

of 78.96 rests. Mattauch and Flüggé<sup>18</sup> report the value from mass spectroscopy as 78.95, and later,<sup>19</sup> in the English edition of "Nuclear Physics," as 78.94.

TABLE VII  
THE  $\text{SeOCl}_2:2\text{Ag}:2\text{AgCl}$  RATIOS

Titrimetric				Gravimetric		
$\text{SeOCl}_2$ , g.	Ag, g.	$\text{SeOCl}_2$ : 2Ag	Atomic weight of selenium	AgCl, g.	$\text{SeOCl}_2$ : 2AgCl	Atomic weight of selenium
3.88093	.....	.....	.....	6.70714	0.578627	78.963
3.91475	5.09206	0.768795	78.961	6.76573	.578615	78.960
3.63360	4.72643	.768783	78.959	6.27987	.578611	78.959
3.81769	4.96600	.768766	78.955	6.59818	.578598	78.955
3.46312	4.50439	.768832	78.969	5.98480	.578653	78.971
3.19867	4.16051	.768820	78.967	5.52788	.578645	78.969
4.15394	5.40331	.768777	78.957	7.17916	.578611	78.959
4.46080	5.80239	.768787	78.960	7.70920	.578633	78.965
6.00116	7.80602	.768786	78.959	10.37136	.578628	78.964
5.39786	7.02111	.768804	78.963	9.32870	.578629	78.964
4.05741	5.27781	.768768	78.955	7.01231	.578613	78.959
4.65053	6.04910	.768797	78.962	8.03731	.578618	78.961
4.53967	5.90490	.768797	78.962	7.84567	.578621	78.962
4.59714	5.97953	.768813	78.965	7.94479	.578636	78.966
2.27775	2.96277	.768791	78.960	3.93648	.578626	78.963
Average		.768794	78.961			.578624 78.962

**Tungsten, Silicon and Boron.**—Inghram<sup>20</sup> determined the isotopic constitution of tungsten, of silicon and of boron. Five isotopes of tungsten

(18) Mattauch and Flüggé, *Ber.*, **76**, 1 (1943).

(19) J. Mattauch and S. Flüggé, "Nuclear Physics Tables and an Introduction to Nuclear Physics," Interscience Publishers, Inc., New York, N. Y., 1946.

(20) M. G. Inghram, *Phys. Rev.*, **70**, 653 (1946).

were observed at masses 180, 182, 183, 184 and 186, with abundances of 0.122, 25.77, 14.24, 30.68 and 29.17%, respectively. Using Dempster's<sup>21</sup> value of  $+1.8 \times 10^{-4}$  for the packing fraction of tungsten and the conversion factor 1.000275, the calculated chemical atomic weight is 183.89, which compares favorably with the chemically determined value of 183.92.

Three isotopes of silicon were observed at masses 28, 29 and 30, with abundances of 92.28, 4.67 and 3.05%, respectively. Calculating the chemical atomic weight, using the packing fractions  $-4.86 \times 10^{-4}$ ,  $-4.54 \times 10^{-4}$  and  $-5.68 \times 10^{-4}$  for the masses 28, 29 and 30, respectively, as given by Pollard,<sup>22</sup> and the conversion factor 1.000275, the value 28.086 was obtained, which is in good agreement with the chemically determined value of 28.06.

Two isotopes of boron were observed at masses 10 and 11, with abundances of 18.83 and 81.17%, respectively. Using the packing fraction  $+16.3 \times 10^{-4}$  for mass 10 and  $+11.8 \times 10^{-4}$  for mass 11, as determined by Bainbridge<sup>23</sup> and the conversion factor 1.000275, the calculated value of 10.821 was obtained, which is in good agreement with the chemically determined value of 10.82.

The chairman wishes to acknowledge the valuable aid given by Raleigh Gilchrist in the preparation of this report.

(21) A. J. Dempster, *Phys. Rev.*, **53**, 869 (1938).

(22) E. Pollard, *Phys. Rev.*, **57**, 1186 (1940).

(23) K. T. Bainbridge, *Phys. Rev.*, **51**, 385 (1937).

