The values of certain important pole potential differences have been ascertained for the temperature of  $25^{\circ}$  with a precision probably reliable to  $\pm 0.0002$  volt. These values are:

 Volt.
 Volt.
 Volt.

 Hg—HgCl 1.0 M KCl......
 0.5648
 Hg—HgCl 0.1 M KCl......
 0.6168

 Hg—HgCl 1.0 M HCl.....
 0.5567
 Hg—HgCl 0.1 M HCl.....
 0.6168

 PtH<sub>2</sub>(1 Atmos.)—1.0 M HCl....
 0.2777
 PtH<sub>2</sub>(1 Atmos.)—0.1 M HCl.....
 0.2179

 New York, N. Y.
 New York, N. Y.
 New York, N. Y.
 New York, N. Y.

[CONTRIBUTION FROM THE KENT CHEMICAL LABORATORY, UNIVERSITY OF CHICAGO.]

## THE RATIO OF MESOTHORIUM TO THORIUM.

By HERBERT N. MCCOY AND LAWRENCE M. HENDERSON. Received June 6, 1918.

The thorium series comprises the following substances: Th,  $Ms_1$ ,  $Ms_2$ , Rt, ThX, Em, A, B, C, D. The first product of thorium called mesothorium-one,  $Ms_1$ , or simply mesothorium, has a period of 5.5 years and is rayless; it produces mesothorium-two,  $Ms_2$ , which has a period of 6.14 hours and gives intense beta and gamma rays. Pure  $Ms_1$ , after an interval of about 3 days, contains the maximum amount of  $Ms_2$ . The  $\gamma$ -ray activity of mesothorium is, therefore, due to  $Ms_2$ . Since mesothorium has never been obtained pure, its amount, in a given case, is only determinable by its activity. One milligram of mesothorium is, by convention, a quantity of  $Ms_1$  containing the equilibrium amount of  $Ms_2$ , which has a  $\gamma$ -ray activity equal to that of one mg. of radium, containing the equilibrium amounts of its short-lived products.

The activities of pure thorium compounds and minerals have been studied by Boltwood,<sup>1</sup> McCoy and Ross,<sup>2</sup> Dadourian,<sup>8</sup> and McCoy and Viol,<sup>4</sup> and others. As a result, it has been definitely shown that the  $\alpha$ -ray activity of a mineral is proportional to its thorium content, correction being made for any radium and uranium present. This proves that there exists a constant ratio of Ms to Th. The object of the work here reported was the determination of this ratio. In anticipation, it may be stated that we found that "one milligram of mesothorium" is in equilibrium with 19.0  $\times$  10<sup>6</sup> mg. of thorium in minerals. In other words, one g. of thorium contains 0.524  $\times$  10<sup>-6</sup> milligrams of mesothorium, a "milligram of mesothorium" being defined as above.

In the uranium series, it was early shown by Boltwood,<sup>5</sup> McCoy,<sup>6</sup>

- <sup>1</sup> Am. J. Sci., 21, 409 (1906).
- <sup>2</sup> Ibid., 21, 433 (1906); THIS JOURNAL, 29, 1709 (1907).
- \* Am. J. Sci., 21, 427 (1906).
- Phil. Mag., 25, 333 (1913).
- <sup>5</sup> Nature, 70, 80 (1904); Phil. Mag., 9, 599 (1905).
- <sup>6</sup> Ber., 37, 2641 (1904); THIS JOURNAL, 27, 391 (1905).

Rutherford and Boltwood,<sup>1</sup> Strutt,<sup>2</sup> and in more recent work by Lind and Whittemore,<sup>8</sup> that there exists a constant ratio between the radium and uranium content of minerals, in which the radioactive products have reached equilibrium. For certain minerals giving abnormal values for this ratio, it was shown by McCoy<sup>4</sup> that the radium had been concentrated by percolating water. These secondary minerals have been further studied by Mlle. Gleditsch,<sup>5</sup> Soddy,<sup>6</sup> Russell,<sup>7</sup> and Marckwald and Russell.<sup>8</sup> It seems probable that for minerals which show abnormal values for the Ra/U ratio, recent alteration has occurred, due to a part of the radium having been washed away, or to its having been concentrated by natural agencies. Therefore, for old and unaltered minerals there exists a constant ratio between the radium and uranium content, which, corrected to the new International Standard,<sup>9</sup> is equal to  $3.23 \times 10^{-7}$  by weight.

