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The Isotopism of Mesothorium and Radium
and the Separation of these Elements
from Barium

DISSERTATION

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BY

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THE ISOTOPISM OF MESOTHORIUM AND RADIUM AND THE SEPARATION OF THESE ELEMENTS FROM BARIUM.

Shortly after the discovery of mesothorium, it was stated by Marckwald¹ that this element is completely similar to radium in its chemical properties, no reaction having been found that gave a separation of the two. Marckwald also found that mesothorium accompanies radium in the process of fractional crystallization of barium chloride containing these 2 radioactive elements. Soddy² also confirmed this conclusion in subsequent experiments in which it was found that if any separation did

¹ Marckwald, *Ber.*, **43**, 3420 (1910).

² Soddy, *Trans. Chem. Soc.*, **99**, 72 (1911).

occur, it did not exceed 2%, approximately the limit of the experimental error of the determinations. In Soddy's work,¹ the concentration of the active elements was 62 times greater in the rich than in the lean fraction.

Such elements as mesothorium and radium, which behave in the same way chemically, Soddy has called "isotopes." Since other methods than the chloride process are available for the enrichment of mesothorium and radium, it seemed desirable to examine some of these in a quantitative manner to ascertain whether mesothorium is concentrated to the same extent as radium in these cases.

Accordingly, in the investigation here reported, a mesothorium-radium-barium mixture was concentrated in 2 ways, first, by the McCoy hydroxide method,² and, second, by the bromide method; and the mesothorium/radium ratio determined at various stages in the process of concentration.

The work may be divided thus:

(a) The preparation from monazite residues of 1100 g. of barium chloride containing about 11 mg. of mesothorium³ and 3 mg. of radium.

(b) The concentration of mesothorium and radium by the fractional crystallization of the hydroxide, by means of which a rich fraction was obtained, containing 8.4 mg. of mesothorium in 17 g. of crystallized barium chloride ($\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$) and a lean fraction containing 0.22 mg. of mesothorium in 746 g. of crystallized barium chloride with the remainder of the material in the form of intermediate fractions.

(c) Mesothorium and radium were determined in the rich and lean fractions and the ratio in each compared.

(d) The rich fraction from the hydroxide concentration was converted into bromide and the mesothorium and radium further concentrated by the well-known method of fractional crystallization of the bromide, whereby 6.4 mg. of mesothorium were obtained in 0.55 g. of crystallized barium bromide ($\text{BaBr}_2 \cdot 2\text{H}_2\text{O}$).

(e) In rich and lean fractions from the bromide treatment, mesothorium and radium were determined and their ratios again compared.

(f) The results of the above hydroxide and bromide treatments showed the mesothorium/radium ratio remained unchanged throughout and that these elements are, therefore, strictly isotopic.

I. The Preparation from Monazite Residues of 1100 g. of Crystallized Barium Chloride Containing 14 Mg. of Mesothorium and Radium.

(1) Nature of the Residues.—These consisted mainly of phosphates of thorium and the rare earths, sand, graphite and sulfates of calcium,

¹ "Chemistry of the Radio-Elements," Part I, 1914, p. 51

² U. S. Pat. 1,103,600, 1914.

³ By convention, one mg. of mesothorium is that quantity which has a γ -ray activity (due to its short-lived product mesothorium-two) equal to that of one mg. of Ra (element).

barium and lead. About 1000 kg. of these residues was generously donated by the Lindsay Light Company, of Chicago, to whom we wish to express our thanks.

(2) Treatment of the Residues.

(a) *Caustic Soda Treatment*.—The monazite residues were worked up in lots of 200 kg. each, by boiling them for 2 hours with a solution of 200 kg. of caustic soda and 20 kg. of soda ash in 2000 liters of water, and filtering while hot. Much lead was removed and the barium changed to carbonate retaining the mesothorium and radium. The total residue while moist usually weighed about 130 kg. per lot.

