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Occurrence of the  $4n + 1$  Series in Nature

D. F. Peppard, G. W. Mason, P. R. Gray and J. F. Mech

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A small quantity of  $Np^{237}$ , the long-lived ancestor of the  $4n + 1$  series, has been isolated from a natural source. The  $Th^{229}$  content of  $Th^{230}$  obtained from Belgian Congo pitchblende concentrate and of  $Th^{232}$  obtained from Brazilian monazite has been determined indirectly through isolation of the  $Ac^{225}$  daughter. The mass ratio of  $Np^{237}$  to  $U^{238}$  in the Belgian Congo pitchblende concentrate has been determined as  $(1.8 \pm 0.4) \times 10^{-12}$ . The mass ratio of  $U^{233}$  to  $U^{238}$  in the same ore deposit is found to be  $(1.3 \pm 0.2) \times 10^{-13}$ . The ratio of the respective neutron-capture cross sections of  $U^{238}$  in the ore body for the  $(n, 2n)$  and  $(n, \gamma)$  reactions is calculated to be  $(1.3 \pm 0.6) \times 10^{-3}$  on the basis of the relative  $Np^{237}$  and  $Pu^{239}$  contents.

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Introduction.

Three radioactive series whose respective long-lived parent nuclides are  $Th^{232}$ ,  $U^{238}$  and  $U^{235}$  have long been known to exist in nature. In reference to the general formula for the mass numbers of the component nuclides these series are referred to respectively as the  $4n$ , the  $4n + 2$  and the  $4n + 3$  series. The "missing"  $4n + 1$  series was reported by Hagemann et al(1). These authors prepared  $U^{233}$ , whose mass number conforms

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 Chief, Declassification Branch

1. French Hagemann, L. I. Katzin, M. H. Studier, G. T. Seaborg and A. Ghiorso, Phys. Rev., 79, 435 (1950). The decay scheme of the  $4n + 1$  series is given in this paper. The values for the half-lives, as well as the characteristic alpha energies, of the members were also taken from this reference.

to the general formula  $4n + 1$ , by the  $Th^{232} (n, \gamma) Th^{233} \xrightarrow{\beta} U^{233}$  reaction. They determined the path of the decay chain between artificially produced  $U^{233}$  and stable  $Bi^{209}$  and reported the properties of the nuclides which are members of the chain. The results are in agreement with those obtained by English et al(2). Since  $Np^{237}$  decays by alpha-particle emission

2. A. C. English, T. E. Cranshaw, P. Demers, J. A. Harvey, E. P. Hincks, J. V. Jelley and A. N. May, Phys. Rev., 72, 253 (1947).

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to form beta-active  $\text{Pa}^{233}$  decaying in turn to  $\text{U}^{233}$ .  $\text{Np}^{237}$  is considered to represent the long-lived genitor of the  $4n + 1$  series, and the complete family of nuclides is referred to as the neptunium series.

Except for the stable terminal member of the chain,  $\text{Bi}^{209}$ , this family of radioactive heavy nuclides corresponding to the formula  $4n + 1$  has not been found in nature<sup>(1)</sup>. It has been pointed out by Seaborg<sup>(3)</sup> that

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3. G. T. Seaborg, Chem. Eng. News, 25, 358 (1947).

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uranium-bearing ores should contain trace quantities of  $\text{Np}^{237}$  formed by the  $\text{U}^{238}(n,2n)\text{U}^{237} \xrightarrow{\beta} \text{Np}^{237}$  reaction; and it has been suggested by Garner, Bonner and Seaborg<sup>(4)</sup> that uranium-bearing ores containing an

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4. G. S. Garner, N. A. Bonner and G. T. Seaborg, J. Am. Chem. Soc., 70, 3453 (1948).

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appreciable relative quantity of thorium should contain some long-lived  $\text{U}^{233}$  formed as the result of the  $\text{Th}^{232}(n,\gamma)\text{Th}^{233} \xrightarrow{\beta} \text{U}^{233}$  reaction. However, isolation of either  $\text{Np}^{237}$  or  $\text{U}^{233}$  from natural sources has not been reported.

In the work presently reported,  $\text{Np}^{237}$  was isolated from a Belgian Congo pitchblende concentrate and the ratios of  $\text{Np}^{237}:\text{U}^{238}$  and  $\text{U}^{233}:\text{U}^{238}$  in this ore source determined.

Although in preliminary experiments  $\text{Np}^{237}$  was isolated from an aqueous waste resulting from the processing of Belgian Congo pitchblende concentrate, it was evident that establishing the  $\text{Np}^{237}$  to  $\text{U}^{238}$  ratio by a direct technique would involve the complete dissolution of approximately one hundred kilograms of ore concentrate. Consequently, an approach based on another member of the  $4n + 1$  series was used.