[CONTRIBUTION FROM THE WARTIME METALLURGICAL LABORATORY, UNIVERSITY OF CHICAGO]

## The First Isolation of Element 93 in Pure Compounds and a Determination of the Half-life of ${}_{93}\text{Np}^{237}$

BY L. B. MAGNUSSON<sup>1a</sup> AND T. J. LACHAPPELLE<sup>1b</sup>

Wahl and Seaborg,<sup>2</sup> who first detected the  $\alpha$ -particles from  ${}_{93}\text{Np}^{237}$  in April, 1942, found a value of  $3 \times 10^6$  years, considered to be accurate within a factor of two, for the half-life of the isotope by measuring the ratio of seven-day  $\text{U}^{237}$  activity to that of its daughter,  $\text{Np}^{237}$ . The corresponding specific counting rate of 500  $\alpha$ -particle counts minute<sup>-1</sup> microgram<sup>-1</sup> in the 50% geometry  $\alpha$ -particle counter was used in subsequent determinations of mass by radiometric assay. A more precise and corroborating value for the half-life was desired for accurate standardization of the radiometric method of mass determination and because of the fundamental importance of this constant.

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(2) A. C. Wahl and G. T. Seaborg, *Plutonium Project Record*, Vol. XIVB, No. 1.5 (1943) (to be issued); *Phys. Rev.*, **73**, 940 (1948) (written on April 14, 1942).

The method of direct weighing on the ultramicro scale of a neptunium compound and measurement of its disintegration rate by  $\alpha$ -particle emission was first attempted by Cunningham and Werner,<sup>3</sup> and Cunningham<sup>4</sup> who, it now appears, had available such extremely small amounts that isolation of the pure material was not feasible. Cunningham found a value for the half-life of  $6 \times 10^6$  years. The purity and composition of the materials isolated were unknown. The work reported in this paper culminated in the preparation and identification for the first time of two pure compounds of neptunium in June and July, 1944.

As part of the Manhattan Project program of research, a more accurate and detailed knowledge of the chemistry of neptunium was needed than

(3) B. B. Cunningham and L. B. Werner, Manhattan Project Report CN-556 (March 31, 1943).

(4) B. B. Cunningham, Manhattan Project Report CN-991 (October 9, 1943).

could be acquired from experiments with trace concentrations. The discoverers of element 93, McMillan and Abelson,<sup>5</sup> showed with trace concentrations of the fifty-six hour isotope,  $\text{Np}^{239}$ , that neptunium existed in at least two oxidation states, one carried by rare earth fluorides and the other by sodium uranyl acetate. The initial objective of the ultramicro investigation was the establishment of one or more of the oxidation states of neptunium together with the formula of at least one dry compound, since the determination of the specific activity by weighing requires that the formula of the weighed compound be known. The decision was made that an oxide could be most easily prepared and duplicated in the subsequent gravimetric determination of the specific activity. The fact that both elements 92 and 94 form relatively insoluble, isomorphous compounds of the type  $\text{Na}_2\text{XO}_2(\text{O}_2\text{C}_2\text{H}_3)_3$  made it likely that neptunium would form the same type of compound. The formation of an insoluble, pure compound was regarded as highly desirable from the point of view of separation from the carrier which would be required in the isolation process.

A concerted effort was begun in 1944 in the Metallurgical Laboratory (now the Argonne National Laboratory) of the University of Chicago to isolate weighable quantities of  $\text{Np}^{237}$ , the only known isotope of neptunium which is sufficiently long-lived to allow convenient separation of practical amounts. Seaborg and Wahl<sup>6</sup> found differences in the properties of plutonium and neptunium which enabled them to devise an efficient method of separating the two elements. This process also eliminated all other radioactive species and was used with little change in the work reported here. The method, briefly, begins with dissolving neutron bombarded natural uranium as metal or compound in nitric acid. The resulting uranyl nitrate solution contains in addition to the uranium principally plutonium, neptunium and fission products. From the uranyl nitrate solution the plutonium, neptunium and much of the fission product activity is carried by a precipitate of lanthanum fluoride in the presence of a suitable reducing agent. A very little uranium is carried down by the lanthanum fluoride. The isolation of neptunium from plutonium, residual uranium and the fission products is accomplished by a series of bromate oxidation cycles which depend on the fact that neptunium is oxidized rapidly by bromate in sulfuric-hydrofluoric acid solution at room temperature to a state which is not carried by lanthanum fluoride, whereas plutonium is oxidized only very slowly. Later work has established that neptunium is oxidized to the plus six state and plutonium remains in the plus four state under these conditions. The fission products in general are carried by lanthanum fluoride to about the same