(b) *Acid Treatment*.—Lots of about 30 kg. each of the residues from the caustic-soda treatment were intimately mixed with an equal weight of water and 15 kg. of conc. hydrochloric acid. The mass was stirred vigorously throughout the whole of this acid treatment until ready for filtration. Live steam was passed into the mixture until the temperature was raised to 65°, and 15 minutes later, a second lot of 30 liters of water, at a temperature of 65° was added. After 15 minutes, the material was filtered. Each filtrate was then treated with 6 kg. of 30% sulfuric acid. The resulting precipitate of the sulfates of barium and lead, containing mesothorium and radium, was allowed to settle and the supernatant liquid decanted. Laboratory experiments showed that the larger part of the mesothorium and radium contained in the original monazite residues was obtained by this process in the final sulfate precipitate.

(c) *Conversion into Carbonate*.—The sulfates were easily converted into carbonates in a small autoclave, by heating them with soda solution under pressure of about 8 atmospheres, for 1/2 hour. The charge consisted of 100 g. of sulfates and 300 g. of soda ash dissolved in 850 cc. of water. The product obtained by this treatment was allowed to settle, the liquor decanted and the residue washed first with soda solution and then with water. A conversion of 95% of the mesothorium, radium and barium was obtained.¹

(d) *Conversion into Pure Chloride*.—The mesothorium-radium-barium carbonate was dissolved in a measured volume of standard hydrochloric acid and the approximate barium content calculated. It was necessary to precipitate with ammonium hydroxide and filter off small quantities of mixed hydroxides of lead, thorium, and rare earths and then to acidify the solution with hydrochloric acid. The barium content was redetermined by precipitating an aliquot portion with sodium hydrogen carbonate and titrating the washed precipitate with standard hydrochloric acid.

(3) *Product*.—The final product obtained by the above treatment was 1100 g. of barium chloride, containing 14 mg. of mesothorium and radium.

II. The Hydroxide Concentration.

(1) *Theory*.—It is a familiar fact concerning the chlorides of calcium,

¹ Several other methods for the conversion of sulfate to acid-soluble form have been proposed.

(a) Sulfide. Soddy, *Trans. Chem. Soc.*, 99, 76 (1911); *Bur. Mines, Bull.* 104 (1915).

(b) Carbonate fusion. McCoy and Viol, *Phil. Mag.*, 25, 336 (1913).

(c) Calcium hydride. Ebler and Bender, *Z. anorg. Chem.*, 83, 149 (1913).

(d) Calcium carbide, alone or with the hydride. Ebler and Bender, *Z. anorg. Chem.*, 88, 255 (1914).

(e) Carbon. *Bur. Mines, Bull.* 104 (1915).

strontium and barium, that the solubility decreases as the atomic weight of the element increases. When the properties of radium were discovered, which placed it in the same group with these elements, the solubility of radium chloride was expected to be less than that of the other chlorides and therefore radium would be more concentrated in the first crystals forming from a radium-barium chloride mixture than in the remaining liquor. Similar reasoning applies to the case of the bromides, this method having been found even more efficient than the chloride method for the enrichment of radium. Both of these methods have an extended use in the production of radium.

A study of the solubility of other compounds led to the discovery of the hydroxide method for concentrating radium and mesothorium.¹ But since the solubility of the hydroxides of calcium, strontium and barium increases with the atomic weight, it was anticipated that radium would concentrate in the mother liquor instead of in the crystals. This was found to be the case. An additional fact, in favor of the hydroxide process, is that the solubility of crystallized barium hydroxide ($8H_2O$) changes greatly with temperature, *viz.*, it melts at 80° in its water of crystallization, and at 0° only 3.2 g. dissolve in 100 cc. of water. Thus it is comparatively easy to obtain a very concentrated solution of barium hydroxide and on cooling, have a relatively small amount of barium in the filtrate, which contains a large fraction of the radium and mesothorium.