The best method of determining the Ra/U ratio is based on the measurement of the radium content of minerals by means of radium emanation. A similar procedure is not possible for the Ms/Th ratio for the reason that thorium emanation arises from ThX which, in turn, is formed from radiothorium, which has a period of over two years. Both for scientific and technical reasons a knowledge of the Ms/Th ratio is a matter of considerable importance. It is probably chiefly due to experimental difficulties that this ratio has not been determined heretofore. The  $\gamma$  activity of a thorium mineral is only partially due to the Ms present. In addition to radium, which, along with uranium, is usually present, ThD gives intense  $\gamma$  rays and is probably responsible for nearly twice as much  $\gamma$  activity as the Ms.

It is possible to get an approximate estimate of the total activity of a thorium mineral directly without separation of the mesothorium. This has been done by Eve,<sup>10</sup> who used thorianite and found that  $6.9 \times 10^{6}$  g. of thorium in a mineral has a  $\gamma$  activity equal to that of one g. of radium. Eve corrected for the activity due to radium contained in the thorianite, but does not state how he corrected for the great absorption of the  $\gamma$  rays in the mineral.

We have repeated Eve's experiment in the following manner: The  $\gamma$  activity of 735.8 g. of thorianite containing 50.7% thorium was first

<sup>1</sup> Am. J. Sci., 20, 155 (1905); 22, 1 (1906).

- <sup>2</sup> Nature, 69, 473 (1904); 70, 222 (1904); Proc. Roy. Soc., 76a, 81, 312 (1905).
- <sup>8</sup> Technical Paper 88, Bureau of Mines (1915).
- 4 This Journal, 29, 1698 (1907).
- <sup>5</sup> Compt. rend., 148, 1451 (1909).
- Phil. Mag., 20, 345 (1910); 21, 652 (1911).
- 7 Nature, 84, 238 (1910).
- <sup>8</sup> Ber., 44, 771 (1911).
- <sup>9</sup> Rutherford, Phil. Mag., 28, 322 (1914).
- <sup>10</sup> Am. Jour. Sci., 22, 477 (1906).

determined by placing the pasteboard cartoon containing the thorianite in a lead dish on top of a brass electroscope. Then half of the thorianite was removed, 368.12 g. remaining. The radium standard (0.355 mg. Ra element) was then placed in a groove of the lead dish. (The groove was used merely to supply a definite position for the tube of radium throughout the series of measurements.) Over the radium standard was placed the cartoon containing 368.12 g. of thorianite, and the  $\gamma$ activity of both determined. The tube of radium was then removed and placed in a corresponding position on top of the thorianite and the time of discharge again taken. Deducting the activity due to the 368.12 g. of thorianite in each case, the apparent loss in activity of the radium standard due to the absorption of the  $\gamma$ -rays by the mineral was found to be 59.2%. Therefore the activity of the 735.8 g. of thorianite as observed represented approximately only 40% of its activity, if no absorption had occurred. Correcting, then, for this absorption, the total  $\gamma$ activity of the mineral was found to be equal to 0.0967 mg. Ra. The mineral contained 0.0422 mg. of radium. The remaining  $\gamma$  activity of the mineral = 0.0545 mg. Assuming that this activity (= 0.054 mg. Ra) was due entirely to thorium products, it follows that the  $\gamma$  activity of 1 g. of radium element is equivalent to that of  $6.85 \times 10^6$  g. thorium in equilibrium with its products. This value is in good agreement with Eve's result,  $6.9 \times 10^6$ . It is obvious that this method is not free from criticism and that the result so obtained cannot be considered as more than approximate, without confirmation by other methods. Since we did not know at the time this work was done the relative  $\gamma$  activities of Ms and ThD, we could not calculate from the above result the ratio of mesothorium to thorium. It might be noted here that on account of the short life of Ms<sub>1</sub> compared with that of Ra and also the fact that thorium disintegrates directly into Ms<sub>1</sub>, there was little likelihood that thorium minerals would show abnormal values for the Ms/Th ratio, due to alteration by external agencies.