extent under either oxidizing or reducing conditions and hence may be removed by the cyclic process to be described. The lanthanum fluoride precipitate from the uranyl nitrate solution is put into 0.5–3 molar sulfuric acid solution by any one of three methods: (1) fuming with hot sulfuric acid to remove hydrofluoric acid, (2) metathesis by sodium hydroxide solution to lanthanum hydroxide with subsequent dissolution in sulfuric acid or (3) dissolution in a fluoride complexing agent, such as zirconyl nitrate solution. To the sulfuric acid solution of lanthanum at room temperature is added potassium bromate to 0.1 molar. Addition of hydrofluoric acid to 1–6 molar precipitates lanthanum fluoride which carries almost all of the plutonium. The neptunium remains nearly quantitatively in the supernatant solution, which is then separated from the precipitate and reduced by excess sulfur dioxide. Evaporation to fumes of sulfur trioxide removes the bromate reduction products and hydrofluoric acid. To complete the cycle, lanthanum is again added but in smaller amount as carrying agent; the solution is diluted to 0.5–3 molar sulfuric acid and made 1–6 molar in hydrofluoric acid to precipitate lanthanum fluoride which carries the neptunium quantitatively along with whatever plutonium may still be in solution. The oxidation–reduction cycling is continued until the amounts of plutonium and lanthanum accompanying the neptunium are reduced to any desired level. The neptunium may be separated from lanthanum carrier by the precipitation of a suitable insoluble neptunium compound. One such compound will be described in this paper. Even under the most advantageous experimental conditions for the formation of  $\text{Np}^{237}$  from natural uranium by neutron bombardment, the  $\alpha$ -activity of  $\text{Np}^{237}$  is associated with at least a hundred-fold larger  $\alpha$ -activity of  $\text{Pu}^{239}$ , so that the neptunium cannot be followed through the separations process by direct alpha assay. To label the neptunium, it is necessary to add a known amount of fifty-six-hour  $\text{Np}^{239}$  ( $\beta$ -particle emitter) activity at the beginning of a separation. Quantitative recovery of the added  $\text{Np}^{239}$  along with the  $\text{Np}^{237}$  which may be present in appreciable amount in the bombarded material depending upon the time of decay after bombardment, assures complete recovery of the  $\text{Np}^{237}$ . Purity of the isolated  $\text{Np}^{237}$  to within a few per cent with regard to  $\text{Pu}^{239}$   $\alpha$ -activity is obtained by continued oxidation–reduction cycling until the (beta)/(alpha) emission ratio of the material attains a constant maximum (with allowance for  $\text{Np}^{239}$  decay). Two different sources yielded approximately equal amounts of  $\text{Np}^{237}$  to make up a total of about 45 micrograms which was available for the ultra-micro determinations reported in this paper. One source was 64 pounds of uranium metal which had received a fast neutron bombardment produced indirectly from deuterons on beryllium by the cyclotron at the University of California, Berkeley, California. The yield of nep-

(5) E. M. McMillan and P. H. Abelson, *Phys. Rev.*, **57**, 1185 (1940).

(6) G. T. Seaborg and A. C. Wahl, *Plutonium Project Record*, Vol. XIVB, No. 1.6 (1948); *THIS JOURNAL*, **70**, 1128 (1948).

tunium element in this bombardment was about two parts per billion parts of uranium by weight. The other source was uranium pile material.

### Experimental

Observation and manipulation of micro and ultramicro amounts of materials and solutions was done with the aid of stereoscopic microscopes and suitable micro manipulators. Precipitates were separated from solutions by centrifugation. All solutions containing hydrofluoric acid were held in platinum or waxed glass vessels, and transferred with waxed pipets.

