represent the average cross-sectional area of the hydrocarbon chain of oleic acid.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF PITTSBURGH]

IONIUM. I. RECOVERY OF IONIUM FROM CARNOTITE. II. ADSORPTION OF IONIUM-THORIUM BY BARIUM SULFATE. III. IONIUM-THORIUM RATIO IN CARNOTITE[1]

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I. Recovery of Ionium from Carnotite Ore

Although a large quantity of carnotite ore has been worked for its uranium, vanadium and radium content during the last ten years, apparently no attempt has been made to recover the ionium. Constancy of the purely α-ray activity of ionium makes it useful in science, and it is probable that commercial uses might be found if sufficient quantities were available.

Ionium is an isotope of thorium, and thorium, in turn, is found in variable quantities in most mineral deposits. The ionium content of an ore is directly dependent on the uranium present, but is independent of the thorium.

Since ionium has little commercial value, it would have to be obtained as a by-product in the extraction of radium, and the extra expense incurred by its recovery would have to be small. This study began with an investigation of the precipitation of ionium and thorium from solution.

Procedure.—Direct precipitation of ionium with oxalic acid from solutions obtained by boiling carnotite with strong acids was unsuccessful. The presence of large amounts of other substances extracted from the ore seemed to prevent the precipitation of the oxalate. Precipitation of the fluoride with hydrofluoric acid gave good results, but the precipitate was bulky and hard to handle. The difficulty in handling hydrofluoric acid also makes this method unsatisfactory.

Ionium can be extracted with dilute acids, but results vary with different types of carnotite. From a relatively high-grade carnotite containing 18% of uranic oxide, boiling with twice its weight of hydrochloric acid (d., 1.09) brought practically all of the ionium into solution, while the same treatment of a carnotite concentrate, containing 3.5% of uranic oxide, seemed to leave about 75% of the ionium in the insoluble residue. As reported by Plum,[2] it was necessary to fume this residue with sulfuric acid to render the ionium soluble.

[1] From a dissertation submitted to the faculty of the University of Pittsburgh in partial fulfilment of requirements for the degree of Doctor of Philosophy.

[2] Plum, THIS JOURNAL, 37, 1797 (1915).

From Debierne's[3] description of the chemical properties of the substance which he named actinium, it is probable that it contained some ionium. His statement that actinium is precipitated with insoluble sulfates, especially barium sulfate, led to an investigation of the crude radium-barium sulfate produced in the extraction of radium. This sulfate is obtained by boiling carnotite with hydrochloric acid, and precipitating barium and radium as sulfates from the acid solution.

After considerable preliminary work, which indicated the presence of ionium in these sulfates, the following two methods were finally adopted as the most convenient and efficient for the extraction of ionium from the radium-barium sulfate.

A. Fusion with Sodium Carbonate.—Radium-barium sulfate is converted to radium-barium carbonate by fusion with sodium carbonate. The melt is extracted with distilled water, and the solid filtered off and washed free from soluble sulfate. Any thorium and ionium present in the sulfate is converted to oxide by the fusion. As the oxide is insoluble in dilute acids, it remains in the residue when the radium-barium carbonate is dissolved in hydrochloric acid and the solution filtered. The ionium-thorium oxide is converted to sulfate by fuming the residue with sulfuric acid, the sulfate dissolved in water, and any insoluble matter is removed by filtration. Ionium and thorium are precipitated from this solution as hydroxides by means of ammonium hydroxide, filtered, washed and dissolved in a slight excess of hydrochloric acid. After precipitation from the hydrochloric acid solution with oxalic acid, the ionium-thorium oxalate is converted to sulfate by evaporating it to fumes with a mixture of sulfuric and nitric acids. The sulfate is again changed to the chloride as described above, and the ionium and thorium are purified by double precipitation with sodium thiosulfate. When absolute certainty as to purity is desired, the precipitate from the second thiosulfate separation is dissolved in nitric acid and further purified by double precipitation as the iodate.