The decay of  $\text{Np}^{237}$  leads to the formation of  $\text{Th}^{229}$  (alpha-active,  $7.34 \times 10^3$  years)<sup>(1)</sup>, and the decay of  $\text{U}^{238}$  leads to the formation of  $\text{Th}^{230}$  (alpha-active,  $8.0 \times 10^4$  years)<sup>(5)</sup>. Since the half-lives of these thorium

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5. The values for certain half-lives have been taken from the Table of Isotopes of G. T. Seaborg and I. Perlman, Rev. Mod. Phys., 20, 585 (1948).

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isotopes are very long with respect to the time involved in processing an ore but very short with respect to the age of the ore deposit, it follows that the ratio of  $\text{Th}^{229}$  to  $\text{Th}^{230}$ , by activity, should be identical to the ratio of  $\text{Np}^{237}$  to  $\text{U}^{238}$ , by activity, assuming that  $\text{Th}^{229}$  has been formed by no means other than  $\text{Np}^{237}$  decay. However, it is to be noted that  $\text{Th}^{229}$  will be formed if neutrons are captured by the  $\text{Th}^{232}$  present in small quantities<sup>(1)</sup>. This correction will be shown to be negligible.

Therefore, a method was devised for measuring the ratio of  $\text{Th}^{229}$  to  $\text{Th}^{230}$  in a sample containing several grams of  $\text{Th}^{230}$  (ionium) which had been isolated, in this laboratory, from an aqueous waste resulting from the processing of Belgian Congo pitchblende concentrate. The first daughter of  $\text{Th}^{230}$  is  $\text{Ra}^{226}$  (alpha-active, 1590 years)<sup>(5)</sup>. The first daughter of  $\text{Th}^{229}$  is  $\text{Ra}^{225}$  (beta-active, 14.8 days)<sup>(1)</sup> and the second is  $\text{Ac}^{225}$  (alpha-active, 10.0 days)<sup>(1)</sup>.

Consequently, it was decided to determine the  $\text{Th}^{229}$  content of a  $\text{Th}^{230}$  sample by determining the  $\text{Ac}^{225}$  content. A procedure was therefore devised whereby  $\text{Ac}^{225}$  could be isolated and then identified by means of the characteristic alpha energies of it and its daughters<sup>(1)</sup>.

The requirements of the technique are stringent, since a virtually weightless sample of  $\text{Ac}^{225}$  is required for determination of alpha energies; and actinium, a trivalent element, must be separated from divalent radium

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and lead, trivalent bismuth, and tetravalent thorium. In order to obviate the much more difficult problem of separating actinium from rare earths, the  $\text{Th}^{230}$  was exhaustively purified from rare earths (and  $\text{Ac}^{225}$ ) and the  $\text{Ac}^{225}$  allowed to grow again.

By means of a solvent extraction technique,  $\text{Ac}^{225}$  of high purity was isolated and an aliquot of the final product evaporated on a platinum disc for alpha pulse analysis(6).

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6. The energies of the alpha particles were determined by means of a multi-channel differential pulse analyzer described by A. Ghiorso, A. H. Jaffey, H. P. Robinson and B. B. Weissbourd, "National Nuclear Energy Series", Vol. IV-14B, Paper 16.8 (1949).

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For determination of chemical yield, a known quantity of  $\text{Ac}^{227}$  was then added to the  $\text{Th}^{230}$  and the sample allowed to age. An actinium fraction was isolated and the quantities of  $\text{Ac}^{225}$  and  $\text{Ac}^{227}$  present in the fraction determined by alpha pulse analysis. From these data, the chemical yield for the actinium isolation step and thereby the  $\text{Ac}^{225}$  content of the  $\text{Th}^{230}$  sample may be calculated.

#### Experimental.

Isolation of  $\text{Np}^{237}$  from a sample of  $\text{Th}^{230}$ .— In the isolation of approximately one microgram of naturally-occurring  $\text{Pu}^{239}$  from a uranium process waste(7), the aqueous effluents from the first thenoyltrifluoroacetone

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7. D. F. Peppard, M. H. Studier, M. V. Gergel, G. W. Mason, J. C. Sullivan and J. F. Mech, J. Am. Chem. Soc., 73, 2529 (1951).

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extraction cycle were combined and set aside for further study. This composite aqueous phase was subsequently evaporated to dryness. The residue was dissolved in 0.5 M  $\text{HNO}_3$  and the resulting solution made 0.1 M in  $\text{K}_2\text{Cr}_2\text{O}_7$ . After a heating period of several hours the solution was saturated with magnesium

nitrate and contacted with eight equal volume portions of diethyl ether (0.3 M in  $\text{HNO}_3$ ) which were scrubbed successively with twelve half-volume portions of a solution 3.5 M in  $\text{Mg}(\text{NO}_3)_2$  and 0.2 M in  $\text{HNO}_3$ . The combined ether extract was allowed to evaporate over water. This aqueous phase was evaporated to dryness.

