An Unsuccessful Search for Transuranic Elements

In 1934 Fermi[1] and his associates after bombarding uranium with neutrons found that the radioactive substances produced were not any of the elements between lead and uranium. They concluded that these bodies very probably were transuranic. This opinion was maintained also by subsequent investigators, especially by Hahn, Meitner and Strassmann, until the recent discovery[2] of the fission process in uranium presented some completely new viewpoints.

It has been recognized by Abelson[3] and others that some of the so-called transuranics are tellurium, iodine and other elements well below uranium. It remained to be proved whether there are any transuranics at all.

From a purely chemical standpoint this problem is obviously extremely difficult since one has to separate from *all* the elements some substances whose properties can only be guessed on the basis of the periodic system. A better line of approach is offered by the observation due to McMillan[4] that the activity produced in a very thin uranium layer by neutrons is of two types: recoiling, containing only fission products, and nonrecoiling containing a 23-minute period and a period of about two days. The cross sections for formation of these are about equal when the uranium is close to the neutron source, with paraffin behind it.

Since transuranics would certainly be found in the nonrecoiling fraction a detailed investigation of these two activities was made. The first is due to a well-known radioactive isotope of uranium, as was easily shown by chemical experiments. The second is not the daughter of the first as shown by a direct experiment in which the decay of the 23-minute activity was followed long enough to rule out the possibility of its tailing into the longer period. It was thought interesting, then, to establish the chemical nature of the second activity. Thin layers of ammonium uranate of a few millimeters air equivalent were irradiated with about 500μ amp. hours of 8 Mev D+Be neutrons close to the target of the Berkeley cyclotron. The nonrecoiling activity showed practically only two periods, the uranium mentioned above and a 2.3-day period due to a rare earth. This second chemical identification is shown by the fact that this activity does not precipitate with hydrogen sulfide in $6n$ or $0.3n$ hydrochloric acid or acetic acid solution using rhenium or lead as a carrier, that it is precipitated from acid solution by hydrofluoric acid or oxalic acid with lanthanum as a carrier, that it is precipitated quantitatively by potassium sulfate in neutral solution and by ammonia. Uranium can be easily separated from the 2.3-day activity by precipitating it in the presence of lanthanum with hydroxyquinoline in acetic acid solution; protoactinium can be separated by zirconium phosphate precipitation in $3n$ hydrochloric acid solution, thorium by an iodate precipitation in nitric acid solution and finally MsTh 2, an actinium isotope, is separated by fractional precipitation of the oxalates in normal nitric acid solution with lanthanum as a carrier.

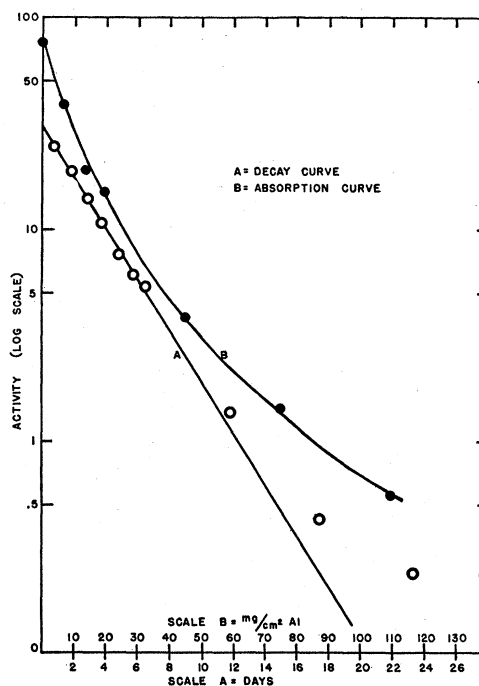In this last process the amount of oxalic acid was

FIG. 1. Decay curve of the activity and the absorption curve of electrons in aluminum.

regulated in such a way as to precipitate about half of the lanthanum in the first fraction and the other fraction upon neutralization of the solution with ammonia. The first fraction contained most of the 2.3-day activity and the second half practically all the MsTh 2. This also shows that the rare earth is probably heavier than lanthanum.

Figure 1 shows a decay curve of the activity and an absorption curve of the electrons in aluminum. The flattening out of the decay curve may be due to UX which has not been separated from this sample.

These experiments seem to show conclusively that no β-emitting transuranics have been so far observed, with the usual reservation of very short or very long periods.

The fact that a rare earth, which is necessarily a fission product of uranium is found among the nonrecoiling activities can perhaps be explained by the very rapid decrease of the range of the fission products when their mass increases.

