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The First Isolation of Element 93 in Pure Compounds and the Determination of the Half-Life of 93 Np237

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Publication Date
1948-07-01

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

By L. B. Magnusson and T. J. LaChapelle

Special Review of Declassified Reports
Authorized by USDOE JK Bratton
Unclassified TWX P182206Z May 79

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

By L. B. Magnusson and T. J. LaChapelle

Department of Chemistry and Radiation Laboratory

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Abstract

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, NpO_2, and sodium neptunium(VI) dioxytriacetate. By the method of weighing and radiometric assay of samples of NpO_2, the specific alpha activity of Np^{237} was calculated to be 1520 disintegrations min^{-1} $microgram^{-1}$ with the corresponding half-life of 2.20×10^6 years.

To be published at a later date.

Contract No. W-7401-eng-37

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[1] This work was done on the wartime Plutonium Project at the Metallurgical Laboratory of the University of Chicago.

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

By L. B. Magnusson and T. J. LaChapelle
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Wahl and Seaborg[2], who first detected the alpha particles from $_{93}Np^{237}$ in April, 1942, found a value of 3×10^6 years, considered to be accurate within a factor of two, for the half-life of the isotope by measuring the ratio of 7-day U^{237} activity to that of its daughter, Np^{237}. The corresponding counting yield of 500 alpha counts minute^{-1} microgram^{-1} in the 50% geometry alpha counter was used in subsequent determinations of mass by radiometric assay. A more precise and corroborating value for the half-life and specific activity was desired for accurate standardization of the radiometric method of mass determination and because of the fundamental importance of this constant. The method of direct weighing on the ultra-micro scale of a neptunium compound and measurement of its disintegration rate by alpha particle emission was first attempted by Cunningham and Werner[3]

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[1] This work was done on the wartime Plutonium Project at the Metallurgical Laboratory of the University of Chicago.

[2] Wahl, A. C., and G. T. Seaborg, Plutonium Project Record, Vol. 14B No. 1.5 (1948); Phys. Rev. May 1, 1948 issue (Submitted on April 14, 1942).

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

and Cunningham[4] 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 6×10^6 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 could be acquired from experiments with trace concentrations. The discoverers of element 93, McMillan and Abelson[5] showed with trace concentrations of the 56 hour isotope, 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 ultra-micro 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 $NaXO_2(OOCCH_3)_3$ 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 weigh-

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[4] Cunningham, B. B., Manhattan Project Report, CN-991, Oct. 9, (1943).

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

able quantities of Np^{237}, the only known isotope of neptunium which is sufficiently long-lived to allow convenient separation of practical amounts. Seaborg and Wahl[6] 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 +6 state and plutonium remains in the +4 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

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[6] Seaborg, G. T., and A. C.Wahl, Plutonium Project Record Vol. 14B, No. 1.6 (1948).

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. 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 usually 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 Np^{237} from natural uranium by neutron bombardment, the alpha activity of Np^{237} is associated with at least a hundred-fold larger alpha activity of 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 56-hour Np^{239} (beta emitter) activity at the beginning of a separation. Quantitative recovery of the added Np^{239}, along with the Np^{239} which may be present in appreciable amount in the bombarded material depending upon the time of decay after bombardment, assures complete recovery of the Np^{237}. Purity of the isolated Np^{237} to within a few percent with regard to 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 Np^{239} decay). Two different sources yielded approximately equal amounts of 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 by the cyclotron at Washington University, St. Louis, Missouri. The yield of neptunium element in this bombardment was about 2 parts per billion parts of uranium by weight. The other source was essentially uranium pile material.

Experimental

Observation and manipulation of micro- and ultramicro materials and solutions was done with the aid of stereoscopic microscopes and suitable micro manipulators. Centrifugation was used in separating precipitates from solutions. All solutions containing hydrofluoric acid were held in platinum or waxed glass vessels, and transferred with wax-coated pipettes.

