[CONTRIBUTION FROM THE CHEMISTRY DIVISION OF THE ARGONNE NATIONAL LABORATORY]

The Isolation of Actinium[1]

BY FRENCH HAGEMANN

Of the known isotopes of actinium, only that of mass 227 has a half-life sufficiently long to permit isolation of macro quantities of the element.[2] The existence of actinium has been known since 1899, shortly after the discovery of radium, when Debierne[3] found a new radioactive substance in a fraction of uranium ore residues. The element, however, has never been isolated in the form of a pure compound from natural sources due to a combination of unfavorable circumstances: (1) it occurs in only extremely small amounts in uranium ores, about 0.15 mg. of actinium per ton of pitchblende, (2) its chemical properties are very similar to those of the rare earths, especially to those of its lower homolog, lanthanum, which also are present in much greater concentration in the ores, and (3) its detection and determination are difficult because of the low energy of its beta radiation.

The most concentrated preparations of actinium from natural sources which have been reported have consisted of several milligrams of lanthanum oxide containing from 1 to 2% of actinium.[4,5] The method of enrichment used in these preparations was fractional precipitation of the oxalates from dilute nitric acid solution, the actinium concentrating in the mother liquor. The rare earth–actinium separation would be greatly simplified by application of the recently developed ion-exchange techniques which have been used so successfully for rare earth separations. McLane and Peterson[6] at this Laboratory have separated tracer amounts of actinium and lanthanum by selective elution from Amberlite IR-1 resin with ammonium citrate solution. However, because actinium occurs so sparingly, the isolation of appreciable amounts of the element from natural sources would require processing tremendous quantities of ore.

A much more feasible method of obtaining actinium has been found to be the transmutation of radium by neutron irradiation

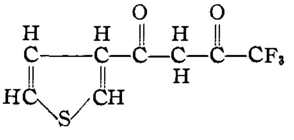
$$\mathrm{Ra}^{226}(n,\gamma)\mathrm{Ra}^{227};\ \mathrm{Ra}^{227} \xrightarrow[\text{short}]{\beta^-} \mathrm{Ac}^{227}$$

This reaction was first demonstrated by Peterson[7] at this Laboratory by irradiation of a milligram of radium in the chain-reacting pile. An amount of actinium was formed which corresponded to a cross-section of about 15×10^{-24} sq. cm. for the over-all reaction. This method of preparation has the obvious advantage that no separation of actinium from the rare earths is necessary.

In order to produce sufficient actinium for chemical studies, one gram of radium has been irradiated with pile neutrons. Isolation of the actinium produced has yielded 1.27 mg. of the element in the form of essentially pure compound.

The isolation of the actinium required separation from radium and from the long-lived daughter elements of radium and actinium, *i. e.*, from thorium, polonium, lead and bismuth. The thallium daughters possess half-lives of only a few minutes. Although conventional precipitation methods could have been used for the separation, a solvent extraction procedure was chosen in order to achieve as complete recovery as possible and because such a method lends itself more readily to the remotely controlled operation necessary for protection from radiation.

The separation was accomplished by extraction from an aqueous solution at a controlled hydrogen ion concentration with a solution of thenoyltrifluoroacetone in benzene. Thenoyltrifluoroacetone (frequently abbreviated as TTA), one of a series of fluorinated β-diketones recently synthesized by J. C. Reid and M. Calvin,[8] has the structure



In its enol form it can react with a metal ion to form a chelate compound which, being neutral and non-polar, is soluble in benzene. The reaction may be represented as

$$\mathrm{Me}^{+n}\ (\text{aq.}) + n\mathrm{HTTA}\ (\text{benzene}) = \mathrm{Me(TTA)}_n\ (\text{benzene}) + n\mathrm{H}^+\ (\text{aq.})$$

and the equilibrium constant at constant TTA concentration by

$$K = \frac{[\mathrm{Me(TTA)}_n]_{\text{benzene}}}{[\mathrm{Me}^{+n}]_{\text{aq.}}}[\mathrm{H}]^n_{\text{aq.}}$$

where $[\mathrm{Me(TTA)}_n]_{\text{benzene}}/[\mathrm{Me}^{+n}]_{\text{aq.}}$ is the extraction coefficient. The conditions to be used in the

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(1) Presented in part at the Chicago Meeting of the American Chemical Society, April, 1948.