The resulting residue was dissolved in 5 M HCl and any plutonium present reduced to the trivalent state (leaving any neptunium present in the tetravalent state). The neptunium was then extracted into four successive portions of 0.4 M thenoyltrifluoroacetone in benzene from the diluted solution<sup>(8)</sup>. These organic phases were then scrubbed successively with

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8. This procedure for separating neptunium from plutonium is reported by L. B. Magnusson, S. O. Thompson and G. T. Seaborg, Phys. Rev., 78, 363 (1950).

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small portions of 1.0 M HCl in order to decrease the content of  $\text{Th}^{230}$  and trivalent  $\text{Pu}^{239}$ , until the total alpha activity of the composite organic phase (determined by measuring the alpha disintegration rate of an aliquot evaporated on a five mil platinum disc) was reduced to 110 counts per minute.

In order to simplify the interpretation of later alpha pulse data the absence of  $\text{Th}^{230}$  was proved. The proof was furnished by the removal of added  $\text{Th}^{234}$ .

Enough  $\text{Th}^{234}$  tracer was added to the organic phase to produce a total beta counting rate, under the counting conditions used, of 12,700 counts per minute. Following several hours of agitation to permit thorium isotope exchange, the organic phase was scrubbed successively with six small portions of 1.0 M HCl in order to strip the thorium from the organic phase. The entire organic phase was then evaporated on a five mil platinum disc. The total alpha counting rate was 26 counts per minute and the total beta counting rate was less than 50 counts per minute.

Alpha pulse analysis showed 7 alpha counts per minute due to  $\text{Mn}^{237}$ .  
Most of the remaining activity was due to  $\text{Pu}^{239}$ .

Isolation of  $\text{Ac}^{225}$  from a Sample of  $\text{Th}^{230}$ , Ac Tracer Added.— A

sample of thorium as the nitrate, containing  $8.77 \pm 0.09$  g. of  $\text{Th}^{230}$  (and 74 g. of  $\text{Th}^{232}$ ), isolated from an aqueous waste resulting from the processing of Belgian Congo pitchblende concentrate for uranium, was extracted into approximately 10 liters of 0.6 M solution of thenoyltrifluoroacetone<sup>(9)</sup>

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9. Thenoyltrifluoroacetone was obtained from Dow Chemical Co.

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in benzene at a pH of unity<sup>(10)</sup>. This solution was scrubbed with several

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10. The extraction coefficients for actinium and thorium from an acidic aqueous phase into a benzene solution of thenoyltrifluoroacetone are given by French Hagemann, J. Am. Chem. Soc., 72, 768 (1950).

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small portions of 0.1 M  $\text{HNO}_3$  to remove traces of rare earths, yttrium, and actinium. The solution was then allowed to age for 80 days to permit the growth of  $\text{Ac}^{225}$  from the  $\text{Th}^{229}$  present.

At the conclusion of the ageing period, the  $\text{Ac}^{225}$  was removed from the organic phase into a small volume of aqueous phase by scrubbing the organic phase with three successive 200 ml. portions of 0.1 M  $\text{HNO}_3$ <sup>(10)</sup>, these aqueous phases being successively contacted with two 300 ml. portions of 0.6 M thenoyltrifluoroacetone in benzene followed by two 300 ml. portions of benzene. The benzene-thenoyltrifluoroacetone extracts containing the  $\text{Th}^{230}$  were combined,  $\text{Ac}^{227}$  tracer was added to a portion, and the extract allowed to age for the experiment described in the section, Isolation of  $\text{Ac}^{225}$  from a  $\text{Th}^{230}$  Sample, Tracer Added.

The composite aqueous phase, containing radium, bismuth and lead daughters of  $\text{Th}^{232}$ , of  $\text{Th}^{230}$ , and of  $\text{Th}^{229}$  and relatively large quantities

of Th<sup>230</sup> and Th<sup>232</sup> in addition to the desired Ac<sup>225</sup>, was evaporated to dryness. The residue was dissolved in a small quantity of water and the solution converted to 10 ml. of saturated ammonium nitrate, 0.3 M in HNO<sub>3</sub>.

This aqueous feed was then contacted successively with four 10 ml. portions of dibutoxytetraethyleneglycol<sup>(11)</sup>, to extract thorium followed

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11. Dibutoxytetraethyleneglycol was obtained from Carbide and Carbon Chemical Corporation.

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by two 10 ml. portions of tributyl phosphate<sup>(12)</sup>, to extract actinium.

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12. Tributyl phosphate, the n-butyl orthoester, was obtained from Commercial Solvents Corporation.

