Studies on the Separation of Alkaline Earth Elements. V. Coprecipitation of Radium in the Induced Precipitate of Lead Sulfate

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In the former papers[1,2] the authors reported on the lead sulfate precipitation induced by barium, and on its usefulness as a method of separation of a small amount of barium from a large amount of lead. In the present paper an analogous method of accumulation of radium is reported by coprecipitation with inductively precipitated lead sulfate by means of barium. In this case barium plays a role of the inducer for lead sulfate and at the same time that of the carrier for radium.

Experimental

Reagents.—The solutions of lead nitrate, barium chloride and ammonium acetate were the same as those prepared in the preceding paper[2].

Radium chloride solution 100 μC/100 ml. was the officially approved article, N. B. S. (U. S. Department of Commerce).

Apparatus.—RIKEN Lauritsen electrometer was used to measure the radioactivity of radium in the sample in a stainless steel cupped planchet with 2.5 cm. diameter.

SHIMADZU Pen-recording Polarograph was used for the amperometric titration, and SHIMADZU glass electrode pH-meter for the measurement of hydrogen ion concentration.

Procedures.—*1) Experimental conditions.* Into a stoppered Erlenmeyer flask was put 40 ml. of a solution of pH 5.50 containing 0.096 M lead nitrate, 2.07 M ammonium acetate, and 2×10^{-4} M barium chloride as their final concentration. The optimum molar ratio of ammonium sulfate to lead for this induced precipitation is $\simeq$20[1]. After the temperature of the mixture was adjusted to 20± 0.05°C, a suitable amount of 0.5 M sulfuric acid was added at a rate of 7—8 sec. per ml. The precipitate obtained in the solution was stirred, kept standing for 2 hr. at 20°C and centrifuged. The supernatant solution was analysed for radium and lead content.

2) The measurement of radioactivity of radium. To determine how much radium is coprecipitated with lead sulfate, it is easier to analyse radium in the supernatant solution than in the precipitate. According to Tompkins et al.[3], when lead is thoroughly precipitated as lead sulfate, radium will be completely coprecipitated with it, and all the disintegrated products will be included without any appreciable loss. For this reason, the following procedure is preferred; 1 ml. of the supernatant sample solution or the standard solution is taken into a stainless steel cupped planchet, and concentrated under an infrared lamp to half of its original volume. Then to it 0.4 ml. of 0.5 M sulfuric acid is added to obtain the lead sulfate precipitate, which is dried up carefully and kept in a calcium chloride desiccator for eight days till it reaches 3/4 of the secular equilibrium for radium, and the radioactivity was measured by Tompkins' alpha-ray method[3].

This procedure was checked as follows; the standard solution was prepared as the supernatant sample solution mentioned above, except that a known amount of radium was added. The drying condition of lead sulfate in the cupped planchet and the amount of sulfuric acid added had a very subtle effect upon the alpha activity. Amount of sulfuric acid (0.2 to 0.6 ml.) was examined and the use of 0.4 ml. was found to be the best, permitting the determination of 1×10^{-3} μC radium with ±4% average deviation, provided that the drying of the planchet was complete. The calibration curve thus obtained is shown in Fig. 1., and serves as the standard measure of the activity.

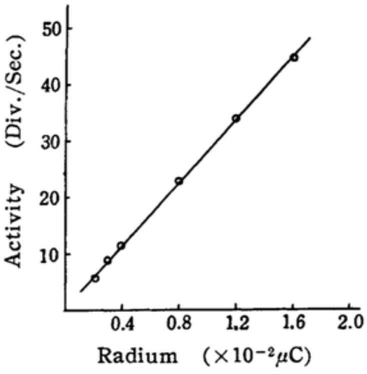

Fig. 1. The calibration curve of radium.

The absorption of alpha rays of radium by lead sulfate was examined and the results were

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[1] M. Shinagawa and T. Murata, *J. Science Hiroshima Univ.*, **A**, **18**, 429 (1955).

[2] M. Shinagawa and T. Murata, This Bulletin, **31**, 162 (1958).

[3] P. C. Tompkins, W. P. Norris, L. Wish and R. D. Finkle, *MDDC.*, 699 (1946).