(2) The value of the half-life recommended by the International Radium Standards Commission Report of 1930 [*Rev. Mod. Phys.*, **3**, 427 (1931)] is 13.5 years; a more recent and perhaps better value of 21.7 years has been reported by I. Curie and G. Bouissieres, *Cahiers Phys.*, No. 26, 1 (1944).

(3) A. Debierne, *Compt. rend.*, **129**, 593 (1899).

(4) W. A. Lub, *J. Phys. Rad.*, **7**, 366 (1937).

(5) M. Perey, *J. chim. phys.*, **43**, 155 (1946).

(6) C. K. McLane and S. Peterson, paper No. 19.6, p. 1385, Vol. 14B, Plutonium Project Record, National Nuclear Energy Series.

(7) S. Peterson, Atomic Energy Commission Document MDDC-1501, paper No. 19.9, p. 1393, Plutonium Project Record, National Nuclear Energy Series; unpublished work, Argonne National Laboratory.

(8) J. C. Reid and M. Calvin, Atomic Energy Commission document MDDC-1405.

separation were determined by a study of the extraction of tracer amounts of the elements by 0.25 *M* TTA solution in benzene as a function of *p*H of the aqueous solution.

Experimental

Tracer Extraction Experiments.—Equal volumes (from 5 to 15 ml.) of aqueous solutions containing radioactive tracers and 0.25 *M* benzene solution of thenoyltrifluoroacetone were equilibrated by vigorous mechanical stirring for fifteen minutes at room temperature. The two phases were then allowed to separate and the *p*H of the aqueous phase measured with a Beckman glass electrode. Fifty or one-hundred-microliter aliquots of each phase were removed and evaporated upon platinum discs for radioactive assay. The *p*H of the solution was then adjusted by addition of sodium hydroxide or hydrochloric acid and the procedure repeated until the range from zero to complete extraction had been covered.

Ionium was used as a tracer for thorium, RaF for polonium, RaE for bismuth, $MsTh_2$ for actinium, Ra^{226} for radium, and Tl^{204} for thallium. The extraction of lead was determined both colorimetrically by the dithizone method[9] using microgram quantities of inactive lead and with RaD tracer. In the latter case the determination of the amount of lead in each sample was made by following growth and decay of the more energetic daughter activity.

Some difficulty was encountered with polonium and bismuth in obtaining a material balance between the known concentration of added tracer and that determined by assay of the aliquots from each phase. It is probable that this was due to slow deposition of some of the activity upon the walls of the vessel as a result of hydrolysis. The difficulty was avoided by preparing a series of aqueous solutions pre-adjusted approximately to the desired *p*H, then adding the tracer and equilibrating with TTA solution. Aliquots were then immediately removed for assay and the equilibrium *p*H measured.

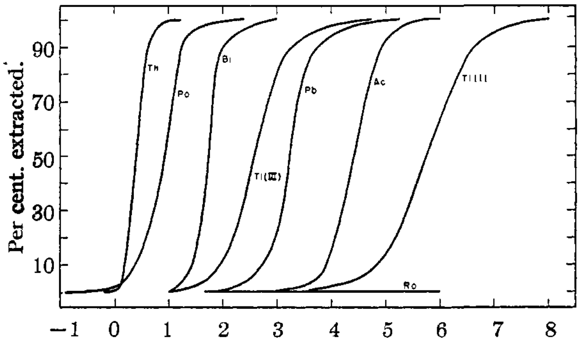

Fig. 1.—Per cent. extraction of tracer quantities of thorium, polonium, bismuth, lead, thallium, radium and actinium from aqueous solution by an equal volume of 0.25 *M* thenoyltrifluoroacetone solution in benzene as a function of *p*H.

