# Some Experiments in the Preparation of the Isotopes U^{239} and Np^{239}

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Some years ago, Starke [1] succeeded in an attempt to obtain a Szilard-Chalmers concentration of the uranium isotope U^{239} by means of the uranyl benzoylacetonate. He had a good concentration factor and his product appears to have possessed a high degree of purity. However, it was not possible to irradiate the compound in solution owing to the rapid exchange between the free, activated uranium ions and the uranium in the complex. In this case the compound, dissolved in the treatment after irradiation, had to be reprecipitated and dried before it could be used again. For the same reason, it was necessary for the activated uranium to be carried down very rapidly by adsorption when the irradiated compound was dissolved.

Duffield and Calvin [2] have made Szilard-Chalmers experiments with metal salts of salicylaldehyde-*o*-phenylenediimine. They achieved good results with the copper complex and mention that they also obtained good results with uranyl salicylaldehyde-*o*-phenylenediimine:
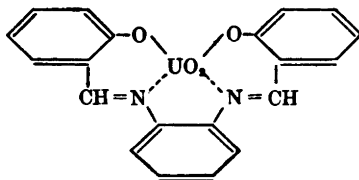
In the present paper some experiments are described, which have been performed with this uranium compound in order to obtain a sample of U^{239} and Np^{239} with high specific activity and as free from other activities as possible.

SZILARD-CHALMERS CONCENTRATION

In their copper experiments, Duffield and Calvin [2] obtained the best result when the complex was irradiated in pyridine solution and this solution was diluted with aqueous acetic acid after the addition of a small amount of copper salt as carrier. The precipitated complex was filtered off and the copper ions in the filtrate were precipitated as CuS.

In the beginning an attempt was made to use a similar method in the case of uranium. After the irradiation with slow neutrons a small amount of an aqueous solution containing a mixture of $U(SO_4)_2$ and UO_2SO_4 was added, and the pyridine solution diluted with ten times its volume of 15 % acetic acid. According to γ-activity measurements about 80 % of the activity accompanied the filtrate. Thus there is only little, if any, exchange between the complex and the liberated uranium.

The difficulty in this method is to find a method for the precipitation of the small quantity of uranium in the large filtrate corresponding to the precipitation of CuS. Several precipitation methods were tried under the appropriate conditions: with Na_2HPO_4, oxine, ammonia and various organic bases (iron was added in order to facilitate the precipitation) and cupferron. Since it was not improbable that the liberated U^{239} was in the quadrivalent state, in the first two cases oxidation was performed with $KBrO_3$. In no instance were both of the following two requirements fulfilled: the uranium (and if possible the neptunium also) should be precipitated with a good yield, and it should be precipitated free from the complex (or its decomposition products formed after the irradiation) still remaining in the aqueous filtrate. The instability of the complex and the buffering action of the solution were serious difficulties.

When minute amounts of a solution containing a mixture of $U(SO_4)_2$, UO_2SO_4, Na_2SO_4, and some H_2SO_4 are added to the pyridine solution, a gelatinous uranium-containing precipitate is formed. In some experiments the pyridine solution was shaken with small amounts of such a precipitate during the irradiation in a shaking device surrounded by paraffin and placed near the D-tank of the cyclotron. After the irradiation the precipitate was filtered off and washed with pyridine. In this manner it was possible to capture more than 50 % of the activity, but the use of uranium carrier reduced the specific activity obtainable.

In order to avoid uranium as a carrier it was attempted to carry down the activity by means of other precipitates, for instance by the addition of Li_2SO_4 solution, but the yeild was very poor.

Adsorption on charcoal after the irradiation was found to be the best method. Though somewhat irregular, yields as high as 80 % have been obtained.

SEPARATION FROM NATURAL DECAY AND FISSION PRODUCTS

Various experiments were performed in order to purify the product resulting from the adsorption on the precipitate containing uranium, but since the results were not very good and the method was abandoned, they are not discussed here.

The most important natural β-emitting decay product in a uranium preparation, the age of which is some months, is UX_1. Its activity is weak, but after some minutes it is already in equilibrium with its decay product UX_2, the β-radiation of which is rather penetrating. In the present case it is possible to handle both products as if the radiation were due to the Th isotope UX_1.