Kithil,<sup>1</sup> in a recent paper, quotes Lorenzen to the effect that, technically, 2.5 mg. of Ms can be obtained from 1 metric ton of monazite, containing 4.3% thorium element. This value is near that obtained by us. In the same paragraph, however, Kithil states that "the mesothorium obtained from one metric ton of monazite, would be calculated as 5.4 mg." Kithil, in calculating that 5.4 mg. of mesothorium can be obtained from 1 ton of monazite containing 4.3% Th element, assumes that the relative  $\gamma$  activities of Ms<sub>1</sub> and Ra are inversely proportional to their periods, which assumption is not warranted unless the  $\gamma$  rays from Ms and Ra produce the same amount of ionization atom for atom.

The large quantity of the minerals necessary to give sufficient meso-<sup>1</sup> Technical Paper 110, U. S. Bureau of Mines (1915). thorium for accurate measurement by the  $\gamma$ -ray method prohibited a direct comparison with the  $\gamma$  activity of radium. Therefore an indirect method was followed which, in brief, was to determine the  $\beta$ -ray activity of the Ms extracted from a known amount of thorium; and then to measure for pure Ms the ratio of  $\beta$  to  $\gamma$  activity. The  $\beta$  activity of the Ms could then be expressed in units of  $\gamma$  activity; and knowing the  $\gamma$  activity in terms of radium, we could find the amount of thorium necessary to produce one mg. of mesothorium.

Two gold leaf electroscopes were used in the work. The bottom of the ionization chamber of the  $\beta$ -ray instrument was made of 0.05 mm. of aluminum. The films were placed 5 cm. below this aluminum screen and all measurements were made by comparison with a constant arbitrary standard.

The  $\gamma$ -ray measurements were made through 2.03 mm. of lead and 1.32 mm. of brass, in the following manner: a circular lead dish with flat bottom was placed on top of a brass electroscope. The film or precipitate on the filter paper was placed directly in this lead dish; and the  $\gamma$ activity determined in terms of our radium standard; this standard contained 0.355 mg. Ra element, as determined by comparison with the  $\gamma$ -ray activity of 2.061 mg. Ra element contained in a similar glass tube and recently standardized by the Bureau of Standards at Washington, D. C.

Since Ra and ThX are isotopes of Ms all new preparations of the latter substance from thorium minerals contain also the two former. For this reason the  $\beta$  and  $\gamma$  activity of new Ms are variable during the first month. By the end of this interval radium emanation and its products have reached maximum amounts and ThX and its products have completely decayed. All activity measurements of Ms were made a month or more after its separation from a mineral. Two procedures were followed: In the first the total  $\beta$  activity of a barium sulfate film was measured and correction was made for the activity due to the radium, the amount of which was determined by the emanation method. The second method, which was used in all except the preliminary experiments, consisted in converting the active barium sulfate into chloride, and after a month's interval separating from a solution of the latter pure Ms<sub>2</sub> and measuring its  $\beta$  activity. During the month, the ThX originally present decayed; and the formation of new ThX was prevented by occasional removal of the radiothorium formed by means of aluminum hydroxide precipitated in the solution. Radium emanation was removed by a current of air blown through the solution for 4 or 5 hours immediately before the separation of the  $Ms_2$  for measurement. The removal of radium emanation allowed its short-lived products to decay completely.

