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THE FIRST ISOLATIONS OF THE TRANSURANIUM ELEMENTS -AN HISTORICAL SURVEY

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J. C. Wallmann

November, 1958

THE FIRST ISOLATIONS OF THE TRANSURANIUM ELEMENTS  
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Berkeley, California

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Any discussion of the history of the isolation of the transuranium elements would not normally include any mention of their discovery. This is because for the transuranium elements the first evidence for unique chemical behavior--the criterion of discovery--has always been based on experiments in which the quantity of material is so small that it is detectable only because of its radioactive decay. This means that for the transuranium elements the discovery has not coincided with the isolation of the element--as it has for most of the other elements discovered in the past three centuries. When we speak here of the isolation we mean the purification of the element from contaminants and the measurement of a property of the element; tracer methods are excluded and the direct observation of a macroscopic property is implied. Among the transuranium elements this observation has generally been made on a compound of the element rather than the elemental matter itself because of the experimental difficulties inherent in producing reactive metals on a microgram scale.

The six transuranium elements and the years in which they were isolated are neptunium, 1944; plutonium, 1948; americium, 1945; curium, 1947; berkelium and californium, 1958. They will be discussed in the chronological order in which they were isolated.

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## Plutonium

Plutonium was the first of the transuranium elements isolated. This was done in August and September of 1942 by B. B. Cunningham and L. B. Werner at the Metallurgical Laboratory of the University of Chicago, a unit of the wartime Manhattan District. Cunningham is now Professor of Chemistry at the University of California, Berkeley, and Werner is at the U. S. Naval Radiological Defense Laboratory in San Francisco. The isotope involved in the isolation was the familiar plutonium-239 with a half-life for alpha decay of approximately 25,000 years. The isolation followed the discovery of the fissionable isotope by Kennedy, Seaborg, Segre, and Wahl by about eighteen months, a period during which all of the investigations of plutonium chemistry had been carried out by tracer techniques.

The three principal objectives of the isolation work were (1) to determine the specific alpha disintegration rate of  $\text{Pu}^{239}$ , (2) to determine the chemical properties of pure plutonium compounds and the chemical behavior of plutonium solutions at ordinary chemical concentrations, and (3) to demonstrate a chemical process for the separation of plutonium from uranium and fission products. The establishment of a reliable value for the specific activity of  $\text{Pu}^{239}$  by a direct weighing and alpha-counting method was a prime objective because this figure entered directly into the calculation of the thermal-neutron-fission cross section of the isotope.

A preliminary isolation yielding about one microgram of  $\text{Pu}^{239}$  was carried out in August, 1942, in order to prove a satisfactory separation and isolation procedure. At the time the isolation was performed it had not yet been shown that a self-sustaining nuclear reaction leading to the production of substantial amounts of  $\text{Pu}^{239}$  could be carried out, and therefore the plutonium used in the preliminary isolation was produced by the irradiation of natural uranium with neutrons produced by a d,n reaction on beryllium. Five kilograms of uranyl nitrate hexahydrate were irradiated using 12-Mev deuterons from the 60-inch cyclotron at the University of California Radiation Laboratory at Berkeley. The plutonium produced, approximately one microgram, was separated by a series of "fluoride cycles" from uranium and fission products and concentrated with 5 mg of cerium and 5 mg of lanthanum in 15 ml of