B. Boiling with Sodium Carbonate.—Radium-barium sulfate is partially converted to the carbonate by boiling with a great excess of sodium carbonate, filtering off and washing. Repeating this procedure several times finally transforms nearly all of the sulfate to the carbonate. Upon dissolving the carbonates in hydrochloric acid, the ionium-thorium is found in the acid solution with barium and radium, and is recovered by precipitation with ammonium hydroxide or oxalic acid. Since thorium forms a soluble double carbonate with sodium carbonate, it should remain dissolved in the sodium carbonate solution. Careful tests have shown that this does not always happen, the ionium-thorium remaining with the barium and radium carbonates.

Several 500g. portions of the crude radium-barium sulfate were treated

[3] Debierne, *Compt. rend.*, **129**, 593 (1899); **130**, 906 (1900).

as described under Method A. The average weight of pure ionium-thorium oxi de extracted was 105 mg. An analysis of the sulfates for radium gave 0.55 mg. of radium element. It can be calculated, using 110,000 years as the average life of ionium, that 0.55 mg. of radium is in equilibrium with 26 mg. of ionium element. Soddy[4] gives the ionium-oxide content of ionium-thorium oxide from Colorado carnotite as 4.26%. Thus, for every 0.55 mg. of radium there should be present in the original ore about 695 mg. of ionium-thorium oxide. The amount recovered from a quantity of radium-barium sulfate containing 0.55 mg. of radium, was 105 mg., or about 15% of the total. As has been mentioned before, about 75% of the ionium is left in the ore residue by a simple treatment with hydrochloric acid, so that a low recovery is to be expected.

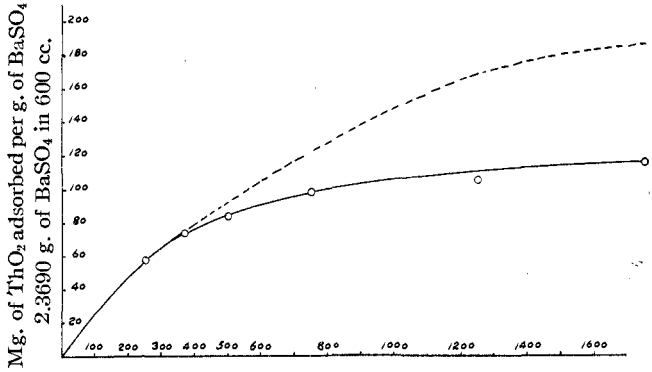

Fig. 1.—Adsorption of thorium (calculated as thorium oxide) by barium sulfate. Observed results, ———. Calcd. from $(x/m)^2 = Kc$, - - -.

Actinium was found in the hydrochloric acid solution with the radium and barium. Cerium nitrate was added to the solution and precipitated as the oxalate to bring down the actinium. α-Ray measurements of the cerium precipitate indicated that only a very small amount of actinium was present.

After a lapse of several months, the α-ray activity of the actinium preparation was less than 2% of the activity of the thorium-ionium oxide extracted from the same amount of radium-barium sulfate. *In other words, about 98% of the activity of the substance adsorbed by the sulfate was due to ionium.*

As the conversion of radium-barium sulfate to the chloride is a necessary step in the production of radium, considerable amounts of ionium-thorium oxide could easily be recovered, particularly if the ore were treated so as to bring the ionium-thorium into solution.

[4] Soddy, *Phil. Mag.*, **47**, 1148 (1924).

II. Adsorption of Thorium by Barium Sulfate

In view of the fact that ionium-thorium was found associated with the barium sulfate in such notable quantities, it seemed advisable to investigate this unusual behavior of thorium in more detail.

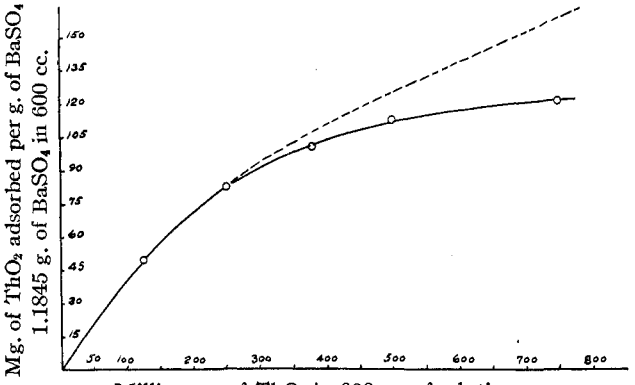

Fig. 2.—Adsorption of thorium (calculated as thorium oxide) by barium sulfate. Observed results, ———. Calcd. from $(x/m)^2 = Kc$, - - -.