The extraction of thallium in the +1 oxidation state was determined after first reducing the tracer with sulfur dioxide, and in the +3 state after preliminary oxidation with aqua regia.

The extraction behavior of these elements is summarized in Fig. 1.

Separation of Actinium from Irradiated Radium.—For protection from gamma radiation all operations were conducted by remote control behind several inches of lead shielding.

The container in which the radium was irradiated is shown in Fig. 2. The material in the form of dry radium bromide was placed in the small inner capsule which was constructed of 3 mil platinum. The capsule was held in place by pressure of a steel spring upon the friction cap. The two concentric 2S aluminum tubes enclosing the capsule were welded shut and the assembly encased in another $^1/_2$-inch aluminum tube not shown in the figure.

After irradiation the whole assembly was cut through at a point near the center by means of a remotely operated milling machine. After removal of the inner rod and attached spring the bottom half of the assembly was inverted and the capsule dropped into a 100-ml. solution flask. The radium bromide was dissolved in about 35 ml. of water and the solution transferred to the first extraction cell of the apparatus shown in Fig. 3. By manipulation of the stopcocks and appropriate application of pressure or vacuum at A or B the aqueous phase could be raised into the bulb containing the electrodes for measuring *p*H, the two phases drawn into the mixing chamber, or the separated benzene phase transferred to the second extraction cell.

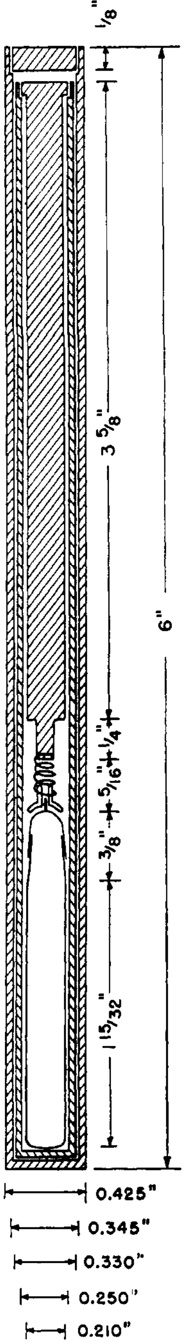

Fig. 2.—Irradiation container: the inner 3 mil platinum capsule contains the dry radium bromide; the outer tubes are of 2S aluminum.

After adjusting the radium solution to a *p*H of 6 by addition

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[9] Colorimetric analyses were carried out by Kenneth J. Jensen of the Analytical Group.

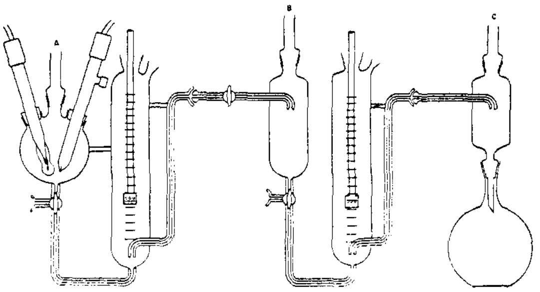

Fig. 3.—Extraction cells for remotely controlled extraction of actinium from irradiated radium.

of sodium hydroxide, an equal volume of 0.25 M TTA solution in benzene was added and the mixture stirred vigorously for fifteen to twenty minutes. The phases were allowed to separate and the benzene solution transferred to the second cell where the actinium was re-extracted into 25 ml. of 6 N hydrochloric acid. The extraction of the original solution was repeated with two more fresh portions of TTA solution to ensure complete recovery of actinium and the benzene phase re-extracted with the same 6 N hydrochloric acid. The acid solution which now contained the actinium, together with radioactinium, radium D and small amounts of the other elements, was transferred from the cell and evaporated to dryness. The residue was dissolved in 25 ml. of 0.1 N hydrochloric acid and extracted several times with equal volumes of TTA solution to remove thorium isotopes, then the pH was adjusted to 6 and the actinium extracted with TTA and re-extracted with 6 N hydrochloric acid as before.