0.5 M  $H_2SO_4$ . These, and later, bulk separations of the large mass of uranium were carried out at Berkeley by A. C. Wahl and J. W. Gofman and at Chicago by A. H. Jaffey, T. P. Kohman, D. E. Koshland, Jr., and E. H. Turk. The solution of cerium, lanthanum, and plutonium was concentrated by evaporation and the fluorides precipitated by the addition of HF and KF solutions. The fluoride precipitate was then converted to a soluble sulfate by fuming with sulfuric acid and the plutonium oxidized to the "fluoride-soluble" oxidation state by addition of solid argentic oxide. Upon addition of hydrofluoric acid the rare earths were precipitated and the plutonium remained in solution. It was separated and recovered by centrifuging the solution, removing the supernatant, and fuming the supernatant with sulfuric acid to convert the plutonium to a soluble sulfate. Repeated cycles identical to this were carried out with ever smaller quantities of rare earth carrier until finally, on August 18, 1942, a pure sample of plutonium fluoride was precipitated -- the first isolation of a synthetic element. This material was not satisfactory for gravimetric work, but it did indicate that the fluoride-cycle method was satisfactory for concentrating and purifying plutonium at all concentrations of plutonium and rare earth carrier. Accordingly, another isolation was performed on about 30 micrograms of plutonium which had been produced by irradiating 90 kilograms of uranyl nitrate hexahydrate with neutrons produced by the reaction of beryllium and deuterons from the cyclotron at Washington University, St. Louis. In this experiment the bulk of the uranium was removed by ether extraction and the plutonium concentrated by means of successive fluoride cycles with decreasing amounts of lanthanum carrier. Finally the lanthanum was removed by a fluoride precipitation carried out with the plutonium oxidized to the fluoride-soluble state. The plutonium in the supernatant solution was fumed with sulfuric acid to yield soluble plutonium sulfate, the hydroxide was precipitated with ammonium hydroxide and washed and then dissolved with dilute nitric acid. From this solution plutonium iodate was precipitated, metathesized to the hydroxide, dissolved in dilute nitric acid, and reprecipitated. Metathesis of this plutonium iodate to the hydroxide yielded a pure material which was dissolved in dilute nitric acid to give a stock solution of about 20 micrograms

of plutonium nitrate with the solution concentration approximately 0.01 M in plutonium.

Several small portions of this solution were used for direct-weighing determinations of the specific activity of Pu<sup>239</sup>. The mass determination was done on a Salvioni type microbalance which had been constructed and calibrated by two independent methods. The first method consisted of constructing two additional Salvioni balances of lesser sensitivity and calibrating the less sensitive of the pair with a standard 1 milligram analytical weight. This calibration was used to determine the mass of a platinum wire, which was then used to calibrate the more sensitive second balance; similarly, a knowledge of the relation between load and displacement for the second balance allowed a calibration to be obtained for the third balance, the most sensitive one and the one on which the plutonium was to be weighed. A check on this calibration was made by an independent method. A 1 liter solution of thorium nitrate was prepared and the concentration of the solution was determined by ordinary analytical techniques. Then a known volume, about 1 microliter, of the solution was delivered onto the previously weighed platinum weighing pan of the Salvioni balance. The pan was then ignited until a constant weight was attained. The two calibrations agreed within 0.3% and indicated a sensitivity of  $\pm 0.00126$  microgram. On September 10, 1942, the first weighing of a pure compound of a synthetic element was made when an aliquot of the plutonium solution was delivered onto the previously weighed platinum weighing pan, dried, and ignited. The deflection of the balance indicated a weight of PuO<sub>2</sub> of 2.77 micrograms. This material was not used for further experimentation but was preserved intact. Two more weighings were made of PuO<sub>2</sub>, sample weights 4.55 and 2.20 micrograms, and these were used for specific-activity determinations which we now know indicated a purity of the plutonium stock solution of >95%. Additional experiments were carried out, using the same plutonium stock solution, to determine the oxidation number of plutonium in plutonium iodate and to determine the approximate solubilities of various plutonium compounds. This information was of importance in connection with the problems involved in designing chemical methods for the large-scale extraction, decontamination, and purification of plutonium. The chemical



separations process at Hanford was successful from the beginning of operation and represented a scale-up factor of  $10^9$  over the ultramicrochemical experiments.

The isolation of plutonium required microchemical techniques of great ingenuity. Both new techniques and the modification of previously developed techniques were used. In the latter the work of P. L. Kirk and associates and M. Cefola and A. A. Benedetti-Pichler should be mentioned.