The  $\text{Np}^{237}$  was freed from  $\text{Pu}^{239}$  by the bromate cycling method described in the introduction. The final bromate cycle resulted in a fluoride precipitate containing 50 micrograms of lanthanum and about 45 micrograms of neptunium. The fluoride was converted to sulfate by adding dilute sulfuric acid and evaporating to dryness. The mixed sulfates were dissolved in 0.3 ml. of 1 molar sulfuric acid and potassium bromate added to 0.1 molar. After one-half hour of standing at room temperature, the solution was made 1 molar in hydrofluoric acid, precipitating lanthanum fluoride and leaving the neptunium in solution. The supernatant solution was transferred, together with a 50 microliter water wash of the lanthanum fluoride, to a 0.5 ml. round-bottom platinum crucible designed for convenient centrifuging. Sulfur dioxide was added until all the bromate was reduced to bromide as indicated by a colorless solution, which was then evaporated to the appearance of sulfur trioxide fumes. The residue was dissolved in 150 microliters of dilute sulfur dioxide solution and aqueous ammonia added to *ca.* 6 molar. A light brown precipitate formed with a solubility at ten hours of 0.1 g. liter<sup>-1</sup> (expressed as neptunium element). The precipitate, which was presumed to be a hydroxide or hydrated oxide of a reduced state of neptunium, was washed with dilute sulfur dioxide/molar ammonia solution, dried in a low temperature oven, and ignited in air at a red heat for fifteen minutes. During the ignition the crucible was covered with a water-cooled platinum dish to condense and collect any neptunium compound which might have been volatile at the high temperature. No detectable increase in  $\alpha$ -activity on the dish was caused by the ignition. The drying and ignition decreased the volume of the neptunium preparation considerably but the color remained light brown. About 10 micrograms was scraped from the platinum crucible and placed in a thin-walled glass capillary for an X-ray diffraction photograph.

For the attempt to prepare sodium neptunium (VI) di-oxytriacetate, neptunium was recovered from the oxide preparation and other sources. The ignited oxide was found to be very resistant to attack by acids. Platinum contamination, caused by heating solutions of hydrobromic and sulfuric acids in platinum dishes gave mechanical difficulties. Precipitation of neptunium hydroxide by ammonia from these solutions also resulted in the precipitation of platinum compounds which were more or less insoluble in acid solutions. The bulk and large liquid hold-up of these precipitates were serious handicaps to the ultramicro operations. About 30 micrograms of neptunium was eventually collected together with 50 micrograms of lanthanum as a fluoride precipitate, which was fumed to dryness with sulfuric acid. The residue was dissolved in 0.1 ml. of 0.5 molar sulfuric acid and transferred to a capillary centrifuge cone. Ammonia was added to excess by directing a jet of the gas at the surface of the solution, forming a white precipitate of about 10 microliters volume after centrifugation. The precipitate was washed with water by stirring with a fine platinum wire and centrifuging. To dissolve the hydroxide precipitate, 6 microliters of 1 molar sulfuric acid was added. About 80% of the precipitate dissolved leaving a brown, insoluble residue which was thought to be platinum. The supernatant solution was transferred to a clean capillary cone and 2 microliters of 0.5 molar potassium bromate solution added. The cone was placed in a water-bath at 80° and immediately colorless crystals precipitated while the solution turned very

pale green. The colorless precipitate was thought to be a lanthanum compound. Most of the neptunium remained in solution and the color change was attributed to the formation of oxidized neptunium. After centrifugation the supernatant solution was transferred to a clean capillary. Additional potassium bromate solution was added with the formation upon heating of a second, though smaller, crop of crystals. The supernatant solution was again transferred to a clean capillary cone to which 7 microliters of 4 molar sodium nitrate, 4 molar sodium acetate solution was added. A fine, granular precipitate containing *ca.* 15 micrograms of  $\text{Np}^{237}$  soon formed which occupied a volume of 0.01 microliter after centrifugation. The supernatant solution was removed and the precipitate sealed off in the capillary for X-ray diffraction analysis.

After an X-ray picture was obtained the capillary was opened and the crystals were washed twice with a 2 molar sodium nitrate, 2 molar sodium acetate solution and dissolved in 1.5 microliters of 1 molar nitric acid. The acetate compound was reprecipitated by the same procedure. The solubility of the compound measured by radiometric assay of the supernatant solution shortly after precipitation was 0.2 gram liter<sup>-1</sup> in 2 molar sodium nitrate and 2 molar sodium acetate solution. The crystals were dissolved in 1.2 microliters of 0.5 molar nitric acid, 0.5 molar sodium nitrite solution to give a pale blue-green solution. Addition of ammonia to excess precipitated a very pale green material which was washed once with strong aqueous ammonia, and then dissolved in 1.2 microliters of 1 molar nitric acid. The neptunium was reprecipitated again by ammonia giving a definitely pale green precipitate. The purification procedure was completed by dissolving the precipitate in 0.25 microliter of 2 molar nitric acid giving a blue-green solution. Two portions of this solution were used for the specific activity determination.

