[CONTRIBUTION FROM THE CHEMISTRY DIVISION, ARGONNE NATIONAL LABORATORY]

# Isolation of Microgram Quantities of Naturally-occurring Plutonium and Examination of its Isotopic Composition(1)

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The plutonium content of a Belgian Congo pitchblende concentrate has been determined as 7.0 ± 0.7 parts of Pu$^{239}$ in $10^{12}$ parts of concentrate. This value is 700 times the value reported by Seaborg and Perlman for the Pu$^{239}$ content of a Canadian pitchblende concentrate. Microgram quantities of Pu$^{239}$ have been isolated from a uranium process waste. No isotopes of plutonium other than Pu$^{239}$ have been demonstrated to be present in the product. On the basis of 100 parts of Pu$^{239}$ the following upper limits have been set: Pu$^{238}$ (0.0003), Pu$^{240}$ (1), Pu$^{241}$ (1), Pu$^{242}$ (0.01), Pu$^{244}$ (1). The quantity of Pu$^{239}$ found is probably too high to be accounted for by absorption by U$^{238}$ of neutrons formed by spontaneous fission of uranium. A mechanism involving interaction of light elements such as oxygen, silicon and magnesium with the more energetic alphas of the uranium series to yield neutrons is suggested as a further source of neutrons. Other presumed contributions to the neutron flux are the U$^{235}$ "multiplication" and cosmic rays.

## Introduction

The existence of plutonium in nature was first reported by G. T. Seaborg and M. L. Perlman.[2] Using fluoride carrying techniques under conditions such that the valence of any plutonium present would alternate between the lower valence states and the six-valent state, so that the plutonium would alternately be carried and fail to be carried, they isolated a plutonium fraction from a 400-g. sample of pitchblende concentrate from the Great Bear Lake region of Canada. The product had an alpha activity of 1.5 counts per minute at 45% geometry.

Behavior of the product in the carrying cycles led to the conclusion that plutonium (or neptunium) had been isolated; and on the assumption that the product was formed through interaction of U$^{238}$ with neutrons produced by the spontaneous fission of U$^{238}$ the product was considered to be Pu$^{239}$. From these data and an assumption of probable yield they estimated the Pu$^{239}$ content of the sample of pitchblende concentrate to be of the order of one part in $10^{14}$.

On the basis of empirical correlations and certain theoretical considerations higher isotopes, such as Pu$^{244}$, might be expected to be longer-lived than Pu$^{239}$[3] and might conceivably have existed throughout geologic time. A further possibility is that such an isotope might be a daughter of an unknown radioactive series containing a very long-lived transuranium progenitor other than plutonium. The isolation of any such higher plutonium isotope would be of interest because of its probable application in the synthesis of a transcurium isotope.

Because of the possible existence, in trace quantities, of longer-lived plutonium isotopes it therefore seemed of interest to undertake an investigation with a threefold purpose: (1) to examine the isotopic composition of natural plutonium, (2) to establish the ratio of plutonium to uranium in a Belgian Congo pitchblende concentrate, (3) to isolate a sufficient quantity of natural plutonium to permit transmutation studies on any higher plutonium isotopes which might be present (Pu$^{244}$, etc.).

In order to perform the necessary measurements in examining isotopic composition it was considered desirable to isolate approximately one microgram of plutonium. Since on the basis of the data of Seaborg and Perlman the isolation of one microgram of Pu$^{239}$ would require the processing of approximately 100 tons of pitchblende concentrate, it was decided to search for plutonium in the aqueous waste resulting from the processing of Belgium Congo pitchblende concentrate for uranium. This waste is a nitrate solution containing essentially all of the soluble gross components of the ore concentrate with the exception of the uranium which has been reduced to a small fraction of its original content. This solution is referred to as uranium process waste in this paper.

## Experimental and Results

**Isolation of Microgram Quantities of Plutonium.**—Microgram quantities of plutonium were isolated from uranium process waste by the following procedure. This aqueous waste, which is essentially a saturated solution of metallic nitrates with a free nitric acid content of approximately 0.4 *M*, was contacted with five per cent. of its volume of tributyl phosphate. The resulting extract was then contacted with 25% of its volume of aqueous 1.0 *M* hydrofluoric acid. The mixed thorium and rare earth fluoride precipitate carried reduced (*i.e.*, trivalent and tetravalent) plutonium.

