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MOUND LABORATORY

Operated By

MONSANTO CHEMICAL COMPANY

MIAMISBURG, OHIO

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REPORT

FOR

GENERAL RESEARCH

DECEMBER 11, 1950 TO APRIL 2, 1951

(Radium Volume)

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SUMMARY

The work presented in this volume concludes the research on methods for the recovery of purified radium from K-65 residues. The completion of a final report and an engineering study of the proposed process are underway.

The preliminary treatment of the K-65 residues with 15 per cent sodium hydroxide was checked and found to give 84 per cent removal of lead and 40 per cent removal of silica. The combined sodium hydroxide, sodium carbonate treatment for removing additional amounts of lead and achieving a preliminary conversion of the radium-barium sulfates to carbonates has been studied at 170°C. under pressure as well as at 100°C. as previously used. A marked improvement was found with the use of higher temperatures. Alternate methods were studied for removing the residual lead content in place of precipitation with hydrogen sulfide. Precipitation of insoluble hydroxides was found to remove about 90 per cent of the lead present.

The overall recovery of radium in the residues treatment has been checked and found to be better than 98 per cent (p. 5). The work on the separation of radium from barium by fractional precipitation of the chromates has shown that in actual practices the results are in good agreement with the results calculated from the observed enrichment factors. The fractionation schemes have been worked out for the use of cyanide at 0° and 25°C. and urea at 100°C. (p. 8). Additional measurements have been made on the solubility of barium chromate in nitric acid to determine the barium concentrations which can be handled in the fractional precipitation of the barium-radium chromates (p. 38).

The use of ion exchange for the separation of radium from barium appears to be most useful for the final purification of the radium. Additional experiments were directed toward increasing the amount of radium to the milligram level and toward determining, by extrapolation, the amount of barium in the radium fractions below the level which can be detected analytically (p. 43).

It has been found that the liquid wastes from the radium process can be effectively decontaminated by neutralization under the proper conditions. The decontamination obtained results largely from the precipitation of the lead sulfate which occurs when the solutions are neutralized. Additional experiments have shown ferrous sulfide to be the most suitable precipitating agent found for a second decontamination step rather than the ferrous ferrocyanide previously suggested (p. 65).

Experiments have shown that the major portion of the nitric acid used for the conversion of the barium-radium chromates to nitrates can be recovered by distillation for reuse (p. 69).

A preliminary report on the engineering study of the radium process has been made (p. 73).

Problem Title - The Extraction and Purification of Barium-Radium Concentrate from K-65 Residue

Report By - E. F. Joy

Work Done By - E. F. Joy

INTRODUCTION

The processes which have been used or recommended for the extraction of radium from its ores may be classified under two general types, depending on the order in which radium is extracted. In the first type, the radium is put into solution in the first step of the process along with certain other constituents of the ore from which the radium is subsequently separated. These processes usually involve treatment with strong acids to dissolve the radium, nitric or hydrochloric acid (when the sulfate content of the ore is small) or sulfuric acid. In the second-type process, other constituents are removed first, reducing the bulk of material to be handled and leaving the radium in the residue in a form readily extracted by dilute acid. These processes usually involve the use of alkaline reagents, sodium hydroxide, and sodium carbonate; in some cases special reagents, hydrofluoric acid for silicon removal, sodium chloride for lead removal, and others have been used in the preliminary steps.

The second general type process has been under study in this Laboratory for the purpose of extracting radium from K-65 residue. Quantitative data not available in the literature have been obtained on the various possible steps and on ways of combining these steps. A number of important points have been developed including the following:

1. The removal of lead from K-65 should be done early in the process since its elimination along with associated sulfate ion gives greatly improved conversions of barium and radium sulfates to carbonate on treatment with sodium carbonate.

2. Direct treatment of K-65 with sodium hydroxide solution reduces the bulk of the residue to be treated to about one-half, because most of the lead and a good portion of the silica content are dissolved. The use of sodium chloride for lead removal and of hydrofluoric acid for silica removal does not appear to offer any advantage over simple treatment with alkali hydroxide.