To separate the Ms<sub>2</sub>, one to two cc. of a 5 % solution of aluminum

chloride was added to the solution of Ms, which was then heated to boiling, and just sufficient ammonia gas was passed in to make the solution alkaline, methyl orange being used as indicator.<sup>1</sup> The time at which the solution turned alkaline was taken as zero time for the Ms<sub>2</sub> thus precipitated. The solution was filtered with suction in 2 or 3 minutes, using a filter paper on a glass plate in a glass funnel; this spreads the precipitate quite uniformly over considerable surface and affords a very thin film, which shows practically no absorption of the  $\beta$  rays. The film of Ms<sub>2</sub> and aluminum hydroxide was rapidly dried and its  $\beta$  activity measured at once. The whole operation, from the time the solution turns alkaline to the time of the first measurement, requires about 15 minutes. This makes the correction for the amount of Ms<sub>2</sub> which decays in this time very small. The  $\beta$  activity of the Ms<sub>2</sub> at time zero, may be readily calculated from the observed activity, at a given time and the decay constant for Ms<sub>2</sub>. Inasmuch as Ms<sub>1</sub>, alone, has very little, if any, activity the  $\beta$ activity of Ms<sub>2</sub> at the instant of separation from Ms<sub>1</sub> respresents the entire  $\beta$  activity of a Ms preparation which contains only Ms<sub>1</sub> and Ms<sub>2</sub>. The activity of the Ms<sub>1</sub> at the time of separation from the original mineral or Th preparation is then readily deduced from the observed  $\beta$  activity of Ms<sub>2</sub> and the decay constant of Ms<sub>1</sub>.

The number of arbitrary  $\beta$  units of Ms<sub>2</sub> equivalent to the  $\gamma$  activity of one mg. of radium was determined in the following manner: An active solution of Ms1 was made from radium free residues of mantel ash, generously donated by the Lindsay Light Company, Chicago. The solution was divided, by weight, into two portions containing 98.896% and 1.104%, respectively, of the total smount of mesothorium-one. The smaller portion was used for the  $\beta$ -ray measurements, according to the scheme outlined above. Aluminum hydroxide was precipitated in the solution at frequent intervals over the course of a month, during which time the ThX had completely decayed. Then the  $\beta$  activity of the Ms<sub>2</sub> obtained from the solution was determined at 3-day intervals. The 98.896% portion was treated in the same way save that its  $\gamma$  activity was determined. The  $\alpha$  activity was measured in terms of a constant arbitrary standard. The  $\gamma$  activity was measured in terms of the  $\gamma$  activity of our secondary standard (0.355 mg. Ra). Knowing the relative amounts of Ms1 in each solution and the  $\gamma$  activity of the stronger in terms of one mg. of Ra and the  $\beta$  activity of the other in arbitrary  $\beta$  units, we could readily calculate the number of arbitrary  $\beta$  units due to Ms equivalent to the  $\gamma$  activity of one mg. of Ra or Ms, when the  $\gamma$  rays from the Ms were due entirely to Ms<sub>2</sub>. Two separate and distinct solutions of Ms<sub>1</sub> were thus divided, and the ratio of  $\beta$  to  $\gamma$  activity determined. The average value of several

<sup>2</sup> McCoy and Viol, Phil. Mag., 25, 336 (1913).

determinations gave 278 arbitrary  $\beta$  units of Ms<sub>2</sub> equivalent to the  $\gamma$  activity of one mg. of radium element.

Various methods of extracting Ms1 from minerals were tried out to see if they gave quantitative separations, and to see if they would check with one another. The first material worked with was thorianite, containing 50.7% thorium and 57.38  $\times$  10<sup>-6</sup> mg. Ra per g. of mineral. In the first method, we separated the Ms1 from the thorium by means of basic carbonate of iron according to McCoy and Viol.<sup>1</sup> About 25 g. of thorianite, containing 50.7% Th and 57.38  $\times$  10<sup>-6</sup> mg. Ra per g. was ground to 100 mesh and dissolved in nitric acid (1 : 1); the small insoluble residue was further treated with aqua regia. The final residue showed practically no activity. To the combined filtrates was added 5 mg. of ferric chloride in dilute solution, and 5 cc. 0.2 N barium chloride, after which the solution was slowly poured into about one liter of a solution of 250 g. of Na<sub>2</sub>CO<sub>3</sub>.-10H2O and 100 g. NaHCO3. A precipitate formed slowly carrying with it the major portion of the Ms<sub>1</sub> and Ra; this was allowed to settle and then filtered, and the precipitate saved. To the filtrate ferric chloride was again slowly added in dilute solution. Three such precipitations suffice for all practical purposes, but five were made to insure complete removal of the Ms<sub>1</sub>. The precipitates were then dissolved in dil. hydrochloric acid and the barium precipitated as sulfate by means of a considerable excess of sulfuric acid. This gave precipitates which were not very thick, and consequently did not show much absorption of the  $\beta$  rays.