The main part of the UX_1 was removed by adsorption on charcoal immediately before the irradiation. However, a quantitative separation was not conveniently achieved in this way, and the remainder had to be removed in the treatment after the irradiation.

In the purification of the product advantage was taken of the (not very common) property possessed by uranium and neptunium [3, 4] of forming soluble complex carbonates with an excess of $(NH_4)_2CO_3$, irrespective of whether their valency is IV or VI. The charcoal was shaken with saturated $(NH_4)_2CO_3$ solution, and in order to provide a carrier for the insoluble carbonates some $Ba(NO_3)_2$ was added.

The Th isotope UX_1 will probably follow U and Np since Th forms soluble complex carbonates. Among the more frequent fission products that might be feared to go the same way are Zr and Ce. These three, however, form iodates, insoluble in nitric acid solution (Ce as Ce^{IV}). (As to Y, see below; Cb seems to give no trouble.) In order to avoid simultaneous precipitation of Np, it is necessary to ensure that it has the valency VI before the addition of iodate.

According to McMillan and Abelson [4], and to Strassmann and Hahn [3], $KBrO_3$ in strong nitric acid solution has the correct oxidizing power to convert Np^{IV} to Np^{VI}. Hence the following procedure was followed.

The carbonate filtrate was acidified with strong nitric acid and the carbon dioxide boiled off. Some $Ce(SO_4)_2$ was added and the mixture boiled with $KBrO_3$. After cooling KIO_3 was added; generally a drop of $Ce(SO_4)_2$ solution was necessary to start the precipitation. The iodate precipitate was filtered off.

In preliminary experiments there was some evidence of a 6—10 hour activity, which later appeared to have a somewhat longer period, 11—12 hours (see below). However, it was first thought to belong to the fission product I^{135} [5], though it seemed strange that the iodine should appear in the product and not be expelled at an early stage of the treatment. It is a well-known fact that there is generally no exchange of iodine between I^- and IO_3^-.

It was therefore thought that if some KI was added to the filtrate, the iodine immediately liberated would ensure a carrier for the activity. The iodine could simply be boiled off. This course was adopted in the experiment, the decay curve of which is shown below. As was to be anticipated, this treatment was without effect.

Finally the solution was made ammoniacal. The residue of Ce, not precipitated by KIO_3, was sufficient as carrier for U and Np. The precipitate was washed thoroughly and ignited.

Alternatively, the precipitate may be dissolved in an acid if it is desired to make radiochemical investigations on neptunium, which may easily be separated from the inactive Ce.

EXPERIMENTAL *

Preparation of uranyl compound. The uranyl salicylaldehyde-o-phenylenediimine was prepared according to Pfeiffer et al.[6] When the complex was prepared from pure salicylaldehyde-o-phenylenediimine and pure uranyl acetate, it had a high degree of purity and no recrystallization was necessary. When prepared in this manner it contains one molecule of ethanol of crystallization.

Treatment before irradiation. 2 g of the uranyl compound is dissolved in 20 ml pyridine and shaken for 10 min. with 500 mg adsorption charcoal. The charcoal is filtered off by suction without washing. This treatment is repeated once.

Irradiation. The solution, which has been newly shaken with charcoal, is placed in the cyclotron behind about 3 cm paraffin near the internal beryllium target, which is bombarded with 6.5 MeV deuterons. The irradiation has usually been continued for 2—3 half-life periods of U^{239}.

Concentration of the activity. 100 mg adsorption charcoal is added to the irradiated solution, and the mixture is shaken for 5 min. The charcoal is filtered off by suction (the filtrate is saved for future experiments) and washed well with pyridine, which is finally sucked off.