The fluoride precipitate was dissolved in 2.4 *M* aluminum nitrate and the resulting solution made 0.05 *M* in sodium dichromate and 0.2 *M* in nitric acid and heated at 90° for six hours. The oxidized plutonium was extracted into diethyl ether and the ether extract allowed to evaporate over water. The water solution was then evaporated to dryness. The residue was dissolved in 0.5 *M* nitric acid.

The valence of the plutonium was then fixed at four, using the method of Crandall, *et al.*,[4] and the solution contacted with one-fourth its volume of 0.1 *M* thenoyltrifluoroacetone (TTA) in benzene for 20 minutes. The aqueous effluent was contacted with a second portion of 0.1 *M* TTA in like manner. The TTA extracts, after dilution to 0.05 *M* TTA with benzene, were scrubbed successively with six equal-volume portions of 0.5 *M* HNO$_3$. The plutonium was then re-extracted from the TTA solution into 10 *M* HNO$_3$. The resulting aqueous phase was evaporated to dryness. The entire TTA procedure described above is essentially that reported by Crandall, *et al.*[4]

The residue was dissolved in 0.5 *M* HNO$_3$ and the resulting solution made 0.1 *M* in K$_2$Cr$_2$O$_7$. After heating for several hours the solution was saturated with magnesium nitrate and the plutonium extracted into diethyl ether (0.3 *M* in HNO$_3$), using four equal-volume passes. The ether solutions were scrubbed successively with four half-volume portions of a solution 3.5 *M* in Mg(NO$_3$)$_2$ and 0.2 *M* in

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(1) This paper was presented at the 118th Meeting of the American Chemical Society, Chicago, September, 1950. The major portion was also presented at a classified Information Meeting at the Oak Ridge National Laboratory, October, 1949.

(2) G. T. Seaborg and M. L. Perlman, THIS JOURNAL, **70**, 1571 (1948); also "National Nuclear Energy Series," Vol. IV—14B, paper 1.3 (1949).

(3) I. Perlman, A. Ghiorso and G. T. Seaborg, *Phys. Rev.*, **77**, 26 (1950).

(4) H. W. Crandall, J. R. Thomas, E. Zebroski, Manhattan Project Report, CN-3773.

$HNO_3$. The combined ether extract was allowed to evaporate over water. The water solution was evaporated to dryness. The residue was dissolved in 0.5 *M* $HNO_3$, and then two more complete TTA cycles performed. No further ether extractions were made.

Following the third TTA cycle the residue resulting from the evaporation of the nitric re-extract was dissolved in a very small volume of 0.5 *M* $HNO_3$ and the plutonium extracted directly into an equal volume of 0.1 *M* TTA. (Evaporation of a plutonium nitrate solution to dryness from concentrated nitric acid results in nearly quantitative conversion of the plutonium to the tetravalent state.) The plutonium was then re-extracted into aqueous 10 *M* $HNO_3$. An aliquot was evaporated on a five mil platinum disc for alpha counting, for measurement of alpha energies, and for determination of thermal neutron fissionability.

**Identification of $Pu^{239}$.**—The alpha disintegration rate was determined using a standard type alpha counter of 52% counting efficiency.

The energies of the alpha particles were determined by means of a multichannel differential pulse analyzer described by Ghiorso, *et al.*,[5] registering the alpha pulses within a selected range of energies.