The results obtained by this method are shown in Table I.

Determination of the Ratio of Ms/Th in Thorianite, Measuring the Activity of the Mesothorium in the Form of a Sulfate Precipitate. Grams Micrograms<sup>2</sup> Obs. β Act. Age of β Act. β Act. Ms/Th

TABLE I.

Expt. No.	Grams of Th.	Microgram of Ra.	Ra + Ms.	. Age of ppt. (days).	β Act. Ms alone.	β Act. per g. Th.	Ms/Th × 107
3-12	10.97	1.232	0.683	36	0.174	0.01586	0.570
3-6	8.23	0.925	0.500	34	0.118	0.01434	0.516
3-43	I3.44	1.360	0.773	46	0.209	0.01555	0.560
						A	7., 0.55

The Ms/Th ratio in the last column was found by dividing the  $\beta$  activity per g. of Th (next to last column) by 278, the  $\beta/\gamma$  ratio.

In the above measurements the correction for the  $\beta$  activity of the radium present was made in the following manner: The radium content of some pitchblende was determined by the emanation method, by fusing it with potassium hydrogen sulfate and measuring the Em produced, as outlined below. A convenient quantity of pitchblende was then dissolved in nitric acid, one mg. of barium chloride added, and the barium precipitated as sulfate. This precipitate was sealed up in an air-tight

<sup>1</sup> Phil. Mag., 26, 334 (1913).

<sup>2</sup> One microgram = 0.000001 g.

case with a thin aluminum foil cover. Its  $\beta$  activity was determined 30 days later.

403  $\times$  10<sup>-6</sup> mg. Ra gave a  $\beta$  activity = 0.1715.

A small quantity of pitchblende was dissolved in nitric acid and the Ra Em determined in the strong acid solution. To the solution was then added one mg. of barium chloride and precipitated as sulfate. This precipitate was not sealed up air-tight.

400  $\times$  10<sup>-6</sup> mg. radium gave  $\beta$  activity = 0.1653.

The second method of extracting Ms from thorianite consisted in adding to the acid solution of the mineral barium chloride<sup>1</sup> and then a large excess of sulfuric acid, for it is only when the concentrations of barium salt and sulfuric acid are sufficient that barium sulfate carries down Ms1 completely.<sup>2</sup> For the quantities of mineral used in each determination (approx. 25 to 35 g. of thorianite) it was found that I to  $I_{.5}$  g. of BaCl<sub>2</sub>.- $_{2H_{2}O}$  were sufficient to carry down all the Ms<sub>1</sub>, provided the solution was not too concentrated with respect to thorium, and that about 3% of sulfuric acid was present. The sulfuric acid (6 N) was added slowly from a dropping funnel, the solution being stirred, and the stirring continued 3 or 4 hours longer to produce as crystalline a precipitate as possible. The entire precipitation was carried out in the cold. The precipitate, together with the residue of the mineral insoluble in acids, was boiled with a strong solution of sodium hydroxide and sodium carbonate to dissolve the lead and convert the Ms<sub>1</sub>, Ra and Ba sulfates into carbonates. The residue was filtered and washed free from sulfates and the whole treatment repeated. The residue was now dissolved in dil. hydrochloric acid, filtered and washed thoroughly. This solution contained all the  $Ms_1$ and Ra of the original sample.

Th  $\beta$  activity was then determined by means of the Ms<sub>2</sub> precipitated with aluminum hydroxide according to the method outlined above. The two methods used for extracting the mesothorium gave nearly the same results for the Ms/Th ratio.