(2) Procedure with 1100 G. of Crystallized Barium Chloride, Containing 14 Mg. of Mesothorium and Radium:

The chloride was dissolved in water and diluted to 4 liters. To this solution, 540 g. of sodium hydroxide, in 1600 cc. of water was added. After being warmed until the barium hydroxide was completely dissolved, the material was cooled to 2° , while being shaken, and then filtered rapidly. The filtrate of 4470 cc. contained the equivalent of 54.5 g. of crystallized barium chloride and 5.2 mg. of mesothorium and radium. The hydroxide crystals were dissolved in 1200 cc. of hot water and the cooling and filtering repeated as before. In this second filtrate 40.1 g. of barium chloride and 3.4 mg. of mesothorium and radium were present. The hydroxide crystals were recrystallized 7 times more, in the same manner. The results are shown in Table I, Run A.

The 5 leaner filtrates, A, 5-9, were combined into B and treated in the same manner as A; see Table I, Run B.

Then the 4 richer filtrates, A, 1-4, were combined with all the filtrates from B, 1-5, and fractionally crystallized as Run C. Table I.

This procedure was followed systematically, as shown in Table II, until, in Run G, 17 g. of barium chloride had been obtained containing 8.4 mg. of mesothorium and radium, that is, 60% of the radioactive elements had been concentrated into 1.5% of the original barium. (See Table III.)

¹ McCoy, Patent, *loc. cit.* For bromates, picrates and ferrocyanides in concentrating Ra, see Ger. Patent 264,901, 1912.

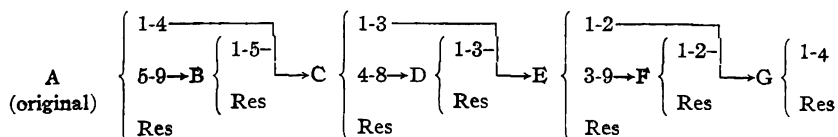
TABLE I.

The Separation of Mesothorium and Radium from Barium by Crystallization of the Hydroxides.

Number of the run and treatment.	Number of the fraction.	Barium Chloride.			Mesothorium and Radium.		Ratio of MsTh + previous Ra fraction. Ba.
		G.	% of original.	% of previous fraction.	Mg.	% of original.	
Run A—BaCl ₂ .2H ₂ O, 3950 cc. solution, 28 g. per 100 cc. of solution. NaOH added, 1600 cc. solution, 540 g. of NaOH (50% excess).	Orig.	1100.0	14.00 1.0
	1	54.5	5.0	5.0	5.26	37	37 7.5
	2	40.1	3.6	3.8	3.35	24	39 6.5
	3	39.5	3.6	3.9	1.96	14	35 3.9
	4	44.5	4.0	4.6	1.17	8	34 2.1
	5	29.1	2.6	3.2	0.66	5	29 1.8
	6	34.7	3.2	3.9	0.45	3	28 1.0
	7	44.6	4.1	5.2	0.38	2.1	33 0.7
	8	34.5	3.1	4.2	0.20	1.4	27 0.5
	9	32.2	2.9	4.1	0.12	0.9	21 0.03
	Resid.	748.0	68.0	...	0.22	1.6	.. 0.01
Run B—BaCl ₂ .2H ₂ O, 900 cc. solution, 19 g. per 100 cc. of solution. NaOH added, 210 cc. solution, 80 g. of NaOH (40% excess).	Orig.	173.0	1.79 1.0
	1	9.5	5.5	5.5	0.80	45	45 8.2
	2	11.0	6.4	6.7	0.40	22	40 3.5
	3	11.0	6.4	7.2	0.18	10	31 1.6
	4	12.0	6.9	8.4	0.13	7	33 1.1
	5	9.5	5.5	7.4	0.06	3	22 0.6
	Resid.	120.0	69.4	...	0.11	6	.. 0.04
Run C—BaCl ₂ .2H ₂ O, 1260 cc. solution, 18 g. per 100 cc. of solution. NaOH added, 270 cc. solution, 105 g. of NaOH (40% excess).	Orig.	228.0	11.50 1.0
	1	17.1	7.5	7.5	4.72	41	41 5.5
	2	19.9	8.7	9.5	2.57	23	38 2.6
	3	13.0	5.7	6.8	1.46	13	35 2.2
	4	11.7	5.1	6.6	0.93	8	34 1.6
	5	11.8	5.1	7.2	0.57	5	31 1.0
	6	9.1	4.0	5.9	0.28	2.4	23 0.6
	7	9.3	4.1	6.4	0.17	1.5	17 0.4
	8	8.8	3.9	6.5	0.09	0.8	12 0.2
	Resid.	110.0	48.2	...	0.10	0.9	.. 0.02

