to construct a curve of the optical density of the solution as a function of the wave length. In drawing the curve random variations of  $\pm 0.004$  in optical density were considered to be within the range of reproducibility of the instrument and a smooth curve was drawn through such points. The optical density curve was then converted to a molar extinction coefficient curve (Fig. 2) by dividing optical density at selected wave lengths by the molar concentration of americium. The concentration of americium in the solution was determined by rough radiometric assay, using a value of  $T_{1/2}$  for  $\text{Am}^{241}$  of 490 years. The molar

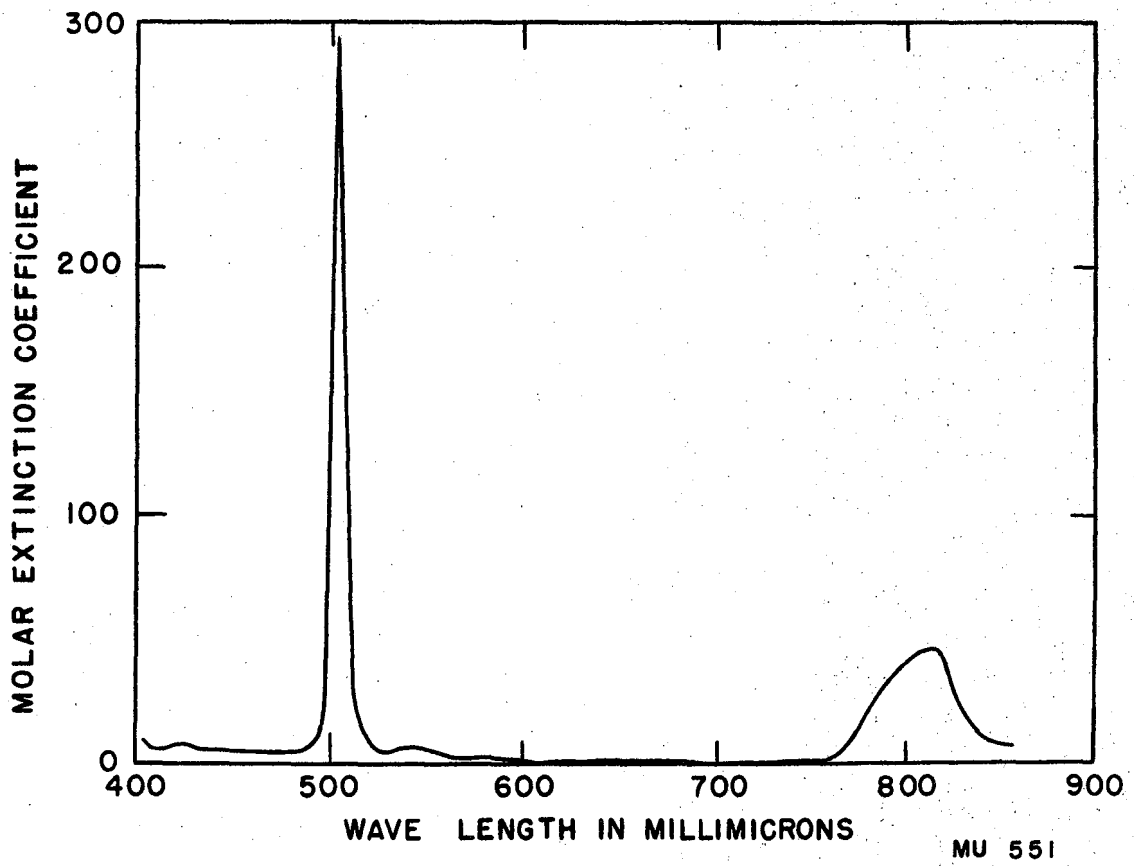


Fig. 2

Absorption Spectrum of 0.0013 M Americium in 1 M Nitric Acid.

extinction coefficients are not claimed to be accurate to better than about  $\pm 6\%$ .