TABLE II.

The Ratio of Ms/Th in Thorianite.				Precipitation with Aluminum Hydroxide.			
Expt. No.	G. of thorium.	Observed activity.	Age of Sol (days)	$e^{-\lambda i}$	β Act. at time zero.	β Act. per g. Th.	Ms/Th × 10.7
3-12	10.97	0.130	506	0.837	0.155	0.0142	0.511
3-43	13.44	0.1746	475	0.850	0.2054	0.0153	0.550
468	12.94	0.1884	158	0.947	0.1988	0.01537	0.553
6-35	17.02	0.245	41	0.985	0.2488	0.01461	0.526

Av., 0.535

<sup>1</sup> Ramsay, J. chim. phys., **3**, 623 (1905); Boltwood, Am. J. Sci., **24**, 99 (1907); Marckwald, Ber., **43**, 3421 (1910).

<sup>2</sup> Soddy, J. Chem. Soc., 99, 72 (1911); McCoy and Viol, Loc. cit.

As a further check on the efficiency of the method of extraction of  $Ms_1$ , the radium contents of the original mineral, the solution of the mineral, and the final  $Ms_1$  solution were determined by the emanation method. Since  $Ms_1$  and Ra are isotopes, if the final solution contained all the Ra of the original sample, it should also contain all the  $Ms_1$ . These determinations gave the following amounts of radium for 1 g. of thorianite:

Thorianite,	$56.7 \times 10^{-6}$
Original solution,	$57.38 \times 10^{-6}$ mg.
Final solution,	57.0 × 10 <sup>-6</sup>

These results show that the total radium content of the sample was present in the final solution which must, therefore, have also contained all the mesothorium.

In determining radium, the emanation was liberated from thorianite by fusion in a hard glass tube with six times its weight potassium hydrogen sulfate. The melt was then sealed up for a known interval of time and the accumulated emanation set free by fusion and transferred to the electroscope. The activity was observed at the end of 15 minutes, instead of after 3 hours, as is usual. In 15 minutes thorium emanation has completely decayed and transformed into inactive ThB, while very little active ThC and ThD have been formed. On the other hand, RaA has nearly reached equilibrium, so that the total activity is not changing fast. We obtained very satisfactory results in this way.

Monazite is readily attacked by hot conc. sulfuric acid. If sufficient acid is used the product dissolves almost completely in water. If some barium is present, the small insoluble residue contains practically all the mesothorium. Our final procedure was as follows: 500 g. of monazite and 2 g. of barium chloride were heated with 500 cc. of conc. sulfuric acid for 6 to 8 hours, with occasional stirring. The cold product was added slowly to 3 l. of ice-cold dil. sulfuric acid and the whole stirred 15 to 20 hours, and then filtered. The small residue consisted largely of quartz, ilmenite and phosphates of thorium and rare earths together with the barium sulfate, containing Ra and Ms. No unchanged monazite was present. The insoluble portion was digested with dil. hydrochloric and sulfuric acids in order to dissolve the phosphates of thorium and rare earths, which have a tendency to hinder the precipitation of barium sulfate in subsequent operations. Then the entire residue was boiled with 100 g. sodium hydroxide and 25 g. sodium carbonate in about 700 cc. of water for 2 hours, and diluted while hot to two liters, filtered, and washed free from sulfates. This removed the lead and converted a portion of the sulfates into carbonates. The alkali filtrates were discarded. The residue was again boiled with alkali 2 to 3 hours, filtered, and washed free from sulfates. It was then treated with dil. hydrochloric acid, filtered and thoroughly washed. The filtrate and washings contained the

major portion of the  $Ms_1$ . The residue was then boiled a third time with a solution of 70 g. sodium carbonate, which nearly always sufficed for complete conversion of the sulfates into carbonates. The small amount of barium with its Ms obtained from the last carbonates was added to the main solution, which then contained all the  $Ms_1$  of the original sand.