### Neptunium

Neptunium was the first of the transuranium elements discovered, but it was not isolated until about two years after Cunningham and Werner had isolated pure plutonium. The neptunium isolation was carried out at the Metallurgical Laboratory of the University of Chicago by L. B. Magnusson, now of the Argonne National Laboratory Chemistry Division, and T. J. LaChapelle, currently employed in industry in California. Neptunium-237 with an alpha-decay half-life of more than one million years was the isotope available. Two objectives stimulated the isolation of neptunium. First, an accurate value for the half-life, determined by means of a direct-weighing specific-activity measurement, was desired because of the fundamental importance of this constant and for accurate standardization of the radiometric method of mass determination. In addition, a more accurate and detailed knowledge of the chemistry of neptunium was needed than could be obtained from tracer experiments. It was especially desired to establish one or more of the oxidation states of neptunium along with the formula of a dry compound.

Two sources of  $\text{Np}^{237}$  yielded approximately equal amounts of neptunium. One source was 64 pounds of uranium metal which had been bombarded by fast neutrons produced by the reaction of beryllium with deuterons from the cyclotron at the University of California Radiation Laboratory, Berkeley. The other source was uranium from a chain-reacting pile. Both sources produced neptunium-237 as a result of the  $n, 2n$  reaction on uranium-238, which yields the beta-decaying  $\text{U}^{237}$  of about 7 days half-life. A total of 45 micrograms of neptunium was isolated by utilizing the fact that neptunium is precipitated by fluoride ion under certain conditions and yet can be rapidly oxidized to a fluoride-soluble state by bromate ion. The neptunium was separated from

uranium by precipitating it, along with lanthanum carrier and plutonium, by adding HF to the solution previously treated with reducing agent. Separation of the neptunium and plutonium was achieved by dissolving the fluoride precipitate and adding potassium bromate. Under the conditions used plutonium was oxidized very slowly, and precipitation of lanthanum and plutonium fluorides left the oxidized fluoride-soluble neptunium in the supernatant. The supernatant solution was then treated with excess sulfur dioxide and the neptunium recovered as a fluoride which could be dissolved by any one of several means. Repeated bromate cycles separated the neptunium from contaminants until finally a pure neptunium fluoride was obtained. This was dissolved and a hydroxide precipitated. After being washed, the precipitate was fired and ignited and about 10 micrograms of the resulting oxide was scraped into an X-ray capillary. The remaining oxide was recovered and used for further preparation of neptunium compounds and measurement of their solubilities and crystal structure.

An X-ray-diffraction analysis of the ignited neptunium hydroxide was made by W. H. Zachariassen. He obtained a diffraction pattern which showed the oxide to be isomorphous with  $\text{ThO}_2$ ,  $\text{UO}_2$ , and  $\text{PuO}_2$ , thus establishing a +4 oxidation state for neptunium. With this information about the preparation of a compound of definite composition, a specific-activity determination was undertaken. Two weighings of 3.82 and 3.75 micrograms of  $\text{NpO}_2$  were made on a Kirk, Craig, Gullberg, Boyer quartz-fiber torsion microbalance, with a precision of about 0.02 microgram, and the balance pans then were counted directly in an alpha counter of ~50% geometry. The half-life calculated from this specific-activity measurement,  $2.20 \times 10^6$  years, is within 1% of the value obtained in recent years by using large quantities of  $\text{Np}^{237}$ , and demonstrates clearly the purity of the neptunium isolated so neatly by Magnusson and LaChapelle.

#### Americium

Element 95, americium, is the third element following uranium in the periodic table, but it was the fourth transuranium element discovered -- following curium, element 96, by a few months -- and unlike all the other transuranics it was isolated in the form of pure compounds less than one year after it was discovered. The isolation was carried out at the Metallurgical Laboratory of the University of Chicago by B. B. Cunningham, who three years previously had

achieved, in association with L. B. Werner, the isolation of the first synthetic element ever isolated, plutonium.