As shown in Fig. 2, the hydrated aqueous ion of Am(III) is characterized by an absorption band of remarkable sharpness and intensity, having a maximum at  $503.0 \pm 1.0 \text{ m}\mu$ , and a second broad band of lesser intensity extending from about 760-820  $\text{m}\mu$ , with a maximum near 810  $\text{m}\mu$ . The assymetry of this second band indicates that it is a composite of two or more overlapping bands.

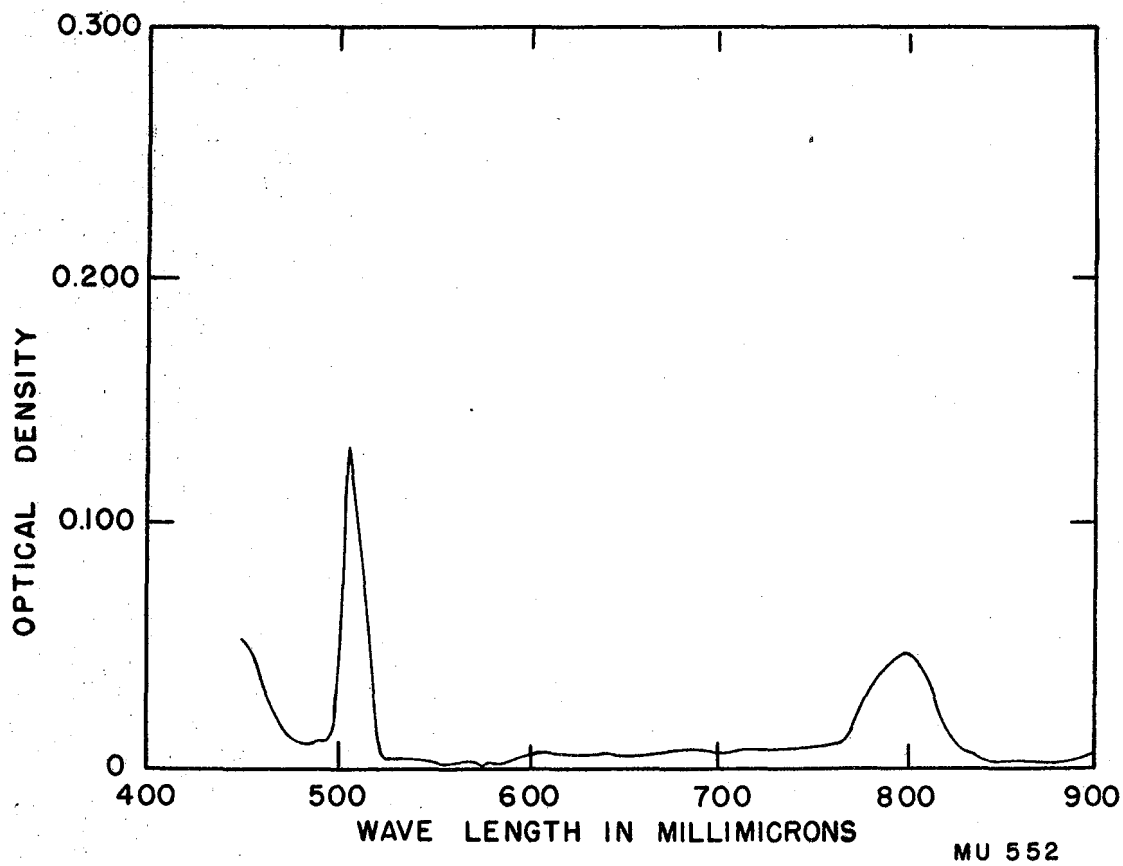
Because of the extreme sharpness of the 503.5  $\text{m}\mu$  band and the limited dispersion of the spectrophotometer, the observed optical density at the maximum probably is substantially less than the true value. Slit widths used in the investigation of the spectrum in the regions near 500 and 800  $\text{m}\mu$  were 0.055 and 0.045 mm., respectively.