At this stage the material was subjected to spectrographic analysis.[10] An aliquot of the solution, which was later shown on the basis of alpha growth curves to contain 6 micrograms of actinium, was found to contain about 54% actinium, 18% lead (probably RaD) and 18% silicon, with iron, aluminum, calcium and magnesium making up most of the other 10%. About 0.1% of radium was present due, probably, to mechanical carryover because of incomplete phase separation. Alpha and beta growth curves indicated that considerable radioactive impurities were also present.

The material was purified by two more TTA extraction cycles. Each cycle consisted of extraction of the thorium isotopes with TTA from 0.1 N hydrochloric acid solution followed by extraction of the actinium at a pH of 5.5–6.0 and re-extraction into 6 N hydrochloric acid. After the second cycle the acid solution was evaporated to dryness and the residue dissolved in 10 ml. of 0.1 N hydrochloric acid. One-half mg. of inactive lead per ml. of solution was added and lead sulfide precipitated to remove any lead, bismuth and polonium activities. Upon passing ammonia gas into the filtrate, the actinium was precipitated as a white gelatinous mass. The actinium hydroxide was centrifuged and redissolved in 0.1 N hydrochloric acid. Spectrographic analysis of an aliquot of the solution containing about 10 micrograms of actinium showed the product to be greater than 95% actinium, with iron, aluminum, calcium and magnesium the only impurities present in detectable amounts. The same amount of impurities was found when a blank of an equal volume of the reagent 0.1 N hydrochloric acid was analyzed in a similar manner.

Determination of Actinium by Alpha Counting.—The energy of the actinium beta particles is too low to permit direct detection with the ordinary thin window Geiger tube, hence quantitative determination by radioactivity methods must depend upon measurement of the more energetic daughter activities. Alpha counting was chosen as the most precise and convenient method of determination.

The alpha activity was measured by evaporating aliquots of the actinium solution upon platinum discs and counting in a methane proportional alpha counter or a parallel plate atmospheric ionization chamber.[11] In view of the high specific activity and chemical purity of the actinium no correction was necessary for counting losses due to self-absorption of alpha particles in the sample. The observed activities were corrected for a resolution loss in the atmospheric counter of 0.8%/1000 counts min.$^{-1}$. The resolution loss in the methane proportional counter was insignificant at the counting rates measured (less than 10,000 counts/min.$^{-1}$). Additional counting losses due to coincidences between the alpha particles from actinon and its short-lived (1.83×10^{-3} second) daughter, AcA, were appreciable in the case of the atmospheric counter because of the relatively long resolving time of this instrument. The magnitude of these losses was found to be about 7% of the total alpha activity at equilibrium. This effect was negligible with the faster methane proportional counter.

It was noticed that when a sample had been in the counter for several minutes a background was left in the chamber after removal of the sample, which decayed completely over a period of several hours. The background amounted to about one per cent. of the activity of the sample for the atmospheric counter and about one-third of one per cent. for the methane counter. This probably was due to loss of actinon and recoil atoms from the sample. Since the sample holder of the methane counter was at negative potential, most of the positively charged recoils would be recollected on the sample plate. A higher background would be expected with the atmospheric

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(10) Spectrographic analyses were performed by John Faris of the Analytical Group.

(11) A. H. Jaffey, "Radiochemical Assay by Alpha and Fission Measurements," Atomic Energy Commission document No. MDDC-1336. To appear as a chapter in Vol. 14A, Plutonium Project Record, National Nuclear Energy Series.

counter in which the sample holder was at a positive potential. A slight correction to the counting yield, which was assumed to be 52%,[11] may be required due to the unknown counting efficiency for the actinon and recoil particles which escape from the sample plate.

Although five to six months after separation are required for the five alpha-emitting daughters of actinium to grow to equilibrium, fairly accurate estimates of the amount of actinium present may be made after one or two weeks by comparison of the experimental and theoretical growth curves.