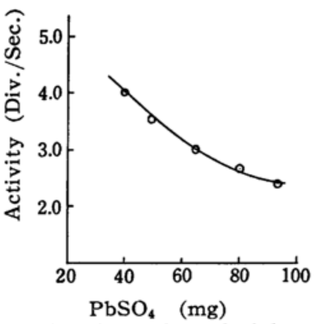

Fig. 2. The absorption of alpha rays by lead sulfate.

obtained as shown in Fig. 2., by which the self-absorption of the sample was calibrated.

3) Measurement of the amount of lead sulfate precipitated. The procedure for amperometric titration was the same as that mentioned in the previous paper[2].

Results

1) The coprecipitation ratio of radium and the induced precipitation ratio of lead as a function of the amount of sulfuric acid added. The solution mixture used had the same composition as in section 1, except 1×10^{-4} M of barium chloride and 40 μC of radium chloride per liter. Forty ml. of this solution was taken and 1.00—3.00 ml. of 0.5 M sulfuric acid was added and aged for 2 hours at 20°C. The analyses of lead and radium were carried out regularly, giving the results as shown in Fig. 3. The amount of lead sulfate precipitate increased as the amount of sulfuric acid added increased, while the amount of coprecipitated radium remained constant on the addition of more than 1.40 ml. of sulfuric acid, where ca. 9% of lead precipitated with ca. 90% of radium. The ratio (Ra)/(Pb) in the precipitate decreased significantly thereafter, just as in the case of coprecipitation of barium[2].

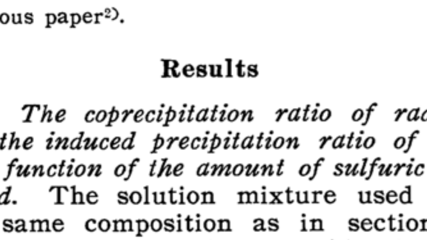

Fig. 3. Results of induced precipitation as a function of the amount of sulfuric acid added.
Curve a: Induced precipitation of lead.
Curve b: Coprecipitation of radium.

2) As a function of the amount of barium present. To each 40 ml. of the mixed solution (see Procedure section 1) which had been mixed with 0.80 μC of radium and a varying amount of barium, 1.20 ml. of 0.5 M sulfuric acid was added. The analyses of radium and lead in these solution gave the results as shown in Table I.

TABLE I

RESULTS OF THE COPRECIPITATION AS A FUNCTION OF THE AMOUNT OF THE BARIUM PRESENT

Solution: 800 mg. Pb^{++} and 0.8 μC $RaCl_2$ in 40 ml. of 2.07 M CH_3COONH_4; 1.20ml. of 0.5 M H_2SO_4 added, aged for 2 hours at 20°C.

Ba added	Ra copptd.		Pb pptd.	
mg.	μC	%	mg.	%
0.549	0.74_9	$93._6$	$66._4$	8.3
1.098	0.76_0	$95._0$	$73._6$	9.2
1.647	0.76_6	$95._8$	$87._2$	10.9
2.196	0.77_2	$96._6$	$98._4$	12.3
2.745	—	—	$113._6$	14.2

It is seen that when a sufficient amount of sulfuric acid, i. e. 1.20 ml. is added in the presence of more barium ions, more lead sulfate precipitates. The percentage of coprecipitation of radium appears to remain constant, although it has an overall trend to increase slightly.

3) As a function of initial concentration of radium. To each 40 ml. of the mixed solution (Procedure section 1), radium was added from 0.2 to 1.6 μC. After the addition of 1.20 ml. of sulfuric acid, the samples were analysed to find the amount of coprecipitated radium. Table II shows the results. In this case, too, the amount of lead sulfate induced was constant (9.2 %), while the amount of coprecipitated

TABLE II

COPRECIPITATION RATIO OF RADIUM AS A FUNCTION OF ITS INITIAL CONCENTRATION

Solution: 800 mg. Pb^{++} and 1.098 mg. Ba^{++} in 40 ml. of 2.07 M CH_3COONH_4. 1.20 ml. of 0.5 M H_2SO_4 was added, aged for 2 hours at 20°C, 9.2% of Pb (73.6 mg.) was precipitated.