TABLE II.

Showing Systematic Treatment in Process of Enrichment of Mesothorium and Radium by Fractional Crystallization from Barium Hydroxide.



NOTE.—Large letters represent the complete fraction. Figures represent the number of individual filtrates in the complete fraction. Res. represents the residue of each fraction

TABLE III.

Showing the Enrichment of Mesothorium and Radium by the Hydroxide Process.

	BaCl ₂ ·2H ₂ O. G.	MsTh & Ra. Mg.	Relative richness.
Original.....	1100	14.0	1.000
A. Residue.....	748	0.22	0.023
B. Residue.....	120	0.11	0.072
G. 1-4.....	17	8.4	38.83

III. Analytical Methods.

Determinations of barium, mesothorium and radium were made in the several solutions by the following methods.

(1) Barium.

In the later barium hydroxide fractions, which were practically free from sodium hydroxide, the filtrate was titrated directly with standard hydro-chloric acid. In earlier fractions where sodium hydroxide was present, the barium was precipitated as crystalline carbonate by first acidifying with hydrochloric acid and then adding sodium hydrogen carbonate to the warm solution. A measured volume of standard hydro-chloric acid was used to dissolve the filtered and washed barium carbonate. The barium content was calculated from the amount of hydrochloric acid so used.

In the case of the work on the bromide, barium was estimated by weighing the anhydrous barium bromide obtained by evaporation and dehydration.

(2) Mesothorium.

For absolute values of mesothorium in the present paper we observed the γ -ray activity of the sample 2 days after separation from radium emanation, radiothorium having been previously removed, and compared this activity with that of our standard tube containing 0.355 mg. of radium element.

For relative values of mesothorium the equilibrium amount of mesothorium-two contained in a definite fraction of the barium salt solution was entrained in aluminum hydroxide and the β -ray activity measured, about 3 minutes after filtering. A gold leaf electroscope having the bottom of the ionization chamber made of aluminum foil 0.05 mm. in thickness was used.

Aluminum Hydroxide Method for Estimating Mesothorium.—A volume of solution sufficient to give a β -ray discharge of about one minute was made up to about 75 cc. in a 150-cc. beaker, a drop of methyl orange added, and the barium salt present brought up to about 5 g.

The solution was treated as follows at intervals of 3 days until constant activity was shown. The solution was boiled on the hot plate for 2 hours (to remove radium emanation) the volume being kept practically constant by occasional additions of hot water; 3 cc. of aluminum chloride solution¹ was added, then 10 cc. of ammonium hydroxide solution² and the boiling continued for 8 to 10 minutes.

The precipitate was quantitatively transferred to a Hirsch funnel fitted with a hardened 7 cm. filter, having its edges turned up about one cm. all round. The time at which the filtration took place was noted as the zero time for the film. The precip-

¹ The AlCl₃ solution was made by dissolving 3 g. of the crystallized salt in 100 cc. of water.

² The NH₄OH solution was made by adding sufficient BaCl₂ to normal NH₄OH to remove any carbonate and sulfate. Passing in NH₃ gas was not found so satisfactory. McCoy and Viol, *Phil. Mag.*, 25, 336 (1913), McCoy and Henderson, *J. Am. Chem. Soc.*, 40, 1316 (1918).

itate, which was well distributed in a thin layer over the paper, was carefully washed and then dried. The filtrate was acidified with hydrochloric acid, and placed aside for the next determination.