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leaving radium in the aqueous phase. (Each of these organic phases had previously been pre-equilibrated with a large volume of saturated ammonium nitrate, 0.3 M in HNO<sub>3</sub>.) The aqueous feed was then followed, in the extraction cycle, by one 10 ml. portion of ammonium nitrate scrub (saturated ammonium nitrate, 0.3 M HNO<sub>3</sub>).

The dibutoxytetraethyleneglycol phases were then discarded. The two tributyl phosphate phases, containing actinium and traces of radium, were contacted successively with two five ml. portions of ammonium nitrate scrub, in order to reduce the radium content, then contacted successively with three 10 ml. portions of 4 M HNO<sub>3</sub> in order to transfer the actinium to an aqueous phase. The aqueous re-extract was scrubbed with carbon tetrachloride to remove traces of tributyl phosphate<sup>(13)</sup> and then evaporated to dryness

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13. This technique for removal of trace quantities of tributyl phosphate is recommended by J. C. Warf, J. Am. Chem. Soc., 71, 3257 (1949).

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with a heat lamp, taking care not to heat beyond dryness.

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The residue was taken up in two milliliters of saturated ammonium nitrate and the above cycle of dibutoxytetraethyleneglycol and tributyl phosphate extractions repeated on a scale one-fifth of the foregoing. The final water re-extract was evaporated to dryness and the residue allowed to age for 24 hours to permit  $\text{Ac}^{228}$  and residual Pb and Bi isotopes, not of the  $\text{Ac}^{225}$  series, to die out to a low value.

Another extraction cycle on the same scale was then performed. The final aqueous re-extract was then evaporated to dryness and the container heated with one milliliter of 0.02 M  $\text{HNO}_3$ , which was then evaporated to about 0.2 ml. This solution was then saturated with ammonium nitrate and contacted successively in a single centrifuge cone with two 0.10 ml. portions of tributyl phosphate. The tributyl phosphate phases were combined and an aliquot evaporated on a five mil platinum disc for alpha counting<sup>(14)</sup>

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14. Alpha counting was done with a methane proportional counter with an approximate 52% geometry factor. Beta counting was done on the first shelf of a Geiger-Muller counter, filled with neon-amyl acetate gas, with a window thickness of approximately 2 mg/cm<sup>2</sup>, using appropriate aluminum absorbers to prevent counting of alpha particles.

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and for measurement of alpha energies<sup>(6)</sup>. The data are listed in Table 1. The alpha pulse analysis curves are shown in Figure 1. The two curves pertain to the identical aliquot counted at different bias settings and for different counting times.

Isolation of  $\text{Ac}^{225}$  from a Sample of  $\text{Th}^{230}$ , Tracer Added.-- Using a shortened version of the preceding procedure a sample of  $\text{Ac}^{227}$  was separated from its daughter activities. This isotope of actinium has two modes of decay, approximately 1.2% of the decaying atoms emitting alpha particles and the remainder emitting beta particles<sup>(15)</sup>. The energy of the beta

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15. M. Perey, J. phys. rad., 10, 435 (1939); J. chim. phys., 43, 155 (1946).  
S. Peterson and A. Ghiorso, "National Nuclear Energy Series", Vol. IV - 14B, Paper 19.10 (1949).

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particles is too low to permit the use of beta counting as an assay technique. However, standardization of an  $\text{Ac}^{227}$  solution by determination of the alpha disintegration rate associated with a certain aliquot is easily accomplished if the alpha particles emitted by the  $\text{Ac}^{227}$  may be distinguished from the alpha particles emitted by the daughters of  $\text{Ac}^{227}$ . Consequently, a solution of this isotope was standardized, immediately after purification, by determining, through alpha pulse analysis, the number of alpha disintegrations per minute resulting from the alpha-branching of the  $\text{Ac}^{227}$  contained in an aliquot evaporated on a platinum disc. (The energy of the particles considered is sufficiently different from that of any of the  $\text{Ac}^{227}$  daughters that no difficulty is experienced if the sample is a freshly purified one.)

An aliquot of the standard  $\text{Ac}^{227}$  solution corresponding to 420 c/s due solely to alpha branching was added to a portion of the benzene-thenyltrifluoroacetone extract, described in the preceding section, containing  $5.31 \pm 0.05$  g. of  $\text{Th}^{230}$  (and 45 g. of  $\text{Th}^{232}$ ). (This portion of the extract had been mixed with 300 ml. of 0.1 M  $\text{HNO}_3$  immediately following the isolation of an actinium fraction as described in the preceding section.) The mixture was agitated for approximately 30 min. each day to prevent the accumulation of  $\text{Ac}^{225}$ , as formed, on the walls of the container. The extract was allowed to age for 56 days.