3. The use of a mixed solution of sodium hydroxide and sodium carbonate gives better lead removal and higher conversion than treatment with equal amounts of the same reagents used separately.

4. The carbonation of K-65 residue by boiling with sodium carbonate solution at atmospheric pressure is essentially complete after two treatments with 5 moles of sodium carbonate per mole of barium sulfate.

5. From a study of the carbonation of cold barium sulfate under pressure, it was found that carbonation with an excess of sodium carbonate of three times the calculated molar concentration at 170°C. is near optimum conditions, considering consumption of sodium carbonate, the reaction pressure, and the per cent conversion obtained.

Based on the above points, an overall process for the extraction of barium and radium from K-65 was set up and tested on a bench scale. The behavior of barium and radium

was followed, and the distribution of silica and lead was determined in the various steps of the process. Particular attention was given to the carbonation of K-65 under pressure, with and without the addition of sodium hydroxide, with the conditions established under point 5. Alternative methods of purifying the barium-radium extract were studied to find the simplest method which would give a product suitable for final separation of radium by the chromate-urea method.

DETAILED REPORT

Based on the best conditions established in the experiments to date, a process for the extraction and purification of barium-radium concentrate from K-65 residue was set up and studied in detail. The proposed process was tested in two bench scale experiments, 21 and 22, on 2-kilogram batches of K-65 residue, the minimum amount of starting material which will supply a workable charge to the 1-gallon autoclave during the carbonation steps. The order of treatment was the same as that used in experiments 8C and 9.

Outline of Process Steps, Experiments 21 and 22

A. Extraction of barium and radium

1. Removal of lead by boiling with 15 per cent sodium hydroxide solution.
2. Treatment with combined sodium hydroxide-sodium carbonate solution for further removal of lead and conversion of barium and radium sulfate to carbonate. Temperature: Experiment 21, 100°C.; 22, 170°C.
3. Extraction of residue with nitric acid to dissolve the carbonates.
4. Second treatment with sodium carbonate solution under pressure to complete the conversion of barium and radium sulfate to carbonate.
5. Second extraction with nitric acid.

B. Purification

1. Precipitation of barium-radium sulfate from the nitric acid extracts.
2. Carbonation with sodium carbonate solution.
3. Extraction with nitric acid.
4. Purification of the barium-radium nitrate solution by precipitation with hydrogen sulfide followed by ammonium hydroxide.
5. Precipitation of barium-radium carbonate from the purified nitrate solution.

From the analysis of K-65 residue, the amounts of the constituents of particular interest, silica, lead, barium, and radium, were calculated for the 2 kilograms of K-65 taken in each experiment. These amounts and the amounts of reagents used in each step of the process are given in Table IA. The figures in the table can be used as a basis for estimating the cost of reagents in a large-scale process, although minor changes in the process based on the results of these experiments indicate that smaller amounts of sodium hydroxide and sodium carbonate would be needed (about 25 per cent less).

Sodium Hydroxide Leach

The removal of the bulk of the lead was effected in the first step of the process by leaching the K-65 directly with 15 per cent sodium hydroxide solution for 1½ hours at 95 to 100°C. The treatment of 2 kilograms of K-65 at one time would require handling about 6 liters of solution. In Experiment 21, for convenience in operation, the K-65 was divided into two batches of 1,000 grams which were leached separately. The leached residues were filtered and washed with hot water, giving filtrates 21A and 21B. Washing was incomplete because of the large amount of residue on the filter. To complete the washing, the two residues were combined, repulped with water, and again filtered, giving filtrate 21C. The three filtrates were analyzed for lead and silica content, see Table IB. In Experiment 22, the initial K-65 was divided into four 500-gram batches for leaching and filtration. This amount of K-65 was readily handled in the equipment available, and no difficulty was encountered in filtration. The analysis of the four resulting filtrates also is given in Table IB. The extraction obtained in these four leaches agreed very closely and gave an average of 84.1 per cent of the lead extracted and 40.6 per cent of the silica extracted. These values are representative of the extraction to be expected in the first step of the process.