The thermal neutron fissionability was determined by subjecting the sample (mounted on a platinum disc) to thermal neutron irradiation in a fission counter following a careful determination of its alpha activity. A quantity of known $Pu^{239}$ approximating the sample in alpha activity, mounted on a similar platinum disc, was subjected to alpha counting and fission counting under like conditions using the same counters. Since the ratio of the number of alpha disintegrations per minute to the number of fissions per minute, as determined in the above manner, for a sample of pure $Pu^{239}$ must be a constant, the data obtained in this way may be used as a measure of the purity of a sample of $Pu^{239}$ (with respect to alpha active contaminants, assuming no other fissionable isotopes present). The results are summarized in Table I. Although the alpha pulse and fission counting data, in conjunction with the chemical behavior of the product during its isolation, were considered very strong evidence for $Pu^{239}$, it was felt that an attempted separation from added $Pu^{238}$ was required to make the assignment unequivocal. Accordingly, a portion of Number 2 Sample of Table I was spiked with $Pu^{238}$ tracer and the solution heated at 90–100° for 24 hours to promote exchange. An aliquot was evaporated for alpha pulse analysis.

TABLE I

ALPHA ENERGY AND THERMAL NEUTRON FISSIONABILITY DATA FOR SAMPLES OF PLUTONIUM ISOLATED FROM URANIUM PROCESS WASTE

| Sample | Total alpha activity (d./m.) | $Pu^{239}$ (d./m.), calculated from: Alpha pulse data | Fissionability data |
|---|---|---|---|
| 1 | 2123[a] ± 10 | 1933 ± 20 | 1906 ± 10 |
| 2 | 1281 ± 10 | 1277 ± 15 | 1279 ± 10 |

[a] The alpha pulse data show this activity to be due solely to alpha particles of energies 5.14 Mev. ($Pu^{239}$) and 4.66 Mev. ($Th^{230}$).

Following dichromate oxidation, the plutonium was extracted into two portions of diethyl ether. The ether layer was scrubbed twice with half-volume portions of a solution 3.5 *M* in $Mg(NO_3)_2$ and 0.2 *M* in $HNO_3$. The scrubbed ether was then allowed to evaporate over water. The aqueous solution was evaporated to dryness. The residue was dissolved in 5 *M* HCl and the plutonium reduced to the trivalent state (leaving any neptunium which might be present in the tetravalent state). The diluted solution was then contacted with 0.4 *M* TTA to remove any neptunium present. Lanthanum fluoride was then precipitated carrying plutonium. The fluoride was metathesized to the hydroxide which was then dissolved in nitric acid. After evaporation to dryness several times following the intermediate addition of 16 *M* $HNO_3$ the cooled residue was dissolved in 0.5 *M* $HNO_3$. The resulting solution was contacted with 0.4 *M* TTA in benzene. The TTA extract was scrubbed twice with half-volume portions of 0.5 *M* $HNO_3$ and then contacted with 10 *M* $HNO_3$ to re-extract the plutonium. An aliquot of the final aqueous phase was plated for alpha pulse analysis.

The ratio of the number of disintegrations per minute corresponding to 5.49 Mev. ($Pu^{238}$) to the number of disintegrations per minute corresponding to 5.14 Mev. ($Pu^{239}$) as shown by this final sample was sensibly the same as that shown by the sample taken before the chemical separation procedure, as shown in Table II.

TABLE II

ATTEMPTED SEPARATION OF PRODUCT ACTIVITY FROM $Pu^{238}$ ACTIVITY

| | Total alpha activity (d./m.) | Ratio o d./m. (5.49 Mev.): d./m. (5.14 Mev.) |
|---|---|---|
| Added | 15,400 ± 50 | 1.36 ± 0.06 |
| Recovered | 12,800 ± 50 | 1.42 ± 0.06 |

**Examination of Isotopic Composition of Naturally-occurring Plutonium.**—By means of the differential alpha pulse analyzer the ratio of the number of alpha particles of 5.49 Mev. energy ($Pu^{238}$) emitted per min. to the number of alpha particles of 5.14 Mev. energy ($Pu^{239}$) emitted per min. was established as less than $8 \times 10^{-4}$ for a 6,500 d./m. aliquot of Number 2 Sample of Table I. Using respective half-lives of 90 and 24,400 years, the ratio of $Pu^{238}$ to $Pu^{239}$ is found to be less than $3 \times 10^{-6}$ by mass.

A search for higher plutonium isotopes was made both by neutron irradiation studies and by mass spectrographic analysis.