An actinium fraction was then isolated by the method described in the preceding section. The final tributyl phosphate extract was evaporated, in approximately equal parts, on two five mil platinum discs. One of these samples was immediately subjected to alpha pulse analysis (to determine that fraction of the total alpha activity due to  $\text{Ac}^{227}$  and that due to  $\text{Ac}^{225}$  and its daughters) and the other was concurrently subjected to alpha counting in a counter calibrated at approximately 52% geometry<sup>(14)</sup>. The data are included in Table 1. The alpha pulse analysis curve is shown in Figure 2. The bias setting and counting time differ from those used in obtaining the data of Figure 1.

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Isolation of an Actinium Fraction from a Th<sup>232</sup> Sample, no Tracer Added.

- A sample of thorium as the nitrate tetrahydrate (16), containing approxi-

16. The thorium nitrate, obtained from Lindsay Light and Chemical Co., had been isolated from a Brazilian monazite concentrate with approximate Th and U contents of 6% and 0.1% respectively.

ately one kilogram of Th<sup>232</sup>, was dissolved in approximately 14 liters of dibutoxytetraethyleneglycol by long stirring at room temperature. The clarified solution was scrubbed with six 500 ml. portions of 6 M ammonium nitrate. The extract, containing 985 ± 10 g. of Th<sup>232</sup>, was then allowed to age for 56 days.

At the conclusion of the ageing period, the extract was contacted with four 250 ml. portions of ammonium nitrate scrub (saturated ammonium nitrate, 0.3 M in HNO<sub>3</sub>) in order to strip the actinium, leaving the thorium in the organic phase. These aqueous phases were then separately and successively contacted with two 250 ml. portions of tributyl phosphate, in order to separate actinium from radium, etc.

The dibutoxytetraethyleneglycol phases were combined with the large dibutoxytetraethyleneglycol extract. Tracer Ac<sup>227</sup> was added and the extract allowed to age for the experiment described in the section, Isolation of an Actinium Fraction from a Th<sup>232</sup> Sample, Tracer Added.

The tributyl phosphate phases were then contacted successively with three 125 ml. portions of 4 M HNO<sub>3</sub>. The combined aqueous re-extract, containing actinium and contaminants, was scrubbed with carbon tetrachloride to remove traces of tributyl phosphate and then evaporated to dryness with a heat lamp, taking care not to heat beyond dryness.

The residue was dissolved in a small quantity of water and the solution converted to 10 ml. of saturated ammonium nitrate, 0.3 M in HNO<sub>3</sub>. The technique used for the isolation of an actinium fraction from a Th<sup>230</sup> sample was then used, beginning at the first dibutoxytetraethyleneglycol and tributyl phosphate cycle. The data are listed in table 2.

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Isolation of an Actinium Fraction from a Th<sup>232</sup> Sample, Tracer Added.

- An aliquot of the standard Ac<sup>227</sup> solution corresponding to 420 c/m due solely to alpha branching was added to the dibutoxytetraethyleneglycol extract, containing  $962 \pm 10$  g. of Th<sup>232</sup>, described in the immediately preceding section. Following a 73 day ageing period, an actinium fraction was isolated according to the procedure of the preceding section, beginning with the saturated ammonium nitrate scrub. The data are included in Table 2.

Results and Discussion.

From the data of Table 1 and the value of the half-life of Ac<sup>225</sup>, 10.0 days<sup>(1)</sup>, the ratio of Ac<sup>225</sup> to Th<sup>230</sup> by mass at secular equilibrium is calculated to be  $9.9 \times 10^{-16}$ . This figure should probably be set at  $(9.9 \pm 0.8) \times 10^{-16}$ . From this ratio, values for the following mass ratios, at secular equilibrium in the ore body, may be derived: Th<sup>229</sup> to Th<sup>230</sup>,  $(3.4 \pm 0.3) \times 10^{-10}$  and U<sup>233</sup> to U<sup>238</sup>,  $(1.3 \pm 0.2) \times 10^{-13}$ .

Table 1  
Isolation of Ac<sup>225</sup> from Th<sup>230</sup>

Expt.*	Th <sup>230</sup> (g)	Ageing (days)	Ac <sup>225</sup> isolated (c/m)	Yield (%)	Ac <sup>225</sup> content (c/m)
1	8.77	80	227	-	-
2	5.31	56	153	44.5	344**

\* Expt. 1 involved no Ac<sup>227</sup> tracer. In Expt. 2, Ac<sup>227</sup> tracer was added so that the chemical yield could be determined.

\*\* Since the feed solution of Th<sup>230</sup> had aged 56 days and the period between isolation of the Ac<sup>225</sup> sample from the Th<sup>230</sup> and alpha pulse analysis of the aliquot was 24 hrs., the "Ac<sup>225</sup> content" represents 76.4% of the maximum value.