In connection with a proposed attempt to oxidize Am(III) in nitric acid to a higher oxidation state, it was of interest to determine the absorption spectrum of Am(III) in concentrated nitric acid. The measurements were made with 250  $\mu\text{l}$ . of 0.001M americium in 15.5M nitric acid. The spectrum is shown in Fig. 3.

The spectrum is greatly affected by the concentrated acid. There is a marked decrease in the molar extinction coefficient of the 503.5  $\text{m}\mu$  band, as well as a pronounced broadening of both the 503.5 and 810  $\text{m}\mu$  bands. Such an effect, indicating a marked effect of the electric field about the Am(III) ion was anticipated from previous investigations on other tripositive actinide and rare earth ions.<sup>16</sup>

#### Oxidation of Americium in Aqueous Solution

Since it had been shown that americium exhibited a stable +4 oxidation state in the compound  $\text{AmO}_2$ , it seemed desirable to reinvestigate the possibility of oxidizing Am(III) to a higher oxidation state in aqueous solution using normal (0.01-0.001M) concentrations in place of the trace concentrations that had been used previously. A number of experiments designed to test this possibility were



MU 552

Fig. 3

Am(III) in Concentrated Nitric Acid Solution



carried out, as follows:

(1) Visual observation of the effect of adding 0.5 mg. of AgO to 20  $\mu$ l. of 0.01M Am(III) in 2M HNO<sub>3</sub> showed that there was no substantial change in the color of the americium solution after the brown Ag<sup>++</sup> ion had disappeared from the solution.

(2) Spectrophotometric observation of the effect of adding 2 mg. of AgO dissolved in 60  $\mu$ l. of 4M nitric acid to 200  $\mu$ l. of 0.001M Am(III) in 4M nitric acid showed no decrease in optical density at 503 or 810 m $\mu$  (after the Ag<sup>++</sup> ion had disappeared from the solution), except for the calculated decrease due to dilution of the Am(III) solution by the Ag<sup>++</sup> solution.

(3) Repetition of the above described experiment after making the Am(III) solution 1M in H<sub>2</sub>SO<sub>4</sub> gave similar results.

(4)<sup>17</sup> Addition of 20  $\mu$ l. of 16M nitric acid saturated with potassium bromate

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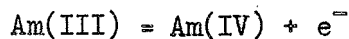
(17) This experiment was suggested by tracer studies by S. G. Thompson, who found occasional increases in the percent of americium carried by zirconium phosphate when this was precipitated from solutions of Am(III) in 15M nitric acid to which bromate had been added.

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to an approximately 0.001M solution of Am(III) in 15M nitric acid caused an apparent slow decrease in optical density at 506 and 800 m $\mu$  when the americium solution was balanced against a reference solution containing a similar amount of potassium bromate in 15M nitric acid. However, these results were not regarded as conclusive evidence for oxidation because of the rapid (and probably unequal) accumulation of bromine in the solutions.

(5) Americium (III) in 1M nitric or hydrochloric acid containing 1-2% of hydrogen peroxide was found to precipitate as a dark reddish brown material when the solution was made alkaline by the addition of excess ammonia. Upon standing further the color of the precipitate faded slowly to a light salmon pink.

The first two experiments show that the oxidation potential for the couple:



is more negative than ca.  $-1.8\text{v}$  since if the couple were less negative rapid oxidation of the Am(III) by  $\text{Ag}^{++}$  would have occurred. (The oxidation potential of the  $\text{Ag}^+ = \text{Ag}^{++} + e^-$  couple is listed by Latimer<sup>18</sup> as  $-2.05\text{v}$ .)

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(18) W. M. Latimer, "Oxidation Potentials," (Prentice-Hall, Inc., New York, 1938).

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The third experiment shows that the potential for the couple is more negative than about  $-2.0\text{v}$ , since the effect of  $1M$  sulfuric acid would be to render the potential less negative by ca.  $0.2\text{v}$ . This conclusion is based upon the assumption that the stability constant for the sulfate complex of Am(IV) would be at least as large as that for the stability constant for Pu(IV).<sup>19</sup> In view

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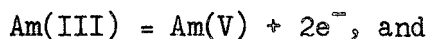
(19) J. J. Howland, Jr., J. C. Hindman, and K. A. Kraus, National Nuclear Energy Series, Plutonium Project Record, Vol. 14B, "The Transuranium Elements: Research Papers," Paper No. 3.3 (McGraw-Hill Book Co., Inc., New York, 1949).