The ultramicro weighings were made on a Kirk-Craig quartz torsion fiber balance with a precision of 0.02 microgram.<sup>7</sup> The torsion scale was calibrated by noting the number of degrees of twist in the fiber required to bring the balance beam to the zero point with a 300 microgram piece of platinum on one of the pans. The scale has been found to be linear over this range. The platinum piece was weighed to a precision of  $\pm 0.6$  microgram on an Ainsworth type FDJ micro balance. The micro balance rider used for weighing was calibrated against a U. S. Bureau of Standards certified one milligram weight, accurate to  $\pm 0.5\%$ . Two flat 5 mm. platinum plates made to fit on the Kirk-Craig balance pan were heated at 800–1000° to constant weight. Roughly equal volumes of the neptunium nitrate solution were placed on the plates and evaporated to dryness under a heat lamp; the plates were then ignited in a muffle furnace at 800° to constant weight. This process required about thirty hours. The plates were counted in the 50% geometry  $\alpha$ -particle counter between each ignition to verify that no loss of neptunium was occurring, and after the final ignition each plate was counted to a probable accuracy of  $\pm 0.5\%$  (so-called 0.9 error).

### Results

An X-ray diffraction analysis of the ignited neptunium hydroxide was made by W. H. Zachariasen who reported<sup>8</sup> that the preparation contained neptunium dioxide,  $\text{NpO}_2$ , based on the fact that the diffraction pattern obtained showed isomorphism with the dioxides of thorium, uranium and plutonium. This evidence established a plus four oxidation state for neptunium, and conditions under which a neptunium compound of a definite

(7) P. L. Kirk, R. Craig, J. E. Gullberg and R. Q. Boyer, *Anal. Chem.*, **19**, 427–9 (1947).

(8) W. H. Zachariasen, *Plutonium Project Record*, Vol. XIVB, Nos. 20.7, 20.8 (1948); Symposium on Chemistry of Transuranium Elements, 1948 Spring Meeting, American Chemical Society, Chicago, Illinois; *Phys. Rev.*, **73**, 1104 (1948).

composition could be obtained were now presumably known. Zachariasen also reported a large percentage of platinum in the neptunium dioxide preparation. This platinum contamination was undoubtedly caused by the fuming operation prior to precipitation of the hydroxide, since solutions containing hydrobromic acid corrode platinum. The following data on the crystal structure of the dioxide are taken from Zachariasen's memorandum:

The crystal is a cubic, face-centered structure containing four molecules per unit cell. The lattice constant is  $5.42 \pm 0.01$  Å. The calculated density is  $11.14$  g. (cc.)<sup>-1</sup>. The oxide has the fluorite structure with 8 oxygen atoms about each neptunium atom. The distance Np-O is  $2.35$  Å.

The lattice constant, density and neptunium-oxygen distance fall between the values of the corresponding constants for the dioxides of uranium and plutonium.

An excellent X-ray diffraction pattern of the acetate preparation was obtained by Zachariasen and isomorphism with sodium uranium (VI) dioxytriacetate was established,<sup>8</sup> confirming the belief that neptunium has a plus six oxidation state. The neptunium compound, therefore, is taken to be sodium neptunium (VI) dioxytriacetate,  $\text{NaNpO}_2(\text{O}_2\text{C}_2\text{H}_3)_3$ . The  $\text{NaXO}_2(\text{O}_2\text{C}_2\text{H}_3)_3$  type of compound has a cubic structure. The lattice constant for the neptunium compound is  $10.659 \pm 0.002$  Å. and the calculated density is  $2.556$  g. (cc.)<sup>-1</sup>. The lattice constant and density are intermediate in magnitude between the corresponding constants for the uranium and plutonium compounds. The precipitate appeared white to pink under incandescent illumination and green under white fluorescent illumination or daylight.