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However, in order to calculate the  $\text{Np}^{237}$  to  $\text{U}^{238}$  ratio the contribution to the  $\text{U}^{233}$  content resulting from the  $\text{Th}(n, \gamma)$  reaction must be evaluated. It is thought that this contribution may be calculated with reasonable accuracy from the experimental value for the ratio of  $\text{Th}^{229}$  to  $\text{Th}^{232}$  in a  $\text{Th}^{232}$  ore.

From the data of Table 2 the ratio of  $\text{Ac}^{225}$  to  $\text{Th}^{232}$  at secular equilibrium is calculated to be less than  $1.1 \times 10^{-19}$  and may certainly be assumed to be less than  $2 \times 10^{-19}$ . From this latter figure the mass ratio of  $\text{Th}^{229}$  to  $\text{Th}^{232}$ , at secular equilibrium in the ore body, is calculated to be less than  $3 \times 10^{-14}$  corresponding to an upper limit for the  $\text{U}^{233}$  to  $\text{Th}^{232}$  mass ratio of  $7 \times 10^{-13}$ .

Table 2  
Isolation of  $\text{Ac}^{225}$  from  $\text{Th}^{232}$

Expt.*	$\text{Th}^{232}$ (g)	Ageing (days)	$\text{Ac}^{225}$ isolated (c/m)	Yield (%)	$\text{Ac}^{225}$ content (c/m)
1	985	56	<5	-	-
2	962	73	<3	51.5	<6**

\* Expt. 1 involved no  $\text{Ac}^{227}$  tracer. In Expt. 2,  $\text{Ac}^{227}$  tracer was added so that the chemical yield could be determined.

\*\* Since the feed solution had aged 73 days and the period between isolation of the  $\text{Ac}^{225}$  sample from the  $\text{Th}^{232}$  and alpha pulse analysis of the aliquot was 24 hrs., the " $\text{Ac}^{225}$  content" represents 85.1% of the maximum value.

In order to correct for the contribution from the  $\text{Th}^{232}(n, \gamma)$  reaction to the  $\text{Th}^{229}$  content of the  $\text{Th}^{230}$  sample of Table 1, use was made of the data of Levine and Seaborg<sup>(17)</sup> who found that the  $\text{Pu}^{239}$  to  $\text{U}^{238}$

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17. G. A. Levine and G. T. Seaborg, J. Am. Chem. Soc., 73, 3278 (1951).

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ratio in a Belgian Congo pitchblende sample was approximately 1.5 times the corresponding ratio for a Brazilian monazite sample. They suggest that the

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lower relative  $\text{Pu}^{239}$  content of the latter mineral is a result of neutron capture by rare earths. On this supposition, it appears logical to assume that for the pitchblende and monazite samples the respective rates of conversion of  $\text{Th}^{232}$  to  $\text{U}^{233}$  should equal the ratio of the respective rates of conversion of  $\text{U}^{238}$  to  $\text{Pu}^{239}$ .

Consequently, the maximum contribution to the  $\text{Th}^{229}$  to  $\text{Th}^{230}$  ratio in the pitchblende sample should be equal to the triple product: ( $\text{Th}^{229}$  to  $\text{Th}^{232}$  ratio in the monazite sample) times (the factor 1.5 mentioned above) times (the  $\text{Th}^{232}$  to  $\text{Th}^{230}$  ratio in the pitchblende sample). In the work being reported, the  $\text{Th}^{230}$  used had been isolated from Belgian Congo pitchblende concentrate, and the  $\text{Th}^{232}$  used had been isolated from Brazilian monazite. Therefore, it is felt that by the introduction of a factor of ten (to cover sample differences within a deposit of Brazilian monazite and within a deposit of Belgian Congo pitchblende) the contribution of the  $\text{Th}^{232}$  ( $n, \gamma$ ) reaction to the  $\text{Th}^{229}$  to  $\text{Th}^{230}$  ratio in the pitchblende concentrate used in the present work may be calculated by the above method.

Since the mass ratio of  $\text{Th}^{232}$  to  $\text{Th}^{230}$  in the sample studied is 8.40 the maximum contribution to the  $\text{Th}^{229}$  to  $\text{Th}^{230}$  mass ratio by the  $\text{Th}^{232}$  ( $n, \gamma$ ) reaction is calculated, by this method, to be  $4 \times 10^{-12}$ . This value is considerably below the experimental error involved in the determination of the  $\text{Th}^{229}$  to  $\text{Th}^{230}$  ratio.

It is concluded, therefore, that the source of the  $\text{Th}^{229}$  is  $\text{Np}^{237}$  formed by the  $\text{U}^{238}(n, 2n)$  reaction. The  $\text{Np}^{237}$  to  $\text{U}^{238}$  mass ratio(5) is then calculated to be  $(1.8 \pm 0.4) \times 10^{-12}$ .