Growth curves of the alpha activity of samples of the purified actinium have now been followed for periods up to one year. The coincidence of the experimental and theoretical curves indicates that the material was free of radioactive impurities. A typical growth curve is shown in Fig. 4.

The yield of actinium calculated from the equilibrium amount of alpha activity was 93 millicuries. Assuming the half-life to be 21.7 years this corresponds to 1.27 mg. of pure actinium.

A large amount of ThB activity was found in the TTA fraction from the original separation which contained the thorium isotopes, indicating the presence of RdTh (Th^{228}). The presence of these members of the thorium series might be ascribed to neutron capture by AcX, Ac^{227} or RdAc; however, since the radium bromide which was irradiated probably contained some $MsTh_1$ impurity, it is not possible to estimate the amount of such second order capture.

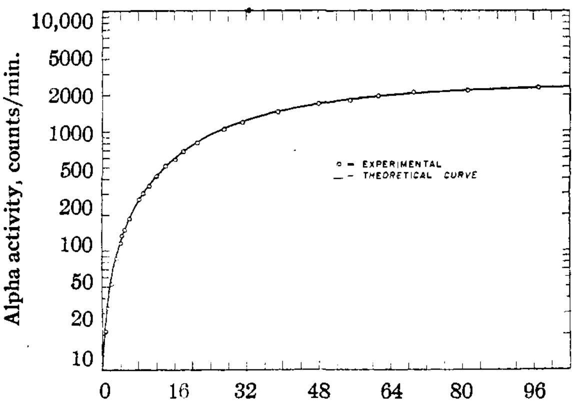

Fig. 4.—Typical curve of growth of alpha activity in purified actinium.

Summary

1. Milligram quantities of actinium, produced artificially by transmutation of radium with pile neutrons, have been isolated for the first time in the form of essentially pure compound.
2. Separation of actinium from radium and daughter elements was accomplished by extraction from aqueous solution at controlled hydrogen ion concentration with thenoyltrifluoroacetone–benzene solution.
3. The extraction of actinium, radium, thorium, polonium, lead, bismuth, thallium(I) and thallium(III) from aqueous solution by 0.25 *M* thenoyltrifluoroacetone in benzene as a function of the equilibrium *p*H of the aqueous phase has been investigated on a tracer scale.

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The Preparation and Identification of Some Pure Actinium Compounds[1]

BY SHERMAN FRIED, FRENCH HAGEMANN AND W. H. ZACHARIASEN

Previous preparations of actinium from natural sources have always contained gross amounts of the difficultly separable rare earths (in particular lanthanum), which occur in much greater concentrations than actinium in uranium ores. Therefore, direct observation of the characteristics of pure actinium compounds has been impossible, and the chemical properties of the element have necessarily been inferred entirely from its coprecipitation behavior with large amounts of inert carrier. Such tracer experiments have indicated that actinium is very similar to, and probably more basic than, lanthanum which is the most basic rare earth. For example, if an actiniferous solution of lanthanum is precipitated as the hydroxide, fluoride, phosphate, oxalate or carbonate, the activity due to actinium in each case is found almost quantitatively in the precipitate. Advantage has been taken of slight differences in solubility of actinium and lanthanum compounds in effecting some enrichment of actinium preparations, but isolation from natural sources has never been achieved.[1a]

Recently, milligram quantities of actinium, produced artificially by transmutation of radium in a chain-reacting pile, have been obtained in a pure state.[2] By applying microtechniques[3] which have been successfully employed in this Laboratory in the past with other heavy elements it has now been possible, for the first time, to prepare and identify several of the compounds of actinium.

Identification of the actinium compounds was

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(1) Presented at the San Francisco meeting of the American Chemical Society, March, 1949.

(1a) Gmelin, "Handbuch der anorganische Chemie," 8 Auflage, Actinium, System-Nummer 40, Berlin, 1942. This reference contains a summary of the literature on actinium to 1940.

(2) Hagemann, THIS JOURNAL, 72, 768 (1950).

(3) Fried and Davidson, *ibid.*, 70, 3539 (1948).