After the discovery of and prior to the isolation of americium, rather extensive tracer experiments on the chemistry had been carried on by the discoverers, Seaborg, James, and Morgan, and also by Thompson, Morgan, James, and Perlman. These investigations demonstrated the pronounced stability of the tripositive oxidation state of americium and the great similarity between the aqueous tripositive ions of the rare earth elements and americium. In three respects the problem of isolating americium differed from those encountered in the isolations of neptunium and plutonium. First, on the basis of the tracer experiments it appeared that it was difficult, if not impossible, to obtain any oxidation state other than +3 for americium. Also, the only methods of separating americium from the naturally occurring rare earths on a microgram scale involved prohibitive losses. Thirdly, the half-life of  $\text{Am}^{241}$ , the principal isotope, was uncertain by at least an order of magnitude, which meant that the amount of americium expected in the isolation was uncertain, and from an amount obtained there was no way of judging its probable purity. The americium-241 was produced by pile irradiation of plutonium, which by multiple neutron capture produced  $\text{Pu}^{241}$ , which yielded  $\text{Am}^{241}$  by beta decay. Necessity for separation of the americium from rare earths was avoided by subjecting the plutonium to extensive purification before irradiation and carefully avoiding any rare earth contamination from reagents or apparatus during the isolation. The americium produced in the irradiated plutonium was concentrated by hydroxide precipitation following precipitation of the bulk of the plutonium as peroxide. This cycle was repeated several times and a final americium-plutonium separation performed by oxidizing the plutonium to the fluoride-soluble +6 state and precipitating the americium fluoride with HF. The americium fluoride was dissolved, and after some further purification a very small portion of the americium solution was subjected to spectrographic analysis carried out by M. Fred and F. Tomkins. Lead and iron were the detected impurities, and these were removed by a lead sulfide precipitation and precipitation of the americium as fluoride to separate it from iron. On the basis of the chemistry which had been carried out on the sample, and from observation of its color, this was believed to be a pure americium compound. This fluoride was therefore used for a direct-weighing specific-activity measurement to determine the half-life of  $\text{Am}^{241}$ . The ignited fluoride yielded a black oxide

which was weighed on a quartz-fiber torsion microbalance and then counted in a low-geometry alpha counter. On the assumption that the several micrograms of oxide was  $\text{AmO}_2^-$ --an assumption later verified by X-ray-diffraction analysis--a half-life of 498 years was calculated. The americium oxide was dissolved off the platinum boat and 20% of it used for spectrographic analysis which indicated 2% La, 0.1% Mg, and 6% Pt, the latter presumably dissolved from the weighing boat when the oxide was dissolved.

The remaining americium was purified and precipitated as hydroxide. The hydroxide was dissolved in dilute nitric acid and used for further studies of the oxidation states of americium in aqueous solution: oxidation states both higher and lower than +3 were looked for without definite success. In addition, the aqueous-solution absorption spectrum of Am (III) was determined. The absorption spectrum tended to verify the validity of Seaborg's actinide hypothesis: the difference between the spectra of americium and plutonium was similar to the difference between the spectra of europium and samarium. This lent weight to the argument of Seaborg that the new elements were part of an actinide series analogous to the rare earth or lanthanide elements.

### Curium

The actinide hypothesis also predicted that element 96, curium, would be the seventh member of a series in which the f orbitals lay at progressively lower levels. Curium was postulated to be an analog of gadolinium and a special stability was expected for Cm (III), presumed to have a configuration of seven 5f electrons. This had been borne out by tracer studies which indicated that only +3 curium was stable in aqueous solution. The problem of isolating curium from irradiated americium thus resolved itself into one of separating two tri-positive ions similar to two adjacent rare earths. This separation and the isolation of curium were successfully accomplished by L. B. Werner, associated earlier with the plutonium isolation, and I. Perlman at the University of California Radiation Laboratory, Berkeley.

A quantity of 4.48 milligrams of  $\text{Am}^{241}$  was irradiated for one year with a high flux of slow neutrons to produce about 150 micrograms of curium-242. The separation of the curium from americium was effected by means of a cation-exchange column using citric acid eluant. Additional ion-exchange separations were made on americium-contaminated fractions until 115 micrograms of  $\text{Cm}^{242}$  was obtained free of americium in 50 milliliters of solution. This material was concentrated