The following experiments on the aluminum hydroxide method were made for the purpose of testing the accuracy of the procedure.

(1) On the Completeness of Removal of Mesothorium-2 with Aluminum Hydroxide.—Aluminum hydroxide was precipitated by the described method in a solution of mesothorium-radium-barium chloride, and very shortly after filtration a second precipitation was made in the filtrate in the same manner as the first.

The activity of the films was observed, and, after allowing for the activity of the mesothorium-2 formed in the time between the first and second filtrations, the percentage of the original activity (that is, the activity of the first film), which the second film should show, was calculated.

Practically complete removal of mesothorium-2 by the first precipitation was found. In one experiment the first precipitation showed 2.132 observed activity in terms of the standard, while the second precipitation showed 0.174 observed activity equivalent to a calculated recovered activity of 0.170, the difference in activities being 0.004 equivalent to 0.2%.

(2) On the Zero Time of Decay of Separated Mesothorium-2.—Two portions, of exactly the same volume, of a solution of mesothorium-radium-barium chloride were tested by the present method. After precipitation of aluminum hydroxide, one portion was allowed to stand for about 10 times as long as the other before being filtered. The time of discharge was observed 30 minutes after filtration, in each case.

The portion which was filtered at once showed a slightly smaller activity, which is to be expected, on account of slight accumulation of β -ray products other than mesothorium-2 in the portion which stood the longer time.

The zero time of decay was thereafter taken as the time at which filtration took place.¹

The time elapsed between precipitation and filtration was 12 minutes for Solution I and 114 minutes for Solution II; while the time of discharge of film 30 minutes after filtration was 81.4 seconds and 81.0 seconds, respectively.

(3) On the Length of Time Taken to Cause the β -Ray Products of Radiothorium to Decay to Values not Detected by Experiment.—Precipitation of aluminum hydroxide removes, along with mesothorium-2, all other elements of a similar chemical nature especially, for the present purposes, radiothorium. By repetition of this precipitation at intervals of 3 or 4 days the accumulation of radiothorium is prevented and its products originally present decay with time. Chief among the products—on account of its long period, during which time thorium D is being produced—is thorium X. In 36 days, 99.9% of thorium X decays.

Three portions of exactly the same volume, of a solution of mesothorium-radium-barium chloride were tested by the present method in identically the same manner.

¹ McCoy and Viol, *loc. cit.*; McCoy and Henderson, *loc. cit.*

After about 23 days, during which time aluminum hydroxide was precipitated every 3 or 4 days, a constant value was reached for the β -ray activity, thorium D no longer affecting the results. See Table IV.

TABLE IV.

Days since first precipitation.	Activity of MsTh-2 after boiling 2 hours, and then precipitating $Al(OH)_3$.			Average.
	Sol. No. 1.	Sol. No. 2.	Sol. No. 3.	
0	..	2.74	2.75	2.745
3	2.58	..	2.56	2.570
7	2.30	2.30	..	2.300
10	..	2.18	2.19	2.185
16	2.05	2.07	..	2.060
19	2.04	2.02	2.04	2.033
23	2.02	2.00	2.01	2.010
26	2.00	1.99	2.01	2.000
30	1.99	2.00	2.00	2.000

NOTE.—Where no determination is shown the solution was used for another purpose.

(4) **On the Effect of the Time of Boiling before Precipitating Aluminum Hydroxide.**—Boiling the solution removes radium emanation as soon as formed and allows radium D originally present to decay.

Three portions, of exactly the same volume, of a solution of mesothorium-radium-barium chloride were tested by the present method in identically the same manner except for the time of preliminary boiling. The results shown in Table V prove that boiling for 2 hours before separating the aluminum hydroxide is sufficient. If the boiling is continued only one hour the measured activity may be more than 2% too great.

TABLE V.