Purification of the activity. The charcoal is transferred to a flask containing 5 ml saturated $(NH_4)_2CO_3$ solution. The flask is shaken for about one minute, a few drops of $Ba(NO_3)_2$ solution, corresponding to 5 mg $Ba(NO_3)_2$, are added, and the shaking is continued for some minutes. The charcoal is filtered off and washed with 2 ml saturated $(NH_4)_2CO_3$ solution. 3 ml HNO_3 is carefully added, and the CO_2 is boiled off. A few drops of a nitric acid solution of $Ce(SO_4)_2$, corresponding to some mg $Ce(SO_4)_2$, and subsequently about 10 drops of $N-KBrO_3$ are added to the boiling solution. The solution is cooled in ice water, and $Ce(IO_3)_4$ is precipitated by means of KIO_3 solution. Generally one or two drops of the $Ce(SO_4)_2$ solution are added at this point in order to facilitate the rapid precipitation of $Ce(IO_3)_4$. After some minutes' shaking the precipitate is filtered off without washing. Finally, the filtrate is made ammoniacal and boiled. The faint colourless precipitate is filtered off and washed with dilute ammonia.

If the preparation is to be used for radiochemical purposes, the precipitate on the filter may be dissolved in a small volume of acid. The only inactive material in this solution will be a minute amount of Ce, which may be removed by an appropriate method.

In the present case, where only the activity was to be measured, the filter was ignited. The weight of the residue was about 1 mg. The uranium content in the ash was not determined, but to judge from the faint colour of the ammonia precipitate and the ash it cannot have exceeded 10 %.

The process was completed in 40—45 min., counted from the end of the irradiation.

For the purposes of β-spectrography the tenfold amount of pyridine solution was irradiated. Ten times the amounts of charcoal given above were used, but the amounts of the other reactants were not more than doubled, except $Ba(NO_3)_2$, the amount of which was not increased. The residue was 2—3 mg.

Measurement of the activity [*]. In order to establish the yield in one of the large-scale experiments a sample of the original irradiated pyridine solution was saved and its γ-activity compared with that of the product. The result, 12 % yield, represents a lower limit since all fission products still remained in the pyridine together with U and Np.

The decay was followed by means of a Geiger-Müller tube with a 12 μ mica window. The sample was covered with a thin film of nitrocellulose. The Al absorption equivalent of the mica window, the air, the nitrocellulose and the self-absorption in the sample was calculated as 32 μ. The decay was followed by this absorption and by the addition of 27 and 59 μ Al, that is by the total absorption equivalents of 32, 59, and 91 μ Al respectively. The decay curves from a small-scale experiment (irradiation 46 min.) are shown in fig. 1 and fig. 2.

