Search for Elements 94 and 93 in Nature. Presence

of 94^{239} in Pitchblende

by

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The discovery¹ of a rather easily prepared form of radioactive element 94 and the subsequent determination of the chemical properties² of 94 with the help of this isotope as tracer makes it possible to conduct a search for 94 in natural minerals. It is convenient to search for 93, whose chemical properties^{2,3} are also known, at the same time. The hope would be to discover a very long-lived 94 or 93 and that this be present in an amount large enough so that useful quantities could be extracted from the minerals. Alpha and beta radioactivity is to be tested for, in the final very thin sample, which, in view of the chemical procedure, would contain the 94 or 93. In case the 94 or 93 is not alpha or beta active, a test for fissions with neutrons should be made, since it appears likely that any isotopes of these elements will undergo fission either with slow or with fast neutrons. The presence of an amount of the order of one microgram can be established by the neutron tests; therefore, starting with about one pound of the pitchblende, the sensitivity for the detection of these elements can be about one part in 10^8 or 10^9 .

1. Seaborg, Vahl and Kennedy, Report "Production and Properties of 50-Year Element 94".
2. Seaborg and Vahl, Report "The Chemical Properties of Elements 94 and 93".
3. McMillan and Abelson. Phys. Rev. 57, 1185 (1940)

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This report describes a careful search for elements 94 and 93 in a sample of pitchblende concentrate obtained from the Great Bear Lakes region of Canada. Since this pitchblende, which is said to contain some 40 different elements, seems to offer more hope to contain 94 and 93 than does any other mineral, it was decided to make an extremely careful search in this mineral. Great care was taken to be sure that all the material was dissolved, even down to the last few milligrams, and the most sensitive means of detection for 94 and 93 in the final fraction, including tests for alpha and beta radioactivity and neutron induced fissions, were employed.

Another reason that seemed to make it definitely worthwhile to extend the sensitivity of the method to the limit was the possibility of establishing the presence of the 30,000-year 94^{239} in this material. From the spontaneous fission rate of uranium, one can calculate the amount of 94^{239} which might be formed as a result of the absorption of U^{238} of the neutrons emitted in the spontaneous fission process. In an amount of pitchblende of the order of one pound, there might be expected to be present an amount of 94^{239} , formed by spontaneous fission neutrons, corresponding to an alpha-counting rate of several thousand counts per hour, provided an appreciable fraction of these neutrons were absorbed by U^{238} to ultimately form 94^{239} . Even if only a small percentage of the neutrons led to the formation of 94^{239} from U^{238} in this manner, it should be possible to detect the 94^{239} , since alpha-counting rates of the order of a few counts per hour are readily determinable. Our experiments indicate that we have discovered the presence of 94^{239} in pitchblende.

centrate were treated successively with a number of reagents, and after each treatment the solution which was obtained was set aside and the residue was subjected to the action of the next reagent. The reagents, in the order in which they were used, were (1) boiling concentrated HCl followed by boiling aqua regia, (2) hot 6 N-NaOH, (3) hot aqua regia, (4) boiling 6 N-HCl, (5) boiling 27 N-HF followed by HNO_3 extraction, (6) fuming hot H_2SO_4 followed by H_2O extraction, (7) NaOH fusion followed by dilute NaOH extraction, (8) boiling 6 N-HCl and (9) HF solution followed by H_2SO_4 , Na_2CO_3 and HNO_3 solutions. After this series of treatments the final undissolved matter was entirely negligible, perhaps of the order of a few milligrams in weight.

The acidity of each of these solutions was adjusted to from 1 N to 6 N, sulfur dioxide was added, and hydrofluoric acid was added to each in order to remove a fluoride precipitate. Lanthanum and cerium carrier material was added when necessary before the addition of the hydrofluoric acid.

The various fluoride precipitates were all combined and dissolved in concentrated sulfuric acid, and, after dilution with water and the addition of dilute nitric acid in order to oxidize any uranous uranium to the uranyl form, the rare earth fluorides were again precipitated by the addition of hydrofluoric acid. This rare earth and thorium fluoride precipitate, which amounted to about 20 grams and which would contain, in their reduced forms, any 94 or 93 which might have been present in the original pitchblende, was dissolved in sulfuric acid and reprecipitated as the fluoride. It was now necessary to go through a chemical procedure designed to isolate any such 94 or 93 into a very thin layer (0.3 mg/cm^2) of rare earth carrier material, special care being taken

to eliminate all the elements in the uranium, thorium and actinium radioactive series which would interfere with the detection of the 94 or 93 in the final sample.