Two samples of plutonium isolated from uranium process waste and containing 0.5 and 1.0 microgram of $Pu^{239}$ were irradiated for one day in the thimble of the Argonne CP-3 pile. The plutonium was purified by lanthanum fluoride cycles, ether extractions, and TTA cycles; a subsequent search was made for plutonium beta emitters. No beta activity which could be assigned definitely to plutonium was found. Failure to detect the five hour beta-emitting $Pu^{243}$ recently reported by Sullivan, *et al.*,[6] indicates that the $Pu^{242}$ content is less than 0.01% of the $Pu^{239}$ by mass.

A mass spectrographic analysis of a sample containing 1.0 microgram of $Pu^{239}$, performed by M. G. Inghram and D. C. Hess,[7] showed that no other isotope of plutonium was present in a concentration as great as one per cent. of the $Pu^{239}$.

The foregoing results are summarized in Table III.

TABLE III

ISOTOPIC COMPOSITION OF NATURALLY-OCCURRING PLUTONIUM

| Isotope | Relative abundance | Method of determination |
|---|---|---|
| 238 | <0.0003 | Alpha pulse analysis |
| 239 | 100 | Alpha pulse analysis and thermal neutron fission |
| 240 | <1 | Mass spect. analysis |
| 241 | <1 | Mass spect. analysis |
| 242 | <0.01 | Neut. irrad. studies |
| 243 | .... | (Five hour beta-emitter) |
| 244 | <1 | Mass spect. analysis |

**Assay of Belgian Congo Pitchblende Concentrate for $Pu^{239}$.**—It having been established that the ratio of $Pu^{238}$ to $Pu^{239}$ (by activity) is less than $8 \times 10^{-4}$ in the plutonium isolated from uranium process waste it was permissible to use $Pu^{238}$ as a tracer in determining chemical yield in the assay of the ore concentrate. A 2.00-kg. aliquot of a sample of Belgian Congo pitchblende concentrate, ground to pass a 100-mesh screen, was leached with six liters of 6 *M* $HNO_3$ at the boiling point for 24 hr. The residue was leached three more times with six-liter portions of 2 *M* $HNO_3$ in the same way.

It should be noted that in the leaching step the residue was equivalent in weight (when dried at 100°) to 8% of the

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(5) A. Ghiorso, A. H. Jaffey, H. P. Robinson and B. B. Weissbourd, "National Nuclear Energy Series," Vol. IV-14B, Paper 16.8 (1949).

(6) J. C. Sullivan, G. L. Pyle, M. H. Studier, P. R. Fields and W. M. Manning, Argonne National Laboratory, Report ANL-4370.

(7) The authors are indebted to M. G. Inghram and D. C. Hess of Argonne National Laboratory for the mass spectroscopy study.

initial pitchblende concentrate. This residue appeared to consist chiefly of gangue.

After addition of $Pu^{238}$ tracer to the combined clarified leaches the solution was evaporated to approximately six liters in a stainless steel beaker. This solution was allowed to age for 14 days (to permit isotope exchange). Following saturation of the solution with sulfur dioxide at room temperature, to reduce hexavalent plutonium, a precipitate was formed by the addition of 600 cc. of 27 $M$ HF (uranium decontamination). This precipitate was dissolved by the addition of two lb. of $Al(NO_3)_3 \cdot 9H_2O$. The resulting solution contained $Pu^{239}$ (a few hundred alpha disintegrations per min.), $Th^{230}$ (approximately $10^9$ alpha dis. per minute), $Th^{234}$ (approximately $10^9$ beta dis. per min.) and some $Po^{210}$.

This solution was made 0.2 $M$ in $HNO_3$ and contacted with dibutoxytetraglycol. The resulting extract was washed with 10 $M$ $NH_4NO_3$ and the plutonium, ionium and uranium removed by water re-extraction. The water re-extract was evaporated to dryness.

The residue was dissolved in 0.5 $M$ nitric acid. The procedure described for the isolation of microgram quantities of plutonium from uranium process waste was then followed in detail, beginning at the fixing of plutonium in the tetravalent state. The entire final solution was evaporated on a five mil platinum disc for alpha pulse analysis and for determination of thermal neutron fissionability. The results are summarized in Table IV.