DISCUSSION OF RESULTS

In the present case, where the decay constants are far apart, it is possible to treat the consecutive activities as quite independent. Apart from U^{239} and Np^{239} the curves indicate the presence of a 11.8 hour activity, the radiation of which is rather penetrating (no influence of the difference in absorption could be detected). For physical and chemical reasons it seems most probable that this radiation originates from the fission product Y with a period of 10 hours (probable mass number 93)[5]. Only a detailed study will confirm this. However, the physical investigations (β-spectrographic studies by Slätis[7]) were not disturbed by this impurity, and radiochemical investigations on Np will also be possible without separation since after only 2 days the foreign
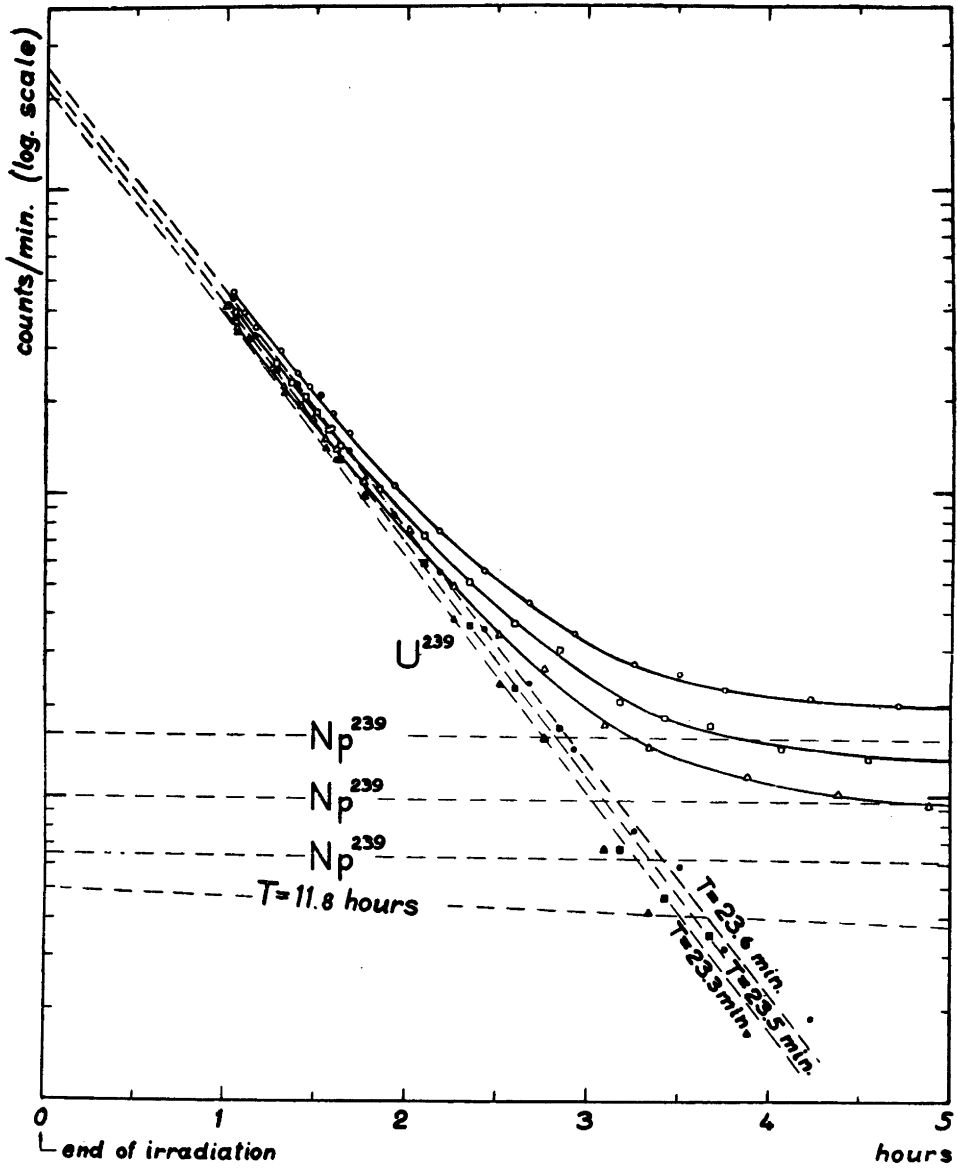
Fig. 1. Decay curves of $U^{239} + Np^{239}$ with 32, 59, and 91μ Al absorption equivalents (first 5 hours).

component of the activity is only about 3 % if measured with 30 μ Al absorption and still less with smaller absorption.

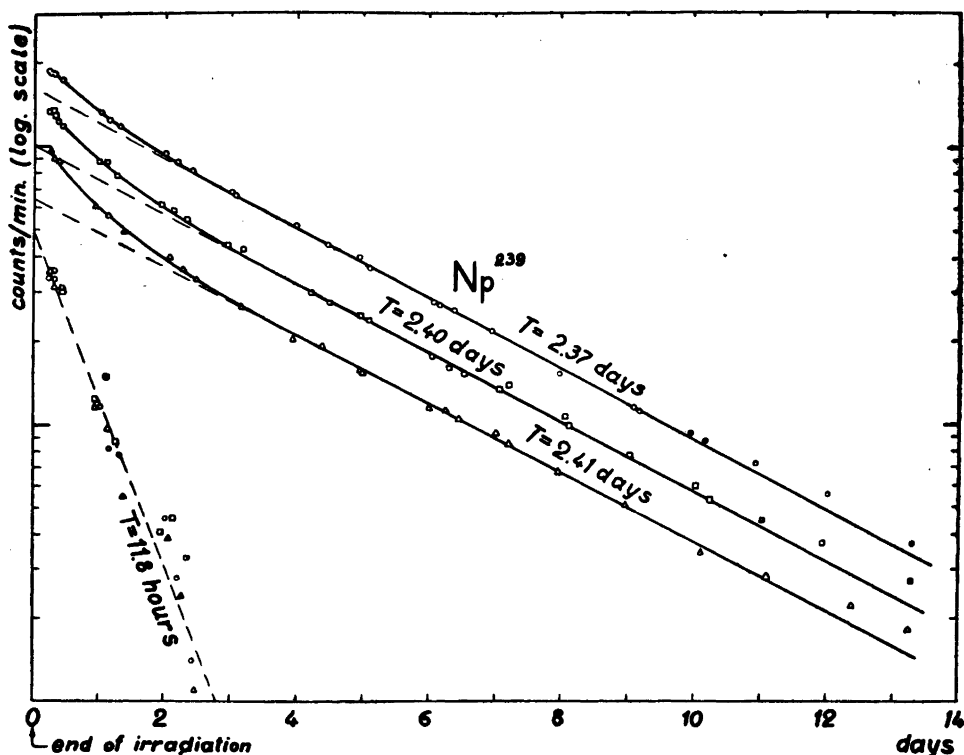At the ends of the curves there are certain indications of a longer period.