This rare earth plus thorium fluoride precipitate was dissolved in sulfuric acid and after the addition of a few grams of potassium peroxydisulfate ($K_2S_2O_8$) and a few tenths of a gram of silver nitrate, hydrofluoric acid was added to again precipitate the rare earth and thorium fluoride. In this procedure the 94 and 93 remain in solution, present in their higher oxidation states. This solution, after the removal of the fluoride precipitate by centrifugation, was boiled in order to remove the hydrofluoric acid and decompose the peroxydisulfate and was then treated with sulfur dioxide in order to reduce the 94 and 93 to their lower, fluoride-insoluble, oxidation states. About 120 milligrams of lanthanum and cerium carrier were then added and the fluoride precipitated by the addition of hydrofluoric acid.

This 120-milligram fluoride precipitate was then dissolved in sulfuric acid and taken through another identical cycle in which the amount of rare earth was reduced to about 5 milligrams. These 5 milligrams of rare earth, which would contain the 94 or 93, were then dissolved in sulfuric acid and, after the addition of peroxydisulfate and silver ion, the rare earths were removed from solution by precipitation as the fluoride. The hydrofluoric acid was removed by boiling the solution until the white fumes of sulfur trioxide appeared and after dilution another 0.2 milligram of rare earth carrier was added. After treatment with peroxydisulfate and silver ion, this 0.2 milligram of rare earth was precipitated as fluoride. The purpose of this precipitation, which

was made just before the final isolation of the material which would contain the 94 and 93, was to establish that there was a negligible amount of isotopes of thorium (U_{10} , Io) present in the solution at this stage. This 0.2 milligram showed no detectable beta-activity, above the background of the Geiger-Muller counter, and an alpha-counting rate of about 45 per hour when placed on one electrode of an ionization chamber in which the calibrated counting efficiency amounted to about 45 percent.

The hydrofluoric acid was removed from the solution by boiling until the dense white fumes of sulfur dioxide, another 0.2 milligram of rare earth was added. This was precipitated as fluoride by the addition of hydrofluoric acid, and centrifuged onto a platinum disk for final measurements. This sample would contain any 94 or 93 which was present in the original pitchblende. (Calibration experiments, starting with 20 grams of rare earth and ending with 0.2 milligram of rare earth fluoride in an identical chemical procedure, in which 50-year alpha-emitting 94 was added as tracer to the original 20 grams, proved that the yield of 94 in this rather lengthy chemical procedure amounted to about 80 percent.) Careful counting experiments proved that the rare earth carrier material and the platinum, upon which the final sample was mounted, were free from alpha-emitting contamination.

Results. This final sample showed no detectable beta-activity, above the background of the Geiger-Muller counter. It showed an alpha-counting rate of about 90 per hour when placed on one electrode of an ionization chamber in which the calibrated counting efficiency was about 45 percent. Since it is likely that any isotopes of 94 or 93

would undergo fission with slow or fast neutrons, a test for fissions with neutrons was made by placing the final sample on one electrode of an ionization chamber connected to a linear amplifier and recording system adjusted to record the impulses due to fissions. When slow neutrons were used, a 300 mg Ra-Pe source with paraffin between the chamber and neutron source and around the chamber and neutron source, there was recorded zero fissions in 7 hours of counting. When the sample was replaced by a "standard" 200-microgram uranium sample, containing therefore 1.4 micrograms of U^{235} , the fission counting rate due to slow neutrons amounted to about 15 counts per hour. Therefore, assuming that the slow neutron fission cross section of the 94 or 93 would be of the same order of magnitude as that of U^{235} , there was present in the final sample no more than a small fraction of a microgram of any isotope of 94 or 93 capable of undergoing fission with slow neutrons. So far as fast neutrons are concerned our experiments place an upper limit of the order of a microgram on the amount of any isotope of 94 or 93 which was present and capable of undergoing fission with fast neutrons; therefore, we can say that there was not present in this pitchblende as much as one part in 10^8 or 10^9 of 94 or 93.

On the other hand, the alpha-counting rate might very well be due to the presence of 94^{239} in view of the expectation that some of this isotope be present as the end product formed as the result of absorption of spontaneous fission neutrons by U^{238} . The chemical procedure is very stringent and specific for the isolation of 94 (and 93). A counting rate of about 90 per hour, amounting to some 10^{-6} microcurie, would correspond to the order of 10^{-5} microgram of 30,000-year 94^{239} . This would correspond to something like one part in 10^{14} of 94^{239} in the

original pitchblende concentrate. This amounts to only a few percent of the amount to be expected if a large proportion of the spontaneous fission neutrons were absorbed by the U^{238} , but this is not surprising in view of the number of other neutron absorbing materials which might be present in the pitchblende.