Days since first precipitation.	Boiled before precipitating and filtering $Al(OH)_3$.						Difference between	
	1 Hour.		2 Hours.		3 Hours.		Average activity of 2 hour and 3 hour samples.	activity of one hour sample and average of 2 hr. and 3 hr.
	Sample.	Act.	Sample.	Act.	Sample.	Act.		
0	1	2.86	2	2.74	3	2.75	2.74	0.12
3	2	2.61	3	2.56	1	2.58	2.57	0.04
7	3	2.36	1	2.30	2	2.30	2.30	0.06
10	1	2.22	2	2.18	3	2.19	2.18	0.04
16	3	2.10	1	2.05	2	2.07	2.06	0.04

(5) **On the Rate of Decay of the Mesothorium-2 Film.**—The decay of the film, which was obtained by the present method, was followed during a period of about 23 hours, until the activity had fallen to about 8% of the original activity. The results obtained are compared with those demanded on the assumption of 6.14 hours as the period of mesothorium-2.¹ Excellent agreement is shown.

The error due to slight initial disturbance was avoided in practise by observing the "time of discharge" about 30 minutes after filtration.

¹ McCoy and Viol, *loc. cit*

TABLE VI.

<i>T</i> (hours) since separation Ms - 2.	<i>T</i> (seconds) corrected for air leak.	Log <i>T</i> observed.	Log <i>T</i> calculated.	Diff. log <i>T</i> .
0	9.21	0.96	0.97	0.01
1	10.42	1.02	1.02	0.00
2	11.63	1.07	1.07	0.00
3	13.44	1.13	1.11	0.02
4	14.85	1.17	1.16	0.01
5	16.66	1.22	1.21	0.01
6	18.47	1.27	1.26	0.01
18	69.2	1.84	1.84	0.00
19	77.0	1.89	1.89	0.00
20	86.0	1.93	1.94	0.01
21	96.6	1.99	1.99	0.00
22.5	114.3	2.06	2.06	0.00

(6) **On the Accuracy of the Present Method.**—(a) In the observation of the time of the γ -ray discharge of the tube of radium, it was possible to check the readings easily to 0.2 second for a discharge of 140 seconds. The error is 0.15%. (b) In the observation of the time of the film, using β -radiation, it was found that, for a 70-second film, it was not possible to be certain of the discharge within less than 0.2 second, an error of 0.3%. (c) In the observation of the time of decay, in which zero time is the moment of separation of mesothorium-2 from mesothorium-1, there must be included (a) the time occupied in filtering, usually about 1.5 minute, and (b) the time occupied by the film in discharging the electroscope, about 1.2 minute. There may be an error of one minute, or 0.2%. (d) Other errors inherent in the method cannot be calculated with accuracy. The known limit of error should, therefore, be 0.65%. The experimentally observed values show satisfactory agreement.

TABLE VII.

Days since first precipitation.	Solution.	Activity of mesothorium-2.	Deviation from average.	
23	1	2.02	0.018	0.9%
	2	2.00	0.002	0.1
	3	2.01	0.008	0.4
26	1	2.00	0.002	0.1
	2	1.99	0.012	0.6
	3	2.01	0.008	0.4
30	1	1.99	0.012	0.6
	2	2.00	0.002	0.1
	3	2.00	0.002	0.1

Av., 2.002

(3) Radium.

In the work on isotopism relative radium content was determined by the emanation method as follows.

A definite fraction—1% was found satisfactory—of the solution, in which mesothorium had been previously determined, was made up to 50 cc. in a 150-cc. emanation

flask, fitted in the customary way, then 10 cc. of 6 *N* hydrochloric acid was added. Air was drawn through the solution for one hour and the tubes sealed. The emanation which accumulated in 3 to 4 days was drawn into an evacuated emanation gold-leaf electroscope and after exactly 2 hours the activity was measured in terms of our γ -ray standard tube containing 0.355 mg. of radium element. The customary corrections were applied and the activity calculated.