On the other hand, the 23-minute uranium must decay into a substance with atomic number 93; hence a search was made for an alpha-emitter. An ionization chamber connected to a linear amplifier or a spherical ionization chamber in which the pressure could be varied[5] were used for this purpose. A sample showing a very strong β-activity due to the 23-minute period showed no alpha-activity above the natural thus ruling out the possibility of the 23-minute uranium decaying into a short life alpha-emitter.

In the hope of finding a long life emitter, U_3O_8 which had been kept intermittently for two years close to the target of the Berkeley cyclotron was used. We believe

that no other uranium sample today has had a stronger irradiation. The alpha-activity of this sample was examined and compared with the activity of U_3O_8 of the same source, but not irradiated. No difference could be detected. Two grams of the irradiated oxide were dissolved in $6n$ hydrochloric acid and rhenium added to the solution and precipitated as a sulphide. No activity was found in the rhenium. Similar experiments were performed also with a bombardment time favorable to the detection of a period of the order of magnitude of some days with negative results.[6]

The necessary conclusion seems to be that the 23-minute uranium decays into a very long-lived 93 and that *transuranic elements have not yet been observed.*

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[4] E. McMillan, Phys. Rev. 55, 510 (1939).
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Concentrating the Uranium Isotope of Twenty-Three-Minute Half-Life*

The uranium isotope of twenty-three-minute half-life[1] can be concentrated with respect to U^{238} by the following procedure. Other products of the uranium bombardment are separated from the twenty-three-minute isotope in the process.

In an acid or neutral solution containing no oxidizing agent stronger than hydrogen ion, a highly excited uranium atom will probably settle down in the tetravalent state. The hydroxide corresponding to this state is a weaker base and less soluble than the corresponding uranyl compound. Consequently, hydrolysis is more complete and probably more rapid for salts of tetravalent uranium than for salts of hexavalent uranium. This results in an increase in the concentration of the tetravalent uranium in the first fraction of a hydrolytic precipitation from a mixture of the two salts. In these experiments, the twenty-three-minute uranium isotope, left in an excited state by the neutron capture and recoil gamma-ray emission, settles down in the tetravalent state and can be concentrated.

Ammonium uranyl acetate $[NH_4UO_2(CH_3COO)_3]$, was the salt used in these experiments. It can be prepared by dissolving ammonium pyrouranate in glacial acetic acid and crystallizing from a hot concentrated acetic acid solution.

Thirty to forty grams of this salt (15–20 g U) are dissolved in 100–150 cc of cold distilled water. The solution is placed in a 175 cc spherical soft glass flask surrounded by paraffin. In the center of the solution is placed the neutron source (110 mC Ra+Be). After a two-hour bombardment, the solution is poured into one liter of boiling water containing 10 g of ammonium acetate. A precipitate of a basic uranyl acetate appears within one to three minutes. To the suspension is added 0.1 g of decolorizing carbon (to aid filtering) and the solid removed by filtering with suction through a sintered glass funnel. The precipitate is dissolved and separated from the carbon by pouring a hot solution of 5 cc concentrated nitric acid and 20 cc glacial acetic acid into the funnel and applying suction. To the resulting solution is added 5 cc of an ammonium acetate solution (1 g/cc) and then a large excess of a hot concentrated solution of sodium acetate. The precipitate (1 to 2 g) of sodium uranyl acetate, $[NaUO_2(CH_3COO)_3]$, is filtered, washed first with cold glacial acetic acid, then with acetone and dried. Activity measurements on this sample are then made.

A modified Geiger-Müller counter with a 50μ mica window gives an observed activity from an activated sample of about 100 counts/minute per gram U. Measurements are started five minutes after the final precipitation and fifteen minutes after the cessation of bombardment. Blank runs on nonirradiated samples give observed activities of about 20 counts/minute/gram U five minutes after the final precipitation. When activated samples are measured without concentrating the twenty-three-minute uranium isotope, activities of 25 to 30 counts/minute/gram U are obtained. These measurements are made five minutes after the sodium uranyl acetate is precipitated and fifteen minutes after cessation of bombardment. This indicates that the procedure described increases the concentration of the twenty-three-minute uranium isotope with respect to U^{238} by a factor of the order of ten.

Decay curves of the activated samples show an initial decrease which changes gradually into an increase in activity. The increase is due to the build-up of the UX bodies. Elements other than uranium whose activities would interfere with the measurements are removed by the two precipitations.

Precipitation of rhenium sulphide from a concentrated sample of the twenty-three-minute uranium isotope should also precipitate the homologue of rhenium, element 93. Activity measurements on such precipitates gave negative results. From these results and from the activity measurements on the concentrated sample it can be concluded that element 93, if beta-active, has a half-life of less than one minute or greater than eleven hours.

Complete details of this work are being prepared for publication elsewhere.

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[1] Hahn, Meitner and Strassmann, Ber. 70, 1374 (1937).