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of the observed regular decrease in ionic radius with atomic number for the compounds  $\text{NpO}_2$ ,  $\text{PuO}_2$ , and  $\text{AmO}_2$ , this assumption can scarcely be doubted.

No conclusions concerning the oxidation of americium (III) are warranted on the basis of the results of the fourth experiment, because of the experimental difficulties mentioned.

Finally, it is emphasized that the experiments described above did not exclude the possibility that the potentials for the couples:



are less negative than  $-1.8\text{v}$  in  $1M$  acid solutions, since oxidation to the (V) and (VI) states might be quite slow. Ions of Am(V) and Am(VI) in acid solution would undoubtedly exist principally as the (hydrated) species  $\text{AmO}_2^+$  and  $\text{AmO}_2^{++}$

with covalently bonded oxygens.<sup>20</sup> Reactions in which it is required to form

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(20) R. E. Connick, M. Kasha, W. H. McVey, and G. E. Sheline, ibid., Paper No. 4.20.

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covalent bonds are often slow.<sup>21</sup>

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(21) R. E. Connick, ibid., Paper No. 3.18.

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Latimer's<sup>18</sup> values for the solubility products of  $\text{La}(\text{OH})_3$  and  $\text{Th}(\text{OH})_4$  may be used in order to estimate the extent to which these solubility relationships would favor the oxidation of  $\text{Am}^{+3} \longrightarrow \text{Am}^{+4}$  in alkaline solution.

Taking  $K_{\text{sp}} \text{Am}(\text{OH})_3 \approx 10^{-20}$ ,  $K_{\text{sp}} \text{Am}(\text{OH})_4 \approx 10^{-50}$ , then in  $1\text{M OH}^-$  (neglecting activity coefficients)

$$\frac{(\text{Am}^{+4})}{(\text{Am}^{+3})} \approx 10^{-30}$$

The free energy for the oxidation reaction is therefore less positive by some 40 kcal. in  $1\text{M}$  base as compared with  $1\text{M}$  acid solution. Oxidation by hydrogen peroxide in basic solution is therefore consistent with an  $\text{Am}(\text{III}) = \text{Am}(\text{IV}) + e^-$  potential which is more negative than ca.  $-2.0\text{v}$  in acid solution.

#### Attempted Reduction of Am(III) in Aqueous Solution

Attempts to obtain evidence for the reduction of  $\text{Am}(\text{III})$  to  $\text{Am}(\text{II})$  in aqueous solution were carried out by polarographic methods, using a Heyrovsky type polarograph, model XI, manufactured by E. H. Sargent and Company. A diagram of the cell employed in these experiments is shown in Fig. 4.

Before the cell was employed for an investigation of americium, it was tested by running several polarograms on 0.5 milliliters of  $0.003\text{M Eu}^{+3}$  in  $0.1\text{M KCl}-0.01\text{M HCl}$  supporting electrolyte. Well defined waves, corresponding to the reversible reduction of  $\text{Eu}(\text{III})$  to  $\text{Eu}(\text{II})$  were obtained at a potential of  $+0.42\text{v}$  (NHE).