TABLE IV

$Pu^{239}$ CONTENT OF LEACH SOLUTION FOR A 2.00-KG. SAMPLE OF A BELGIAN CONGO PITCHBLENDE CONCENTRATE

| | |
|---|---|
| $Pu^{238}$ added (c./m.) | 778 |
| Total Pu recovered (c./m.) | 77 |
| Ratio $Pu^{239}$: $Pu^{238}$ recovered (by activity) | 1.28 |
| $Pu^{238}$ recovered (c./m.) | 33.7 |
| Chemical yield (%) | 4.34 |
| $Pu^{239}$ present in leach solution (c./m.) | 996 |
| $Pu^{239}$ present in leach solution (micrograms) | $1.40 \times 10^{-2}$ |
| $Pu^{239}$: pitchblende concentrate (by mass) | $7.0 \times 10^{-12}$ |

It is felt that within reasonable limits the last figure of Table IV may be set at $(7.0 \pm 0.7) \times 10^{-12}$. It should be borne in mind that this is a lower limit, since the pitchblende concentrate was not completely solubilized. Consequently, an indeterminate amount of $Pu^{239}$ may have been lost before the addition of $Pu^{238}$ tracer. However, it is likely that the leaching of plutonium from the ore concentrate was quite efficient, since the plutonium is probably present in the tetravalent state; and its behavior ought, therefore, to resemble that of thorium which is leached with an efficiency of well over 99%. (The ratio of total thorium to uranium is approximately $1 \times 10^{-4}$. The efficiency of leaching is obtained by assay of the alpha-active $Th^{230}$.)

Since the pitchblende concentrate was found to contain 45.3% uranium, the mass ratio of $Pu^{239}$:$U^{238}$ is estimated to be equal to or greater than $(1.5 \pm 0.2) \times 10^{-11}$.

## Discussion

Assuming that the $Pu^{239}$ has been formed through neutron capture by $U^{238}$, the $Pu^{239}$:$U^{238}$ ratio appears to be too high to be attributable in its entirety to the neutron flux produced by spontaneous fission of natural uranium (24.2 ± 0.5 f./g./hr.).[8] Assuming secular equilibrium and a $Pu^{239}$:$U^{238}$ ratio of $(1.5 \pm 0.2) \times 10^{-11}$ the present rate of formation of $Pu^{239}$ is calculated to be 128 ± 17 atoms per hour per gram of $U^{238}$. This rate of formation corresponds to 5.3 ± 1.0 neutrons captured by $U^{238}$ per fission of natural uranium. The number of effective neutrons emitted per fission is probably considerably less than this.

However, the additional neutron flux made available by the interaction of high energy alpha particles from the uranium series with light elements such as oxygen, silicon and magnesium present in the ore is probably sufficient to compensate for the assumed deficiency. A further contribution to the neutron flux by cosmic rays is presumably a function of the depth of the ore deposit. A third contribution to the neutron flux results from $U^{235}$ "multiplication"—a $U^{235}$ atom may capture a neutron (produced through the spontaneous fission of $U^{238}$) and then undergo fission to produce several neutrons.

It is difficult to discuss, quantitatively, these modes of contribution to the neutron flux in view of the interaction of so many variables, *i.e.*, depth of the ore deposit, concentration of uranium in the ore (as opposed to ore concentrate), composition of the gangue (content of Mg, Si, O, B, etc.), etc.

There remains the possibility that part of the $Pu^{239}$ is present as a daughter in a radioactive decay chain not yet reported as naturally-occurring. This presumably requires the presence of a long-lived trans-plutonium progenitor. It seems necessary that such a series should include one or more isotopes of americium or/and curium.

Since the tetravalent state of plutonium appears to be a stable state and the chemistry of tetravalent plutonium resembles that of thorium very closely, it is possible that any long-lived plutonium isotopes would have been laid down in thorium ores. From this point of view, it is perhaps not surprising that no long-lived isotope of plutonium has been found in pitchblende concentrate, since this concentrate is not an ore of thorium.

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(8) W. G. Whitehouse and W. Galbraith, *Phil. Mag.*, **41**, 429 (1950).