The absolute amount of radium was determined, using the emanation method, by comparison with a known amount of radium in a similar solution. Measurement on bromide Sample 18 showed that 0.116 mg. of radium accompanied 0.382 mg. of mesothorium. Since these elements are isotopic and no mesothorium or radium was added at any stage, it is evident that 0.30 mg. of radium was present along with every 1.00 mg. of mesothorium throughout the whole of the work.

IV. Results of Mesothorium and Radium Determinations in the Original Solution and in Rich and Lean Fractions from the Hydroxide Enrichment.

The original solution of mesothorium-radium-barium chloride was assayed for mesothorium and radium by the methods described, as were also rich and lean fractions after systematic treatment by the hydroxide method. The results given in the last column of Table VIII show that no separation of mesothorium and radium takes place when they are subjected to fractional crystallization by the hydroxide method. The slightly higher ratio found for the B residue is doubtless the result of analytical error, since the total activity was too small to be measured with great accuracy.

TABLE VIII.
Comparison of Mesothorium-Barium and Mesothorium-Radium Ratios after Hydroxide Enrichment.

Solution.	Relative richness (Table III).	Relative MsTh/Ra ratio.
Original.....	1.000	0.900
G, 1-4.....	38.83	0.898
B, residue.....	0.072	0.921

V. The Bromide Method of Concentration.

(I) **Introduction.**—Although the fractional crystallization of the chloride was the first method adopted in the enrichment of radium, it was soon discovered that the bromide is a more efficient salt to use. A description of the bromide process is given in connection with an unsigned article on the production of radium in *Le Radium*, March¹ and April,² 1904. The method is in common use, especially for the final concentration of radium previously enriched to the desired stage by cheaper methods. The United States Bureau of Mines³ has published the method used and results found in their work on this process.

¹ P. 5.

² P. 7.

³ *Bull.* 104, 80-84 (1915)

(2) **Procedure with 17 g. of Barium Chloride Containing 8.4 mg. of Mesothorium and Radium.**—The solution was treated with colorless ammonium sulfide and filtered to remove lead sulfide. The filtrate was acidified with hydrochloric acid, boiled to remove hydrogen sulfide, and the barium precipitated as sulfate in dilute solution by addition of pure dil. sulfuric acid.

The dried precipitate of barium sulfate was mixed with a large excess of a mixture of sodium and potassium carbonates and fused in a platinum crucible. The fused mass was extracted with water and the insoluble carbonate filtered, washed and finally dissolved in pure hydrobromic acid.

The solution of mesothorium-radium-barium bromide was evaporated in a beaker (No. 1) on the hot plate until surface crystals formed on blowing across the solution. After cooling, the liquor was poured into a second beaker (No. 3) and water and hydrobromic acid added to the first beaker (now called No. 2) (see Table IX). The mesothorium and radium were more concentrated in No. 2 than in No. 3. This was called Series 2.

Then the solutions in (No. 2 and No. 3) were evaporated to crystallization and cooled as before. The liquor of No. 3 was poured into a third beaker (No. 6), the liquor from No. 2 onto the crystals remaining in No. 3, which latter was now called No. 5, leaving the crystals in No. 2, which was now called No. 4, and water and hydrobromic acid added to No. 4. This gave Series 3.

Further treatment by the same systematic process outlined in Table XI, was carried on until Series 6 was obtained, the fractions 16 to 21 in this series were evaporated, dehydrated and weighed as barium bromide and the γ -ray activity measured, through 2 mm. of lead and 2 mm. of brass.

The enrichment obtained by this treatment is shown in Table X.

TABLE IX.

Showing Systematic Treatment in Process of Enrichment of Mesothorium and Radium by Fractional Crystallization from Barium Bromide.

Series number.