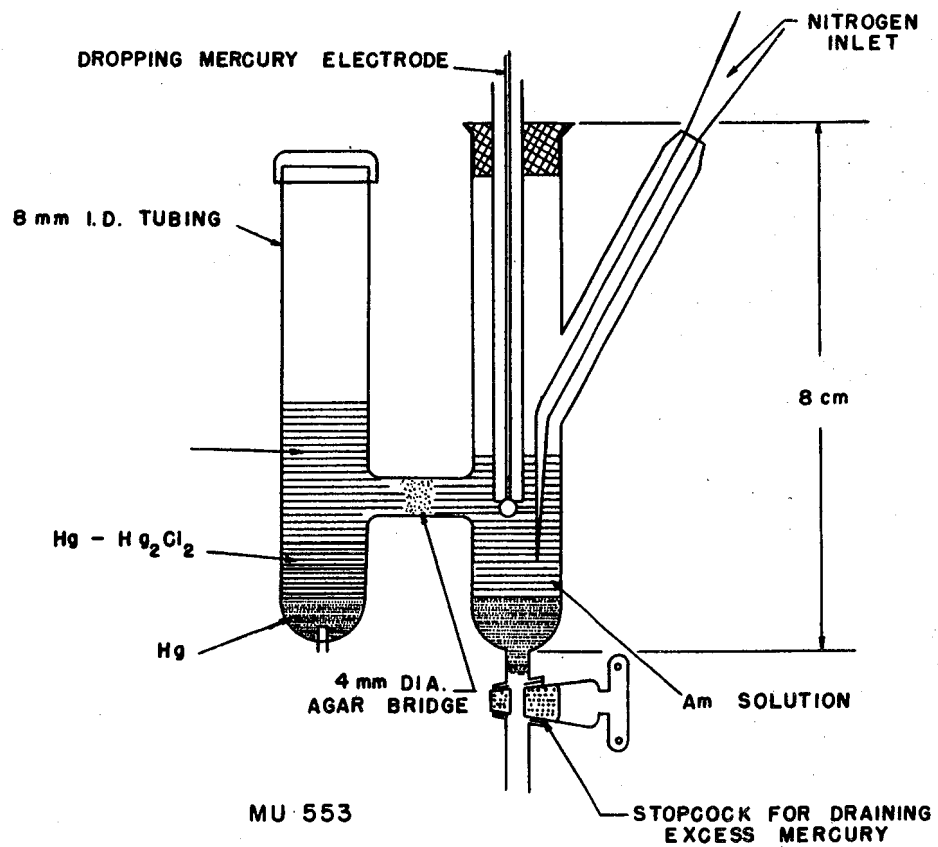
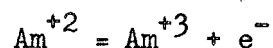


Fig. 4

Micro Polarographic Cell

When these experiments were repeated with americium, no well defined wave corresponding to the reversible reduction of americium (III) preceded the reduction of hydrogen ion (at an NHE potential of about +0.9v). It was thus shown that the potential for the half reaction



is more positive than about +0.9v, and that it is thus more difficult to reduce tripositive americium to the dipositive state than is the case with  $\text{Eu}^{+3}$ .

#### DISCUSSION

A point of interest in connection with the magnitude of the oxidation potential of the Am(III)-Am(IV) couple is that of its relationship to the corresponding couples of the preceding elements, uranium, neptunium, and plutonium. Although the heats of formation of the tripositive aqueous ions of these elements vary in an irregular manner, (being -123.6, -159.8, and -141.9 kcals./mole at 298°K., respectively),<sup>22</sup> the heats and free energies of formation of the tetra-

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(22) L. Brewer, U. S. Atomic Energy Commission Declassified Document AECD-1899, (Feb. 10, 1948).

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positive ions from the tripositive ions shows a remarkably regular increase of  $18.8 \pm 0.6$  kcals. per unit increase in atomic number. This regularity does not extend to americium, for which the free energy of formation of the tetrapositive from the tripositive ion is at least 24 kcals. more positive than the case for plutonium.

This information may be used to estimate the stability of other tetrapositive compounds of americium. After the oxide, the tetrafluoride might be expected to be the most stable compound of tetrapositive americium.

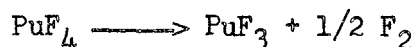
Using data provided by Brewer, Bromley, Gilles, and Lofgren,<sup>23</sup>  $\Delta F_{298}$  for the

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(23) L. Brewer, L. Bromley, P. W. Gilles, and N. L. Lofgren, National Nuclear Energy Series, Plutonium Project Record, Vol. 14B, "The Transuranium Elements: Research Papers," Paper No. 6.40 (McGraw-Hill Book Co., Inc., New York, 1949).