This ratio may be compared with the  $\text{Pu}^{239}$  to  $\text{U}^{238}$  mass ratio of  $(1.5 \pm 0.2) \times 10^{-11}$  for a sample of pitchblende concentrate from the same deposit.(7) Since the ratio of the respective rates of formation of

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$\text{Np}^{237}$  and  $\text{Pu}^{239}$  is the same as the ratio of their respective activities as measured in the present ore body, assuming no appreciable variation in the neutron flux over past ages, it follows that the ratio of the respective neutron capture cross sections of  $\text{U}^{238}$  in the ore body for the (n, 2n) and (n, gamma) reactions may be calculated to be  $(1.3 \pm 0.6) \times 10^{-3}$ .

The neutron flux is assumed to be contributed to by neutrons resulting from: spontaneous fission of  $\text{U}^{238}$ , the  $\text{M}_1(\alpha, n)\text{M}_2$  reaction where  $\text{M}_1$  is a light element such as Li, Si, Mg etc., induced fission of  $\text{U}^{235}$  and cosmic rays. The importance of these various neutron sources in ore bodies has been discussed by Seaborg et al(3)(18) Garner et al(4), Levine et al(17)

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18. G. T. Seaborg, and H. L. Perlman, J. Am. Chem. Soc., 70, 1571 (1948).

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and Peppard et al(7).

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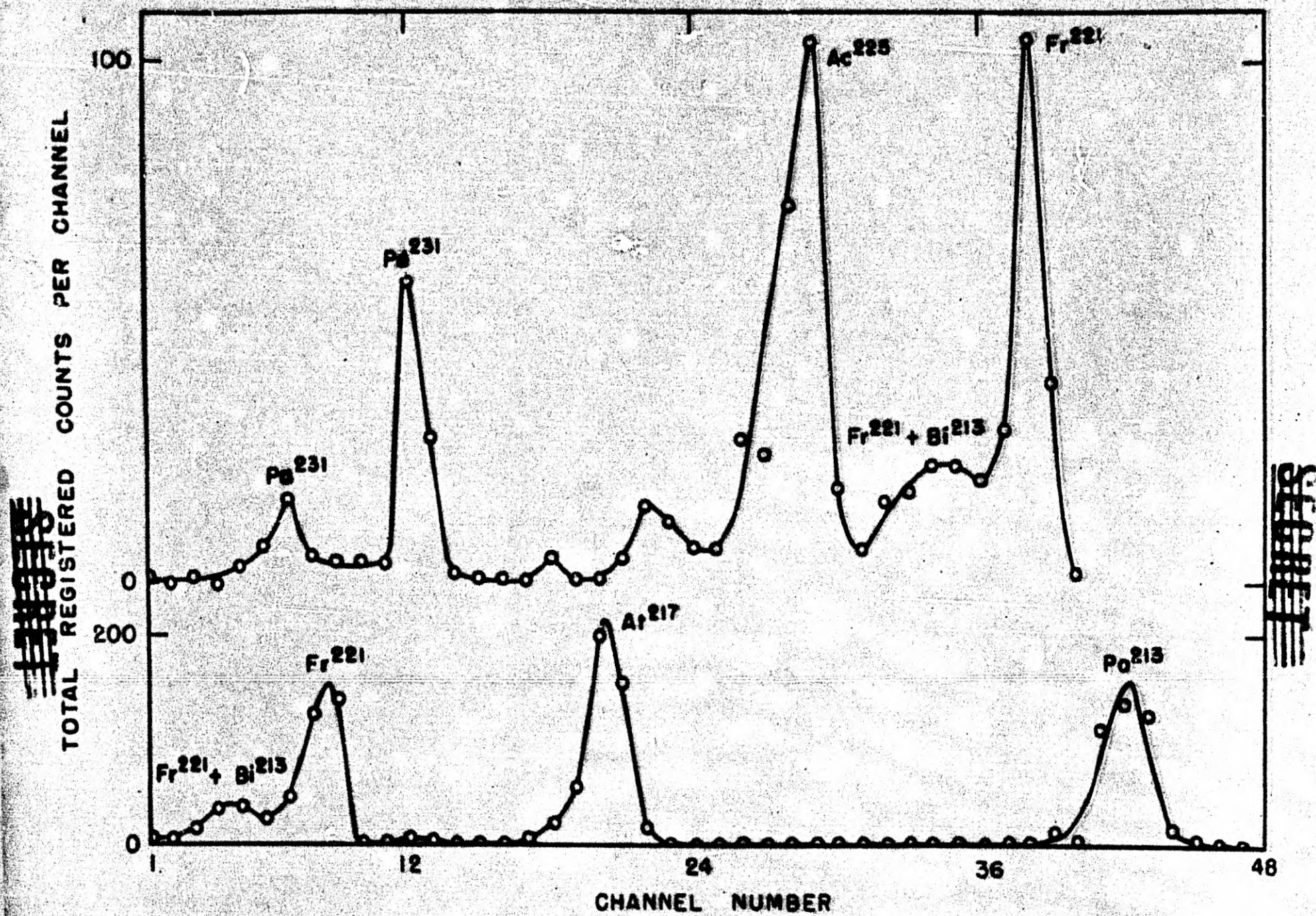


FIG. 1. ALPHA-SPECTRUM OF NATURALLY OCCURRING  $Ac^{225}$ .