However, this solution of Ms could not be used for the determination of the Ms present by the aluminum hydroxide method given above, as it always contained some phosphoric acid, which in an alkaline solution precipitated some of the Ms<sub>1</sub> and Ra. Therefore, the barium was again precipitated as sulfate; and the precipitate fused with sodium and potassium carbonates and reconverted into a chloride solution. This solution was free from phosphoric acid, and the Ms could then be determined by the aluminum hydroxide method. The volume of the chloride solution was about 60 cc. and was kept small to permit rapid filtration of the aluminum hydroxide. The quantities of Ms<sub>1</sub> thus obtained from monazite sand, and the corresponding values for the ratio Ms/Th are given in Table III. The thorium content of the monazite was determined according to the method of Campbell and Carney,<sup>1</sup> which we found to give concordant results.

			TUBLE III			
The Ratio	Ms/Th in M	Ionazite.	Precipitation	ı by Means	s of Aluminu	n Hydroxide
			Indian San	d.		
Expt. No.	G. of thorium.	Obs. activity.	Age of sol. in days.	β Act. at time zero.	β Act. per g. Th.	$ \frac{Ms/Th}{\times 10^7} $
6-2	39.24	0.6055	12	0.555	0.01415	0.509
		0.550	30			
6-42	39.24	0.585	20	0.585	0.0149	0.536
6-60	39.24	0.535	20	0.535	0.01363	0.491
6-24	39.24	0.530	27	0.535	0.0136	0.491
					Average	= 0.507
			Brazilian Sa	nd.		
6-104	28.83	0.3833	39	0.387	0.01345	0.484

# The Mesothorium Content of Pure Thorium Nitrate Solutions of Known History.

Next, a series of thorium solutions, of known age and history, were studied. These solutions were samples of pure thorium nitrate made from mantle-ash by the Linday Light Co., of Chicago. This ash contained about 95% of ThO<sub>2</sub>, which was obtained from gas mantles that had been made from pure thorium nitrate. Each sample bore the exact date of its manufacture. That practically all the Ms<sub>1</sub> had been removed from the thorium during the process of its manufacture was shown by the fact that a solution 17 days old made by the same process contained

<sup>1</sup> THIS JOURNAL, 36, 1134 (1914).

no more Ms than that formed in the solution during the 17 days since the purification of the thorium nitrate. Knowing the decay constant for  $Ms_1$  we may, therefore, calculate the fraction of the total equilibrium amount of  $Ms_1$  present in these solutions at any time.

In the extraction of the Ms from these solutions, two methods were used. In the first after the addition of 5 cc. of 0.2 N barium chloride, the thorium was precipitated as hydroxide by means of ammonia gas, which leaves the major portion of the Ms<sub>1</sub> in the filtrate. The solution was filtered and the filtrate set aside, as it contained the larger part of the Ms. The precipitate was dissolved in dil. hydrochloric acid and reprecipitated with ammonia gas. This was repeated 5 to 6 times, to insure the complete removal of the Ms. All the filtrates were combined, save the last one which was kept as a check, to determine whether the Ms had been completely removed by the previous treatments. From the combined filtrates, the Ms and Ba were precipitated as sulfates, by means of dil, sulfuric acid. The barium sulfate contained all the Ms<sub>1</sub> of the original solution, which had grown since the manufacture of the thorium nitrate. Thus, knowing the time of the last removal of  $Ms_1$  and the thorium content of the solutions, we could readily calculate the equilibrium amount of the Ms<sub>1</sub> from the observed activity, and consequently the amount of Ms<sub>1</sub> in equilibrium with one g. of thorium.

TABLE IV.

The Ratio Ms/Th for Pure Thorium Nitrate Solutions of Known Age and History, Measuring the Mesothorium as a Sulfate Precipitate.