The Np^{237} was freed from 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 H_2SO_4 and evaporating to dryness. The mixed sulfates were dissolved in 0.3 ml of 1 $\underline{M}$ H_2SO_4 in a 0.5 ml waxed centrifuge cone and $KBrO_3$ added to 0.1 $\underline{M}$. After one-half hour of standing at room temperature, the solution was made 1 $\underline{M}$ in HF, precipitating LaF_3 and leaving the neptunium in solution. The suspension was centrifuged to separate the LaF_3. The supernatant solution was transferred, together with a 50 microliter water wash of the LaF_3, to a 0.5 ml roundbottom platinum crucible designed for convenient centrifuging. SO_2 was added until all the bromate was reduced to bromide as indicated by the resultant colorless solution, which was then evaporated to the appearance of white SO_3 fumes. The residue was dissolved in 150 microliters of ca. 0.3 M SO_2 solution and aqueous ammonia added to ca. 6 M. A light brown precipitate was obtained, the solubility of which on standing overnight was 0.12 gram liter^{-1}. The precipitate, which was presumed to be a hydroxide or hydrated oxide of a reduced state of neptunium, was washed twice with 150 microliter portions of a 0.3 M SO_2-6 M NH_3 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 caused a considerable decrease in the volume of the neptunium preparation 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 neptunyl acetate a total of 30 micrograms of Np^{237} was recovered from the oxide preparation and other sources. Considerable loss was sustained in the recovery operations which was attributed to unknown chemical properties. The ignited oxide was found to be very resistant to attack by acids and much of it was not recovered. Another source of difficulty was platinum contamination caused by heating solutions of HBr and H_2SO_4 in platinum dishes. Precipitation of neptunium hydroxide by ammonia from these solutions also resulted in the precipitation of platinum compounds which were more or less insoluble in H_2SO_4 solutions. The bulk and large liquid hold-up of these precipitates was a serious handicap to the ultra-micro operations. 30 micrograms was eventually collected as a fluoride precipitate with 50 micrograms of lanthanum, which was fumed to dryness with H_2SO_4. The residue was dissolved in 100 microliters of 0.5 M H_2SO_4 and transferred to a capillary centrifuge cone. To reduce the volume of the solution, 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 twice with 50 microliter portions of water by stirring with a fine platinum wire and centrifuging. To dissolve the hydroxide precipitate, 6 microliters of 1 M H_2SO_4 were 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 M $KBrO_3$ solution added. The cone was placed in a water bath at 80°C and immediately colorless crystals precipitated while the solution turned very pale green. The colorless precipitate was thought to be a potassium lanthanum sulfate. 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 $KBrO_3$ 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 M $NaNO_3$-4 M $NaOOCH_3$ solution was added, yielding concentrations of about 2 M $NaNO_3$ and 2 M $NaOOCH_3$. A fine, granular precipitate containing ca. 15 micrograms of 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 M $NaNO_3$ - 2 M $NaOOCCH_3$ solution and dissolved in 1.5 microliters of 1 M HNO_3. Addition of 1.5 microliters of 4 M $NaNO_3$ - 4 M $NaOOCCH_3$ solution failed to reprecipitate the neptunium possibly because it had been reduced by traces of impurities in the reagents. Sulfur dioxide gas was added for a few minutes resulting in the formation of a white precipitate which was not identified. Radiometric assay showed the neptunium to be still in solution. The solution was made ammoniacal, precipitating a buff colored neptunium hydroxide which was washed with two portions of water. The hydroxide was dissolved in 2.5 microliters of 1 M H_2SO_4 - 0.15 M $KBrO_3$ solution, yielding a pale green solution. To assure complete oxidation the capillary was placed in a water bath at 80°C for an hour. 2.5 microliters of 4 M $NaNO_3$ - 4 M $OOCCH_3$ solution was added to give concentrations of 2 M $NaNO_3$ and 2 M $NaOOCCH_3$. The characteristic, small crystals of the neptunium compound again formed and were centrifuged. The solubility of the compound measured by radiometric assay of the supernatant solution shortly after precipitation was 0.16 gram $liter^{-1}$. The crystals were dissolved in 1.2 microliters of 0.5 M HNO_3 - 0.5 M $NaNO_2$ 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 1 M HNO_3. 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 microliters of 2 M HNO_3 giving a blue-green solution. Two portions of this solution were used for the specific activity determination.

The ultra-micro weighings were made on a Kirk-Craig quartz torsion fiber balance with a precision of 0.02 microgram.[7]

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[7] Kirk, P. L., R. Craig, J. E. Gullberg, and R. Q. Bayer, Anal. Chem. 19, 427-9 (1947).

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 ±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 ± 0.5%. Two flat 5 mm. platinum holders 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 30 hours. The plates were counted in the 50% geometry alpha counter between each ignition to make certain that no loss occurred and after the final ignition each plate was counted to a probable accuracy of ± 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[8] that the preparation consisted essentially of neptunium dioxide, NpO_2, based on the fact that the diffraction pattern obtained showed isomorphism with UO_2 and PuO_2. This evidence established a (IV) oxidation state for neptunium, and conditions under which a neptunium compound of a definite composition could be obtained were now known. Dr. Zachariasen also reported a large percentage of platinum in the NpO_2 preparation. This platinum contamination was undoubtedly caused by

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[8] Zachariasen, W. H., Plutonium Project Record, Vol. 14B, Nos. 20.7, 20.8 (1948).

the fuming operation prior to precipitation of the hydroxide, since solutions containing hydrobromic acid corrode platinum to some extent. The following data on the crystal structure of NpO_2 are taken from Dr. Zachariasen's memorandum:

The crystal is a cubic face-centered structure containing four molecules per unit cell. The lattice constant is 5.42 ± 0.01Å. The calculated density is 11.14 $gm.cc.^{-1}$. The oxide has the fluorite structure with eight oxygen atoms about each neptunium atom. The distance Np - O is 2.35Å.