For this purpose, solutions of pure thorium chloride and barium chloride were prepared. Known portions of these solutions were mixed and the barium was precipitated as the sulfate with sulfuric acid. The thorium remaining in the filtrate was determined and the amount adsorbed by the barium sulfate obtained by difference. Table I gives the results of a series of tests in which the concentration of the thorium was constant, and the quantity of barium sulfate precipitated in the solution varied. As the barium sulfate increased beyond the values cited in the table, a condition resulted where it was impossible to detect thorium qualitatively in the filtrate by the ammonia test.

TABLE I

ADSORPTION OF THORIUM BY BARIUM SULFATE

The volume of the solution was 600 cc., containing 0.250 g. of thorium oxide as the chloride.

$BaSO_4$, g.	1.1845	2.3690	3.5535	4.7380	5.9225	7.1070
ThO_2 adsorbed, g.	0.096	0.137	0.171	0.191	0.199	0.206

Table II gives the results for a similar solution where the concentration of the barium was kept constant, and the thorium varied. The volume of solution was 600 cc. and contained 2.3690 g. of barium sulfate as the chloride.

The effect of concentration on adsorption was studied with the results given in Table III.

TABLE II

THORIUM ADSORPTION WITH BARIUM SULFATE CONSTANT

ThO_2 in original soln. G.	ThO_2 adsorbed G.	ThO_2 adsorbed per g. of $BaSO_4$ G.	Theoretical wt. of ThO_2 per g. of $BaSO_4$ $(x/m)^2 = Kc$
1.750	0.277	0.116	0.207
1.250	.249	.105	.170
0.750	.236	.099	.122
.500	.198	.084	.093
.375	.176	.074	.076
.250	.137	.058	.057
.125	.083	.035	.035

TABLE III

EFFECT OF CONCENTRATION ON ADSORPTION

$BaSO_4$, g.	ThO_2 adsorbed G.	Volume of soln. coutaining 0.250 g. of ThO_2, cc.
2.3690	0.134	200
2.3690	.133	400
2.3690	.137	600
2.3690	.127	800
2.3690	.126	1000

According to the Freundlich adsorption equation, $(x/m)^n = Kc$, adsorption should increase with increasing dilution. Results show that in this particular instance adsorption is almost independent of dilution, decreasing with dilution if it changes at all.

The conclusion is drawn that barium sulfate, when precipitated in a solution containing thorium, adsorbs the thorium to an extraordinary degree. When the ratio of barium sulfate to thorium oxide is 28:1, approximately 80% of the thorium is adsorbed. As the ratio of barium sulfate to ionium-thorium oxide is about 650:1 in carnotite, it seems probable that a high recovery of ionium could be effected if it were all in solution.

III. Ionium-Thorium Ratio in Carnotite

Soddy[4] and Hitchens recently reported the average life of ionium as 1.1×10^5 years. This value of the average life of ionium made possible a determination of the quantity of ionium in an ionium-thorium compound by observing the rate of growth of radium in the compound. Soddy and Hitchens made a determination of the quantity of ionium oxide in a specimen of ionium-thorium oxide obtained from Colorado carnotite, and found 4.26%, or a ratio of IoO_2:ThO_2 of 1:23.

Since the authors were in a position to obtain an unusually representative specimen of thorium-ionium oxide derived from Colorado carnotite, it was thought to be worth while to make a similar determination with this material.

Samples of radium-barium sulfate produced by the Standard Chemical

Company over a period of eight months were collected and combined. The material used was representative of between 4000 and 5000 tons of ore, collected from various mines covering an area of at least 2000 square miles in the Paradox Valley in Colorado.

The ionium-thorium was extracted by the carbonate fusion method, and subjected to a rigorous purification. It was first purified by two precipitations with sodium thiosulfate, then converted to the nitrate and subjected to four precipitations with potassium iodate in 2:1 nitric acid solution. The iodate was dissolved in hydrochloric acid, the thorium precipitated with aqueous ammonia as the hydroxide, and again dissolved in hydrochloric acid. The solution was made up to 250 cc., and a 10cc. portion taken for analysis. The result showed that the solution contained 1.9250 g. of ionium-thorium oxide. A second determination gave 1.9245 g.