Initial Ra	Ra copptd.		pptn. ratio (Ra)/(Pb)
μC	μC	%	$\times10^3$
0.200	0.18_7	$93._6$	2.5
0.400	0.38_2	$95._4$	5.2
0.800	0.76_4	$95._5$	10.4
1.200	1.15_0	$95._9$	15.6
1.600	1.53_0	$96._1$	20.8

radium increased as the initial concentration of radium increased according to Freundlich's adsorption isotherm as in the case of barium in the previous report²⁾.

4) *In the absence of barium.* The mixed solution mentioned in Procedure section 1, but without barium was used. To obtain the same amount of lead sulfate much more sulfuric acid was required than when barium was present. The experimental results are shown in Table III.

TABLE III

COPRECIPITATION IN THE ABSENCE OF BARIUM

Solution: 800 mg.Pb^{++} and 0.80 μC Ra^{++} in 40 ml., 2.07 M of CH_3COONH_4, 0.5 M H_2SO_4 was added, aged for 2 hours at 20°C.

H_2SO_4 added	Ra copptd.		Pb pptd.		pptn. ratio (Ra)/(Pb)
ml.	μC	%	mg.	%	$\times 10^3$
2.80	0.77_6	$97._0$	$92._0$	11.5	8.4
3.00	0.77_4	$96._7$	$139._0$	17.4	5.6
3.40	0.77_4	$96._8$	$174._0$	21.7	4.4
3.80	0.77_3	$96._6$	$191._0$	23.9	4.0

It can be understood that even when the amount of lead precipitate increases to a large extent, the coprecipitation ratio for radium remains constant and the precipitation ratio (Ra)/(Pb) decreases accordingly.

5) *In the absence of acetate.* The solution mixture containing 0.096 M lead nitrate and 20 μC/l radium chloride was used. To 40 ml. of this solution, an equivalent amount of sulfuric acid to the measured quantity of lead sulfate precipitate was added. The results of analyses are shown in Fig. 4, curve a. Curve b was derived from the same data shown in Fig. 3, curve b for comparison. In Fig. 4, curve b shows clearly that a small amount of induced precipitate of lead sulfate carries off radium from solution as efficiently as a relatively large amount of it does (curve a). While the ordinary precipitate of lead sulfate catches radium in an almost proportional amount to itself.

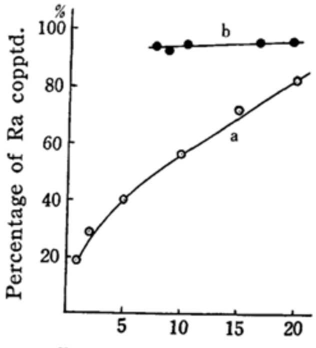

Fig. 4. Comparison of coprecipitation of radium.
Curve a: Ordinary precipitation of lead sulfate.
Curve b: Induced precipitation of lead sulfate in the presence of barium.

Summary

A solution of pH 5.50 composed of 0.096 M lead nitrate, 2.07 M ammonium acetate, $1-5\times10^{-4}$ M barium and 5—50 μC radium per liter, produces an induced precipitate of lead sulfate in proportion to the amount of 0.5 M sulfuric acid added. Under the same conditions, in the absence of barium, a lead sulfate precipitate is obtained in proportion to the amount of sulfuric acid added. But the required amount of sulfuric acid to obtain the same amount of precipitate is larger in this case than that in the case of induction by barium.

In both of the above cases, the ratio of the amount of the radium coprecipitated to the original amount of radium in sample solution is almost constant, i. e. 92—97%, irrespective of the amount of lead sulfate precipitate or of sulfuric acid added. This tendency is the same as in the case of coprecipitation of barium with the induced precipitate of lead sulfate as shown in the previous paper. More than 90% of radium is carried down by a precipitate of lead sulfate of 8—20% of lead. Such an extent was not found in the case of the ordinary precipitation of lead sulfate, i. e. in the absence of the masking agent, ammonium acetate for lead ions.

In conclusion, the induced precipitation of lead sulfate by barium can be made use of as an efficient method of separation or concentration of radium. For a practical usage of this method, more detailed examination according to each sample should be conducted.

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