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[8], confirming the belief that neptunium has a +6 oxidation state. The neptunium compound, therefore, is taken to be sodium neptunium(VI) dioxytriacetate, $NaNpO_2(OOCCH_3)_3$. The $NaXO_2(OOCCH_3)_3$ type of compound has a cubic structure. The lattice constant for the neptunium compound is 10.659 ± 0.002 angstrom units and the calculated density is 2.556 $gm.cc.^{-1}$. 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 NpO_2, the neptunium content in micrograms being calculated from stoichiometrical equivalence. The observed alpha activities as counts per minute were corrected for resolution loss in the counter (0.8%/100 c/m) and for an assumed self absorption loss in the samples of 0.5% since the sample densities were ca. 0.1 mgm/cm^2. The values are given in the table as counts minute^{-1} microgram^{-1} of Np^{237} as metal. The specific activity was calculated as disintegrations minute^{-1} microgram^{-1} of Np^{237} by assuming a 52% counting yield for Np^{237} alpha particles on platinum in the 50% geometry alpha counter. The half-life, $T_{1/2}$, was calculated from its relation to the decay constant, λ, given by

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

λ may be determined using the appropriate units from the first order equation for decay,

$$\frac{dN}{dt} = \lambda N$$

where $\frac{dN}{dt}$ = disintegration rate per minute of N atoms.

Table 1

Specific Activity and Half-Life of Np^{237}

NpO_2 µg.	Np^{237} µg.	Counts min^{-1} µg.$^{-1}$	Spec. Act.	$T_{1/2}$ x 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^{-1} microgram^{-1}, 1520 disintegrations minute^{-1} microgram^{-1} and 2.20 x 10^6 years. The two determinations are in agreement to 0.8% and σ for the sum of the absolute counting and weighing errors was calculated from estimates of individual errors to be 0.9%.

Discussion

Several possible sources of error in the determination of the specific activity and half-life of Np^{237} can be emphasized from the point of view of more recently acquired evidence. The original neptunium dioxide, it will be noted, was prepared by igniting a tan hydroxide in which the neptunium was certainly in the +4 state. The green "hydroxide" precipitated prior to the specific activity determination, however, came from a 1 M HNO_3 solution in which it is now known that Np(V) is the stable form. It is quite certain that the green "hydroxide" is a compound of Np(V). An x-ray diffraction pattern was obtained from a later preparation of this compound, but the structure has not been ascertained. "Hydroxide" precipitates made from Np(VI) solutions are consistently very dark brown. The question arises as to the composition of the oxide formed by drying a Np(V) solution and igniting the residue. The appearance of the ignited residues on the specific activity plates was identical with that of NpO_2. It is believed that Np(V) is unstable in high acid concentration by reason of a high hydrogen ion dependence of the disproportionation to Np(IV) and Np(VI) and probable complexing of Np(IV) and Np(VI) at high anionic concentrations, so that very little Np(V) should remain in the residue from a dried nitrate solution. If such were the case, the Np(VI) nitrate formed by disproportionation could reduce to NpO_2 upon ignition of the nitrate. Any Np(V) nitrate remaining could likewise reduce to the dioxide. Strong supporting evidence that the compound weighed was actually NpO_2 and not a higher oxide comes from recent work by Fried and Davidson[9] who ignited a neptunium residue from a nitrate solution under a pressure of 28 atmospheres of oxygen. The resulting sample gave principally the x-ray diffraction pattern of NpO_2.

The purity of the weighed neptunium dioxide is dependent upon the efficiency of the purification process with regard to removal of all other

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[9] Fried, S., and N. R. Davidson, Manhattan Project Report CN-2689, Feb. 27 (1945).

non-volatile substances. The double precipitation of $NaNpO_2(OOCCH_3)_3$ 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°C would leave on the plate only the dioxide. A gravimetric determination of the non-volatile matter in the 1 M 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 those connected with the radiometry of the determination.

A possible large error is in the purity of the Np^{237} 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^{237} alpha particles. If no isotope emitting alpha particles of shorter range than those of Np^{237} 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% compensates for most of 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^{237} 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%. The self absorption and counting yield errors may be compensating.

Some rather 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. It is believed that an error greater than 5% in the specific activity value would have been detected in these titrations. The values for the specific activity and half-life obtained from the ultra-micro measurements are very probably accurate to within 5%.

Acknowledgement

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 many 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, NpO_2, and sodium neptunium(VI) dioxytriacetate.

By the method of weighing and radiometric assay of samples of NpO_2, the specific alpha activity of Np^{237} was calculated to be 1520 disintegrations min^{-1} $microgram^{-1}$ with the corresponding half-life of 2.20×10^6 years.

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