Three 10cc. samples, each containing 77 mg. of the oxides, were sealed in suitable glass containers. Radium measurements were begun about six weeks later, when enough radium had accumulated to give measurable readings. The results of these measurements are given in Table VII. A large portion, containing 1.1460 g. of the oxides, was carefully freed from radium. This was done by precipitating the ionium from the solution as the hydroxide and filtering. The radium remained in the filtrate. The process was repeated five times, when a test showed that the ionium solution was completely free from radium. The time of purification was taken as the zero time, and the growth of the radium determined from time to time by means of emanation measurements. In making these measurements, the radon was removed from the solution and held in a separate vessel for 15 minutes in order to allow thoron to decay before introducing the radon into the electroscope. Thus, any possibility of an error due to the presence of thoron was avoided. The electroscope was frequently standardized during the progress of the measurements, using exactly the same procedure as in making the measurements.

The following equation (1), developed by Professor Soddy,[4] was used for calculating the growth of radium in the solutions before the separation of the thorium-ionium from the radium. In measurements where the ionium had been separated, Equation 2 was used.

$$\text{Ionium} = \frac{4.08 \times 10^7\ (\text{Ra})}{t - 5.555 + [T/(1 - e^{-\lambda e T})]} \qquad (1)$$

In Equation 1, t is the time from purification to time of seal, T is the time during which the solution remained sealed to allow the accumulation of radon, λ is the average life of radon and Ra is the quantity of radium which grew, as determined by the radon measurement.

In measurements where the radium was first separated from the ionium, the quantity of radium is constant and the equation is simplified to the following form, where λ is the average life of ionium, t is the time from

purification to the separation of the radium and ionium, and Ra is the quantity of radium which grew during time t.

$$\text{Io} = \text{Ra}/\lambda t, \text{ or Io (g.)} = \text{Ra}/\lambda t \times 230/226 \quad (2)$$

TABLE IV

SERIES I[a]

Date	Ra, g. × 10^9	t, days	T, days	Ionium, g.
12- 5-24	1.45	0	1	...
12-15-24	15.58	9	2	0.063
12-19-24	23.40	13	2	.068
12-29-24	36.90	23	2	.062

[a] The solution contained 1.1460 g. of ionium-thorium oxide. Purified 12-4-24 at 2 P.M. No radium present.

The radium was separated from the solution at 2 P.M. on January 8, 1925, and measured nine times, with the following results.

Record No.	1	2	3	4	5	6	7	8	9	Av.
Ra, g. × 10^9	53.8	56.5	53.8	53.8	55.6	56.8	57.2	54.8	56.9	55.47

$$\text{Io (g.)} = \frac{55.47 \times 10^{-9}\,(4.08 \times 10^7)}{35} = \frac{2.26}{35} = 0.0646$$

TABLE V

SERIES II[a]

Date	Ra, g. × 10^9	t, days	T, days	Ionium, g.
1- 9-25	0.756	0	0.75	...
1-17-25	12.90	8.25	2.0	0.060
1-26-25	25.80	16.0	0.75	.062
2- 5-25	41.20	26.25	.75	.060
2-12-25	50.80	33.25	.75	.061
2-15-25	56.0	36.25	.75	.065
2-19-25	57.8	39.25	.75	.059

[a] Purified 1—8—25 at 4 P.M.; the solution contained ionium separated from Series I.

The radium was removed from Series II, and measured separately, with the following results.

Record No.	1	2	3	4	5	Av.
Ra, g. × 10^9	57.60	58.5	58.2	58.4	57.9	58.1

$$\text{Io} = \frac{4.08 \times 10^7\,(58.1 \times 10^{-9})}{40} = \frac{2.37}{40} = 0.059\text{ g.}$$

TABLE VI

SERIES III[a]

Date	Ra, g. × 10^9	t, days	T, days	Ionium, g.
2-19-25	0.364	0	0.75	...
2-27-25	12.90	8.25	.75	0.060
3-13-25	34.60	22.25	.75	.062
3-19-25	43.70	28.25	.75	.058
3-23-25	47.50	31.00	2.00	.060
3-25-25	51.40	34.25	0.75	.056
3-30-25	58.80	38.00	2.00	.060

[a] Purified 2—18—25 at 3 P.M. The solution contained ionium from Series II.