Fig. 2. Decay curves of U^{239} + Np^{239} with 32, 59, and 91μ Al absorption equivalents
(the values for the first 5 hours not represented).

The influence of the absorption on this radiation cannot easily be settled, and it may be due to traces of UX_2 or U^{237} (formed by fast neutrons) as in the case reported by Starke[1].

The mean values of the half-life periods are found to be 23.5 min. for U^{239} and 2.39 days for Np^{239}.

The yield in the entire process, determined as above, was 12 % or more. In a large-scale concentration 7.6 g U (calculated as the element) is used. The U content of the product must be less than 0.7 mg. This together with the yield gives a concentration factor of 10^3 or more.

In order to gain information about the behaviour during the chemical operations of the Np already formed, the (extrapolated) activities at the end of the irradiation were extrapolated to the absorption 0 as shown in fig. 3. For purposes of comparison the figure includes the absorption curve of Np^{239} obtained by Segrè[8], to a certain extent confirmed by Starke[1]. The curve obtained in the present investigation (almost unchanged throughout three
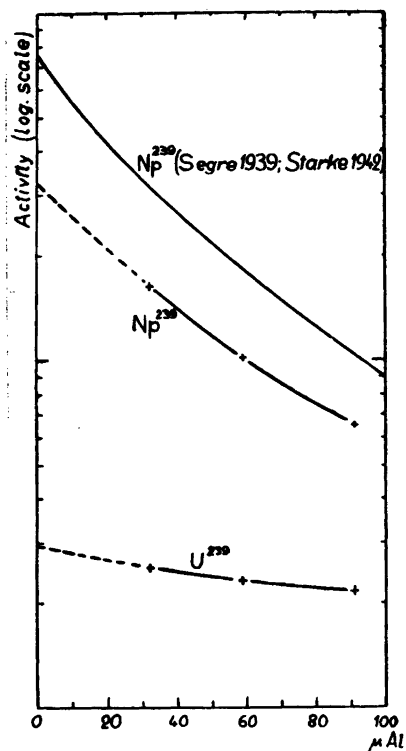
Fig. 3. Extrapolation of the (extrapolated) activities at the end of the irradiation to the absorption 0, compared with the absorption curve obtained by Segrè (confirmed by Starke).

half-life periods) corresponds to a somewhat smaller absorption coefficient than that found by Segrè.

If the extrapolation is performed as indicated in fig. 3, a ratio between the initial activities of Np and U of 1 : 89.8 is obtained, corresponding to an atomic ratio of about 1.60 : 1 if the period values 2.3 days and 23 min. are used. The theoretical atomic ratio (U + Np) : U after 46 min. uniform irradiation is 1.85. The extrapolation of the Np absorption curve is very uncertain, and if the strong curvature in the beginning of Segrè's curve is correct, a higher experimental value would have been obtained. The lower limit of the self-absorption in the sample has been used; an increase here will act in the same direction.

It therefore seems as if U and Np are concentrated in about the same proportions.

SUMMARY

The technique, proposed by Duffield and Calvin[2], of employing uranyl salicylaldehyde-o-phenylenediimine for the Szilard-Chalmers process on uranium, has been developed, and the method applied to the preparation of U^{239} and Np^{239}. A method for the purification of the product is described. The overall yield in the process is at least 12 %, about the same for U and Np, and the concentration factor at least 10^3. The product is somewhat contaminated by a 12 hour activity, which, however, does not influence physical and chemical applications.

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