The Table contains the experimental data and calculated values from the specific activity determination. The composition of the weighed neptunium preparation was assumed to correspond to the formula  $\text{NpO}_2$ , the neptunium content in micrograms being calculated from stoichiometrical equivalence with an atomic weight of 237.0 for  $\text{Np}^{237}$ . The observed  $\alpha$ -particle activities as counts per minute were corrected for resolution loss in the counter ( $0.8\%/1000$  counts min.<sup>-1</sup>) and for an assumed self absorption loss of  $\alpha$ -particles in the samples of  $0.5\%$  since the sample densities were *ca.*  $0.1$  mg. (cm.<sup>2</sup>)<sup>-1</sup>. The values are given in the table as counts minute<sup>-1</sup> microgram<sup>-1</sup> of  $\text{Np}^{237}$  as element. The specific activity was calculated as disintegrations minute<sup>-1</sup> microgram<sup>-1</sup> of  $\text{Np}^{237}$  by assuming a  $52\%$  counting yield for  $\text{Np}^{237}$   $\alpha$ -particles on platinum in the  $50\%$  geometry alpha-particle counter. The half-life,  $T_{1/2}$ , was calculated from its relation to the decay constant,  $\lambda$ , given by

$$T_{1/2} = 0.693/\lambda$$

$\lambda$  may be determined using the appropriate units from the first order equation for decay

$$dN/dt = \lambda N$$

where  $dN/dt$  = disintegration rate per minute of  $N$  atoms.

SPECIFIC ACTIVITY AND HALF-LIFE OF  $\text{Np}^{237}$

$\text{NpO}_2$ , μg	$\text{Np}^{237}$ , μg	Counts min. <sup>-1</sup> μg <sup>-1</sup>	Specific activity	$T_{1/2} \times 10^{-6}$ yr.
3.82	3.37	787	1513	2.213
3.75	3.30	793	1525	2.195

The average values for the specific counting rate, specific activity, and half-life are  $790$  counts minute<sup>-1</sup> microgram<sup>-1</sup>,  $1520$  disintegrations minute<sup>-1</sup> microgram<sup>-1</sup> and  $2.20 \times 10^6$  years. The two determinations are in agreement to  $0.8\%$  and the probable maximum counting and weighing error was calculated from estimates of the individual counting and weighing errors to be  $0.9\%$ .

### Discussion

Several possible sources of error in the determination of the specific activity and half-life of  $\text{Np}^{237}$  can be emphasized from the point of view of more recently acquired evidence. The accuracy of the determination is dependent in part upon the validity of the assumption of a definite, known composition for the weighed material. It was assumed that the isomorphism of the neptunium oxide with the dioxides of thorium, uranium and plutonium indicated the exact composition  $\text{NpO}_2$ , and, furthermore, that the oxide prepared under similar conditions for weighing was also  $\text{NpO}_2$ . It now appears that we cannot state with certainty that the composition corresponded precisely to the formula  $\text{NpO}_2$ . Brewer, Bromley, Gillis and Lofgren<sup>9</sup> point out that the oxides of uranium, neptunium, and plutonium may be expected, in general, to form solid solutions of variable composition. The X-ray diffraction patterns of these oxides may not, therefore, be accepted as *a priori* evidence for definite composition. In the absence of chemical analytical data, the X-ray diffraction evidence permits us to say only that an oxide phase was prepared of the approximate composition  $\text{NpO}_2$ .

An additional uncertainty was introduced in the preparation of the oxide for the specific activity determination. The original neptunium dioxide for X-ray diffraction, it will be noted, was prepared by igniting a tan hydroxide in which the neptunium was in the plus four state.<sup>10</sup> The green "hydroxide" precipitated prior to the specific activity determination, however, came from a 1 molar nitric acid solution containing nitrite in which it is now known that  $\text{Np(V)}$  is the stable form.<sup>10</sup> It is quite certain that the green "hydroxide" is a compound of  $\text{Np(V)}$ . Dissolution of this compound in nitric acid yields a solution of  $\text{Np(V)}$ . The question arises as to the composition of the oxide formed by drying the  $\text{Np(V)}$  solution and igniting

(9) L. Brewer, L. A. Bromley, P. W. Gillis and N. L. Lofgren, Atomic Energy Commission Report MDDC-1543 (September 20, 1945); *Plutonium Project Record*, Vol. XII.