It is evident from the above data that the solution used in these tests contained an amount of ionium element closely approximating 0.060 g. or, calculated as oxide, 0.0683 g. The solution contained 1.1460 g. of the mixed ionium-thorium oxide. Therefore, the percentage of ionium oxide present is 5.96.

The results of the measurements on the three duplicate samples, described in a preceding paragraph, are probably not as reliable as those of Series I, II and III, as they were made with much smaller quantities of the oxide. Measurements were extended over a period of eight months, however, so that the last few results should be fairly reliable. These results are given in Table VII.

TABLE VII

SERIES IV[a]

Days	Ra, g. × 10^9 present	Ra, g. × 10^9 increase	Ionium, g × 10^4
0	14.2	0	..
10	15.3	1.1	44.8
23	16.8	2.6	46.0
37	18.2	4.0	44
81	23.7	9.5	48
113	27.2	13.0	47
147	29.1	13.9	39
175	31.9	19.7	46
214	35.1	20.9	40
217	35.7	21.5	40

[a] Each value is the average for three samples.

The average value for the ionium content is 0.0044 g. The ionium-oxide content is 0.0050 g. or 6.5%. If the last two figures of the series are taken, and they are probably the most reliable as they were made only three days apart and represent the largest total increase, the ionium oxide content is 5.9%.

Thus, the evidence seems conclusive that the specimen of ionium-thorium oxide contained a quantity of ionium oxide very closely approximating 5.9%, and the ionium-thorium ratio is 1:15.8. As previously stated, the specimen of ionium-thorium oxide used in this work represents an average for a very large tonnage of carnotite ore, and would seem to be representative for the greater portion of the commercial carnotite of Colorado.

The radium standard used in these measurements was prepared by dissolving standardized specimens of pure radium bromide in water acidified with hydrochloric acid. This standard was compared with two other standards prepared in the same way, so any uncertainty in the value of these standards would not exceed 1%.

Grateful acknowledgment is made of the valuable coöperation of Drs. Charles H. Viol and Gebhard Stegeman, and Mr. A. L. Miller in connection with this investigation.

Summary

1. The direct precipitation of ionium from an acid solution of carnotite ore is impracticable on a large scale. Attempts to precipitate ionium with oxalic acid are unsuccessful when large quantities of ore are used. Precipitation with hydrofluoric acid is good, but tedious and difficult because of the corrosive and poisonous properties of hydrofluoric acid.

2. Radium-barium sulfate, as obtained from any ore in the commercial process for the production of radium, contains considerable ionium. Methods have been devised for the recovery of ionium from this product; Method A (fusing sulfates with sodium carbonate) and Method B (boiling the sulfates with sodium carbonate) give equally good results. As Method B can be used advantageously as a commercial method, considerable quantities of ionium can easily be obtained as a by-product in the manufacture of radium salts.

3. In the commercial treatment of low-grade carnotite, most of the ionium remains in the ore residue. It is necessary to fume the ore with sulfuric acid to render all of the ionium soluble. From high-grade carnotite, containing more than 15% of uranium oxide, the ionium is readily extracted with hydrochloric acid.

4. It is evident from this work that in addition to radium, the active substance adsorbed by barium sulfate when it is precipitated in solutions containing the radioactive constituents of uranium ores is chiefly ionium, accompanied by a *relatively small amount of actinium*, and that it is *not solely actinium* as has often been assumed. The short-lived element, uranium X, is also adsorbed.

5. This investigation indicates that the ionium-thorium ratio in average Colorado carnotite is 1:15.8.

6. The adsorption of ionium by barium sulfate is confirmed by a series of experiments employing thorium, the isotope of ionium. The investigation indicates that barium sulfate has an extraordinary capacity for the adsorption of thorium, 1 g. of barium sulfate adsorbing as much as 16% of its own weight of thorium sulfate.

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