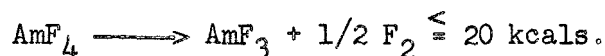
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reaction:



is calculated to be +44.1 kcal.

Assuming now that the difference between the free energies of formation of Pu(III)<sub>(aq.)</sub> and Pu(IV)<sub>(aq.)</sub> on the one hand and Am(III)<sub>(aq.)</sub> and Am(IV)<sub>(aq.)</sub> on the other also extends to their fluorides, the free energy for the corresponding reaction for americium will be at least 24 kcal. less positive than that for plutonium. Hence,  $\Delta F_{298}$  for the reaction:



Unless the potential for the couple is as negative as about -3.0v, it should be possible to prepare AmF<sub>4</sub> stable at room temperature.

At the time the work described in this paper was carried on, the question of primary interest was the extent to which the available data on the chemistry of the actinide elements was consistent with the concept, proposed by Seaborg,<sup>24</sup>

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(24) G. T. Seaborg, ibid., Paper No. 21.1.

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that the transuranium elements constituted a series of actinide "5f" elements in the same sense that the rare earths were a series of "4f" elements.

That "f" electrons were present in most of the aqueous ions of uranium, neptunium, and plutonium could scarcely be doubted since sharp absorption bands of these ions were observed even in aqueous solutions at room temperature. The intensities of these bands, while corresponding to transition probabilities some 10 to 100 times as great as those observed for the rare earths, were still so low as to exclude the possibility that they were due to allowed dipole radiations.

The absorption spectrum of americium (III) was of particular interest in that the band at 503  $\mu$  was entirely comparable in sharpness to the absorption bands of many rare earth ions and distinct in this respect from the absorption bands of any of the ions of the transition elements. The regular decrease in lattice constant of the isomorphous compounds  $\text{NO}_2$ ,  $\text{NpO}_2$ , and  $\text{PuO}_2$  also pointed to an orderly filling of a sub-shell.

While it was generally accepted, on the basis of this kind of evidence, that there was a progressive filling of the 5f shell in the transuranium elements, there was some question concerning the number of "f" electrons in the various ions. According to the actinide concept, it would be expected that ions of the transuranium elements in their ground states would have the same number of electrons in f orbitals as their rare earth analogs. The absorption spectrum of americium provided support for this view. It was as a result of the examination of this spectrum that it became evident that the absorption spectra of analogous members of the lanthanide and actinide elements exhibited a definite qualitative resemblance. Analogous ions tended to show a similarity in the complexity of their spectra in the visible and ultraviolet frequency range. This was regarded as evidence that the ground states and types of transition involved in the two series were analogous.

In other respects the chemical properties of americium were found to be consistent with a progressive filling of the 5f shell. The persistent decrease in lattice constant of the isomorphous compounds  $\text{UO}_2$ ,  $\text{NpO}_2$ , and  $\text{PuO}_2$  was found to extend to  $\text{AmO}_2$ , in a manner quite analogous to that due to the lanthanide construction in isomorphous compounds of the rare earths.

## ACKNOWLEDGMENT

The authors take pleasure in acknowledging the assistance of Mr. D. C. Stewart in several of the experiments described herein. Most of the work described in this paper was carried out under the auspices of the U. S. Atomic Energy Commission.

## SUMMARY

The microgram scale isolation and preparation of pure compounds of americium is described. Data are presented to show that the alpha-half-life of the isotope  $\text{Am}^{241}$  is  $490 \pm 14$  years. The absorption spectrum of  $\text{Am(III)}$  in  $1M$  nitric acid in the range 3500-8000  $m\mu$  is given. The wave lengths of 10 of the most prominent lines in the copper spark emission spectrum of americium are given to the nearest  $0.01 \text{ \AA}$ . Evidence is presented to show that the potential for the  $\text{Am(III)-Am(IV)}$  couple in acid solution is more negative than  $-2v$  and that the potential for the  $\text{Am(II)-Am(III)}$  couple is more positive than  $+0.9v$ .