1	0C0 (1)									
2	1C1 (2)					1L1 (3)				
3	1C2 (4)			1L2 (5)		2C1 (6)		2L1 (7)		
4	1C3 (7)		1L3 (8)		2C2 (9)		2L2 (10)		3C1 (11)	
5	1C4 (11)		1L4 (12)		2C3 (13)		2L3 (14)		3C2 (15)	
6	1C5 (16)		1L5 (17)		2C4 (18)		2L4 (19)		3C3 (20)	
	3L3 (21)		4C2 (22)		4L2 (23)		5C1 (24)		5L1 (25)	

C = crystals, L = mother liquor.

Five complete series of fractional crystallizations were made: each horizontal row represents a series.

Numbers before C and L represent the number of the fraction counting from rich side in the given series.

Numbers after C and L represent the number of the fraction counting from the lean side in the given series.

Sum of numbers before and after C and L gives series number, beginning with original as Series 1.

Small numbers from 1 to 21 are the fraction numbers.

TABLE X.

Showing the Enrichment of Mesothorium and Radium by the Bromide Process.

Number of Fraction.	BaBr ₂ ·2H ₂ O.		Mesothorium and Radium.		Relative Richness.	
	G.	% of total.	Mg.	% of total.		
Original	10.319	100.00	8.363	100.00	1.00	80
16	0.546	5.29	6.388	76.38	14.40	1170
17	1.304	12.63	1.564	18.70	1.50	120
18	2.440	23.65	0.382	4.57	0.20	16
19	3.137	30.40	0.026	0.31	0.012	1
20	2.428	23.53	0.002 (Calc.)	0.024
21	0.464	4.50	0.00004 (Calc.)	0.0005

After 5 head crystallizations (Table IX) 10.319 g. of barium bromide containing 8.363 mg. of mesothorium and radium yielded 0.546 g. of barium bromide containing 6.388 mg. of mesothorium and radium (Table X). Therefore an average of 55% of the barium bromide and 95% of the active material are separated at each crystallization. In consequence, the enrichment ratio for each crystallization is $95/55 = 1.7$.

VI. Results of Mesothorium and Radium Determinations in Rich and Lean Fractions from Bromide Enrichment (This Investigation).

The rich and lean fractions obtained after systematic treatment by the bromide method were assayed for mesothorium and radium.

As shown in Table XI, the ratio of mesothorium to radium remains unchanged, just as was the case for the hydroxide enrichment (Table VIII).

TABLE XI.

Comparison of Mesothorium-Barium and Mesothorium-Radium Ratios after Bromide Enrichment.

Solution.	MsTh/Ba ratio.	MsTh/Ra ratio.
Original (G, 1-4)	1.000	0.898
16	14.4	0.902
19	0.01	0.911

The fact that the ratio of mesothorium to radium remains unchanged (within the limit of experimental error) throughout various chemical transformations and numerous crystallizations as hydroxide and as bromide confirms the conclusions drawn from less elaborate earlier work that these 2 active elements are isotopic.

Summary.

1. Eleven hundred g. of barium sulfate containing mesothorium and radium, equal in γ -ray activity to 14 mg. of radium (element), was extracted from about 1000 kg. of monazite residues. About 80% of the activity was due to the mesothorium.

2. The radioactive elements were concentrated by subjecting the mixture to fractional crystallization by the hydroxide method, whereby

60% of the active material was obtained in 1.5% of the barium compound. (This corresponds to 8.4 mg. of mesothorium and radium in 17 g. of barium chloride.)

3. The rich fraction from the hydroxide crystallization was fractionally crystallized as bromide and 76% of the active material obtained in 5.3% of the barium compound. (6.4 mg. of mesothorium and radium in 0.55 g. of barium bromide.)

4. The ratios of mesothorium to radium in the rich and lean fractions from the hydroxide crystallization and in the rich fraction from the bromide crystallization were practically identical with one another and also with the ratio of these elements in the starting material. The ratio of active elements to barium was over 7000 times as great in the rich fraction from the bromide process as in the lean fraction from the hydroxide process. These facts furnish further evidence for the isotopism of mesothorium and radium.

The present work was carried on under the direction of Dr. Herbert N. McCoy, to whom I wish to express my sincere thanks for inspiration and valuable instruction.