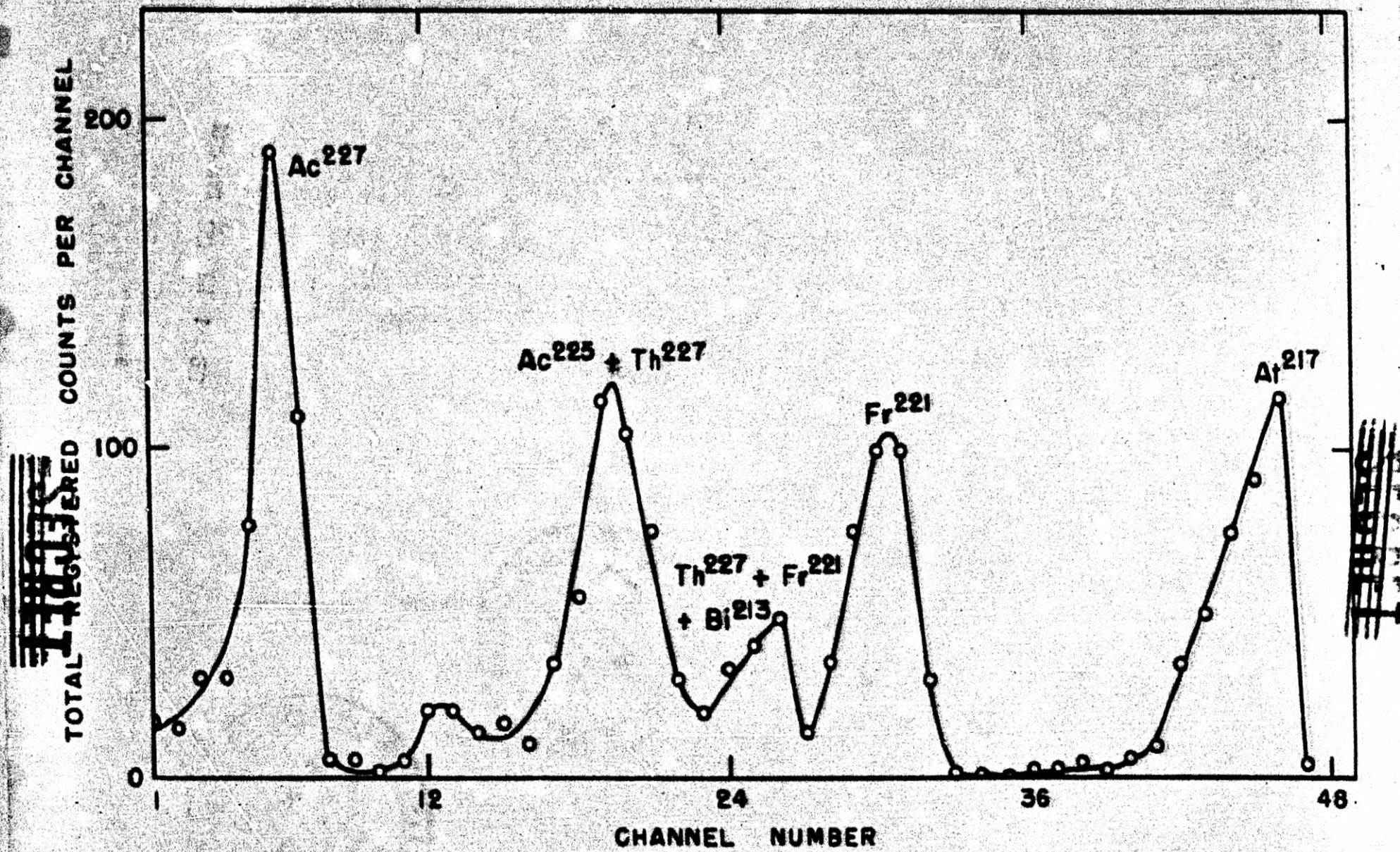


FIG. 2. ALPHA-SPECTRUM OF NATURALLY OCCURRING  $Ac^{225}$  WITH  $Ac^{227}$  TRACER.

**END**