Expt. No.	Age of sample (years).	Grams or thorium.	Act. of ppt.	Age of ppt. in days.	β Act. per g. Th at time of ob- servation.	1e <sup>λt</sup> .	β Act. per g. Th in equilibrium.	Ms/Th × 107.
3-61	3.633	15.397	0.0945	63	0.0061	0.3687	0.01656	0.596
3-53	3.625	13.375	0.0806	67	0.00626	0.3687	0.01634	0. <b>58</b> 8
379	3.875	16.785	0.0919	49	0.00549	0.3863	0.0142	0.511
376	3.952	14.61	0.0868	51	0.00594	0.393	0.0151	0.543
							Average =	0.559

In the second method of separating the mesothorium from the thorium solutions, one to two g. of crystallized barium chloride was added and then precipitated by adding a very large excess of sulfuric acid, as outlined for thorianite. The best results were obtained when the following concentrations were observed: for about 30 g. of thorium element present in a volume of 600 cc., 1.5 g. of barium chloride was added, and then 45 cc. of 6 N sulfuric acid was slowly run into the solution in the cold and stirred for several hours. The barium sulfate thus precipitated was fused with sodium and potassium carbonates in a nickel crucible and the carbonates thus formed were converted into chlorides and the activity of the resulting solution determined as  $Ms_2$  with aluminum hydroxide. The values thus

obtained from pure thorium nitrate solutions of known history and age are given in Table V.

TABLE V.

The Ratio Ms/Th for Pure Thorium Nitrate Solutions of Known Age and History, Precipitation with Aluminum Hydroxide.

Expt. No.	Age of sample (years).	Grams of thorium.	Obs. act.	Age of sol. Ms <sub>1</sub> in days.	$\frac{1-e^{-\lambda t}}{Th \text{ sol}}$	β Act. of equil. amt. of Ms <sub>1</sub> .	βAct.per g.Th.	$\stackrel{\mathrm{Ms/Th}}{\times 10^{7}}$ .
6-97	5.75	59.85	0.445	<b>2</b> 0	0.5158	0.858	0.0143	0.516
6-100	5.3	45.58	0.300	25	0.4872	0.612	0. <b>013</b> 6	0.490
6-112	5.792	25.99	0.1946	<b>2</b> 6	0.5181	0.376	0.01446	0.520

Average = 0.508

## TABLE VI.

Summary of the Results Obtained for the Ratio Ms/Th.

		Ratio Ms/1h.
Ι.	Thorianite, BaSO4 method	$0.550 \times 10^{-7}$
II.	Thorianite, Al(OH) <sub>3</sub> method	0.535
$\mathbf{III}$ .	Indian Monazite, Al(OH) <sub>8</sub> method	0.507
	Brazilian monazite, Al(OH) <sub>8</sub> method	o.484
IV.	Pure thorium nitrate, BaSO4 method	0.559
V.	Pure thorium nitrate, Al(OH) <sub>8</sub> method	0.508

Average =  $0.524 \times 10^{-7}$ 

The average value of the ration of mesothorium to thorium is seen to be  $0.524 \times 10^{-7}$ . The reciprocal of this ratio 19.0  $\times$  10<sup>6</sup>, is the weight in grams of thorium in equilibrium with one g. of mesothorium, one g. of mesothorium being that quantity which has a  $\gamma$  activity equivalent to that of one g. of radium. The approximate measurements of Eve and of ourselves showed that 6.9  $\times$  10<sup>6</sup> g. of thorium give a total  $\gamma$  activity equal to one g, of radium, while 19.0  $\times$  10<sup>6</sup> g, of thorium are required to yield mesothorium having this same  $\gamma$  activity. Therefore the  $\gamma$  activity of mesothorium is only 6.9/19.0 or 36.3% of the total  $\gamma$  activity of thorium in equilibrium with all its products. Since mesothorium two, and thorium D are the only products that emit penetrating rays, the difference between the  $\gamma$  activity found for thorium in equilibrium with all its products and when in equilibrium with only mesothorium must be due to thorium D.

We consider the results obtained by the use of aluminum hydroxide more accurate than those from barium sulfate precipitates. It is of interest to note that the Ms/Th ratio,  $0.52 \times 10^{-7}$ , is only about onesixth as great as the Ra/U ratio,  $3.23 \times 10^{-7}$ .

CHICAGO, ILLINOIS.

1326