by readsorption on several small portions of ion-exchange resin and then batchwise elution from the resin with citrate solution. After decomposition of the citrate with nitric and sulfuric acids, curium hydroxides was precipitated. Handling  $\text{Cm}^{242}$ , which decays by alpha-particle emission with a half-life of only 162 days, leads to problems other than just those of manipulating small quantities of radioactive material. Decomposition of the aqueous solution occurs as a consequence of the high alpha-decay rate, and both buildup of peroxide and evolution of gas are observed. This gas formation in the solution causes a precipitate to be stirred up within a few seconds after it has been compacted by centrifugation. Another concomitant of the short half-life of curium-242 is the growth in the curium at the rate of 0.5% per day of daughter  $\text{Pu}^{238}$ . Except immediately after a separation plutonium is always present as an impurity.

The curium hydroxide was dissolved and the absorption spectrum of the solution examined. After purification of the curium from plutonium two 1-microgram samples were used for spectrographic analysis, which indicated that only lead was a major impurity. After precipitation of lead sulfide a 5-microgram sample was sparked to obtain a more complete measure of the spectral lines attributable to curium and to check for impurities. A further check on impurities was made by performing a direct-weighing specific-activity determination. Unlike the transuranium elements isolated earlier, the curium-242 had a half-life so short that it was known from direct decay observations. A specific-activity determination on curium would thus check the purity of the compound weighed. On the assumption that the composition of the oxide was  $\text{Cm}_2\text{O}_3$ , about 40 micrograms of curium was weighed on a quartz fiber torsion microbalance and then dissolved and counted. A purity of 85 to 93% was found for the curium oxide preparation.

#### Berkelium and Californium

In September 1958, at the 2nd Geneva Conference on the Peaceful Uses of Atomic Energy, a paper was presented entitled "First Macroscopic Observations of the Chemical Properties of Berkelium and Californium." Thus the fifth and sixth transuranium elements have now been isolated. This work was done during the spring and summer of 1958 by B. B. Cunningham and S. G. Thompson at the University of California Radiation Laboratory, Berkeley.

Prolonged neutron irradiation of Pu<sup>239</sup> produced about a microgram each of berkelium, element 97, and californium, element 98. A mixture of isotopes was produced in each case, but those present in greatest abundance were Bk<sup>249</sup>, a 300-day  $\beta^-$  emitter, and Cf<sup>252</sup>, a 2-year  $\alpha$ -emitting isotope. Prior to this work by Cunningham and Thompson the only knowledge of the chemical properties of these elements had been obtained by tracer experiments. This knowledge was actually extensive enough to allow the transplutonium elements to be concentrated by means of ion-exchange techniques which had been tested repeatedly. The final purifications of both berkelium and californium also consisted of elution from a very small ion-exchange column. The solution coming off the column passed directly into a capillary cell with optically flat windows, where the absorption spectrum of the elements could be studied. Approximately 1/2 microgram of berkelium and double that amount of californium in dilute HCl were studied in the cell, and revealed no absorption lines in the visible region of the spectrum. The absence of detectable absorption lines of Bk (III) in the visible region of the spectrum was expected, but the absence of lines for Cf (III) suggested that in the heavier (as contrasted with the lighter) actinides the transition probabilities were decreasing for transitions from the  $^6H_{15/2}$  ground state to the various  $^6F$  levels. Additional studies of the absorption spectrum of Cf (III) by photographic methods revealed the presence of two broad weak absorptions which may correspond to transitions in analogous states of Dy (III).

Magnetic-susceptibility measurements on tripositive berkelium and californium were also made. The separate ions were sorbed on single beads of Dowex-50 resin and the beads suspended in a magnetic field by means of a plastic basket sealed to a fine quartz fiber. Gd (III) was used as the reference standard. The experimental results agreed best with moments derived on the assumption that the electrons occupy f orbitals and interact by unperturbed pure L-S coupling.

Ten transuranium elements are now known, and of these ten, six have been isolated in amounts such that macroscopic properties could be observed or pure compounds weighed. Element 99, einsteinium, will perhaps be isolated in the near future, but it may well be the last element available in macro quantities. Thereafter the half-lives are so short a that even if sufficient quantities of the transeinsteinium elements could be produced the isolation would be difficult.

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