(10) L. B. Magnusson, J. C. Hindman and T. J. LaChapelle, *Plutonium Project Record*, Vol. XIVB, No. 15.1 (1948).

the residue. The appearance of the ignited residues on the specific activity plates was identical with that of the original neptunium dioxide. It is also known that Np(V) is oxidized to Np(VI) in hot, strong nitric acid. Drying the solution, therefore, probably produced initially a hydrated Np(VI) nitrate. If our assumption is correct, this compound must decompose at 800° to give a composition approaching that of neptunium dioxide. A trend observed in the heating to constant weight tends to confirm this idea. The samples were first dried at low temperatures and then fired for an hour at 800°. The weights of the samples at this point were 0.1–0.2 microgram larger than the final constant weights obtained upon long firing. Weight losses of this order of magnitude correspond to that expected for the loss of 0.5–1.0 gram atom of oxygen per gram molecule of neptunium oxide. The error introduced by a deviation of the true composition from NpO<sub>2</sub> is relatively small. If the weighed oxide had the true composition NpO<sub>2.5</sub>, for example, the calculated value for the half-life would be 3% high. It is likely that any actual deviation would be of smaller magnitude.

The purity of the weighed neptunium oxide is dependent upon the efficiency of the purification process with regard to removal of all other non-volatile substances. The double precipitation of NaNpO<sub>2</sub>(O<sub>2</sub>C<sub>2</sub>H<sub>3</sub>)<sub>3</sub> should have reduced the lanthanum content to a negligible quantity. The double precipitation of the green "hydroxide" from ammonia solution likewise should have removed all sodium and sulfate so that the nitrate solution placed on the platinum plates probably contained, besides the neptunium nitrate, only nitric acid and a small amount of ammonium nitrate. The ignition at 800° would leave on the plate only the dioxide. A gravimetric determination of the non-volatile matter in the 1 molar nitric acid used to dissolve the "hydroxide" precipitates showed that the error from this source was entirely negligible. Although an accurate limit cannot be placed on the non-volatile impurities present, it is believed that the error from this source is considerably less than that connected with the radiometry of the determination.

A possible large error is in the purity of the Np<sup>237</sup> with respect to traces of other  $\alpha$ -emitting isotopes. To place a limit on this error, an aluminum absorption measurement of the  $\alpha$ -particles from one of the plates was undertaken by A. H. Jaffey who was able to report that at least 95% of the  $\alpha$ -particles was absorbed by a thickness of aluminum equivalent to the extreme range of Np<sup>237</sup>  $\alpha$ -particles. If no isotope emitting  $\alpha$ -particles of shorter range

than those of Np<sup>237</sup> were present, the lower limit of purity of the measured radiation is set at 95%.

Two other possible sources of appreciable error are the self absorption of  $\alpha$ -particles in the samples themselves and the somewhat uncertain counting yield in the 50% geometry counter. Some self absorption undoubtedly occurred since the samples had a finite surface density. It is believed, however, that the applied correction of 0.5% essentially compensates for the absorption. A value of 52.9% for the counting yield was obtained at one time, but this determination is not believed to be sufficiently accurate to justify its application. More recent comparisons of the counting rates of accurate aliquots of Np<sup>237</sup> on quartz and platinum plates indicate that the counting yield on platinum is very near 52%, if the assumption is made that the counting yield on quartz is 50%.

Some rough checks on the specific activity were obtained in later work on the milligram scale by an independent method involving titrations with standard oxidizing and reducing agents.<sup>9</sup> It is believed that an error greater than 5% in the specific activity value would have been detected in these titrations. Thus, the values for the specific activity and half-life obtained from the ultramicro weighings of the dioxide samples are probably accurate to within 5%.

**Acknowledgment.**—The inception of and opportunity for this work is the result of the early and sustained interest of Professor G. T. Seaborg in the chemistry and isotopes of neptunium. Invaluable aid in a number of the experimental details was obtained from B. B. Cunningham and J. C. Hindman. This work was done under Contract No. W-7401-eng-37 at the Metallurgical Laboratory at the University of Chicago under the auspices of the Manhattan District.

### Summary

Element 93, synthesized by nuclear reactions, was isolated for the first time in visible amount in the form of pure compounds.

Plus four and plus six oxidation states for neptunium were established by the preparation and X-ray identification of neptunium (IV) dioxide and sodium neptunium (VI) dioxytriacetate.

By the method of weighing and radiometric assay of samples of neptunium dioxide, the specific  $\alpha$ -activity of Np<sup>237</sup> was calculated to be 1520 disintegrations minute<sup>-1</sup> microgram<sup>-1</sup> with the corresponding half-life of 2.20 × 10<sup>6</sup> years. The values are estimated to be accurate to within 5%.

BERKELEY, CALIFORNIA

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