Combined Sodium Hydroxide-Sodium Carbonate Leach - Extraction of Silica

The combined residues from the sodium hydroxide extraction were treated with mixed sodium hydroxide-sodium carbonate solution in the second step of the process. In Experiment 21, the treatment during this step was carried out at 100°C. while in Experiment 22, it was done at 170°C. under pressure. The increase in temperature was expected to extract a somewhat greater portion of the silica and to give a higher conversion of barium sulfate to carbonate. These expectations were more than reached when a comparison of the extractions of silica, barium, radium, and lead was made for the two experiments. The remainder of the steps in the outlined process were carried out identically for the two experiments so that differences between them would be caused only by the temperature difference in this step.

The distribution of silica in the various process solutions is tabulated in Table IC. The amount of silica extracted in the second step increased from 35.2 grams to 435.2 grams. The resulting decreased bulk of the residue allowed more effective treatment in the following steps. For the overall process, the total silica extracted increased from 44.3 per cent to 90.2 per cent. The final residues were 33.3 per cent and 11.9 per cent of the original K-65 in the two experiments. While these advantages were gained, a somewhat longer filtration time was required because of the higher sodium silicate content of the solution.

Alternative treatments suggested by these results were not tried but will be listed for further consideration. The advantage of carbonation at 170°C. over 100°C. in the second step is obvious, and the higher temperature should probably be adopted. The quantity of sodium hydroxide used in excess of the minimum needed to dissolve lead, however, might well be reduced to lessen the amount of silica dissolved. A change in this direction is recommended as a possible improvement in the process. A second alternative would be the treatment at some intermediate temperature between 100°C. and 170°C., although this possibility is not so favorable because of the reduced conversion to carbonate which would result. A third possibility is that of extracting lead and silica in the first step (sodium hydroxide leach) at temperatures above 100°C. A considerable reduction in the sodium hydroxide required would be expected, and this might more than offset the disadvantages of operating in an autoclave under pressure.

Barium-Radium Recovery

The barium extracted from the carbonated residues in the first and second nitric acid treatments was carried through the purification steps separately and recovered as two samples of purified barium carbonate. These were weighed and analyzed for radium content. The recovery of barium and radium in the purified barium carbonate is summarized in Table ID. The sodium carbonate used in each carbonation of the residue in these experiments was 40 per cent less than that used in previous experiments (molar ratio sodium carbonate to barium sulfate reduced from five to three). In Experiment 21, this reduction is reflected in the reduced recoveries of barium and radium obtained from the first carbonation, (combined sodium hydroxide-sodium carbonate at 100°C.). The barium recovered was 44.3 per cent and the radium 49.1 per cent. However, the second carbonation at 170°C. gave essentially complete conversion for a total recovery of 97.5 per cent of the barium and 101 per cent of the radium. These high overall recoveries indicate the desirable effect of carrying out the carbonation reaction under pressure at elevated temperatures.

In Experiment 22, both carbonations were made in the autoclave at 170°C. In the first carbonation 89.8 per cent of the barium and 88.8 per cent of the radium was converted. Since the second carbonation was made with the same quantity of sodium carbonate and only one-eighth of the barium was left to be converted, the molar ratio of sodium carbonate to barium sulfate was very high, approximately 24 to 1, and essentially complete conversion could be expected. Total recoveries of 102.2 per cent for barium and 102.1 per cent for radium were obtained. Considering the small bulk of residue left for treatment in the second carbonation and the low barium-radium content, it seems feasible to accumulate this residue from several batches before making a second carbonation in a large-scale process. This would eliminate Steps 4 and 5 from the extraction process except for a clean-up treatment on every fourth or fifth run.

Lead Removal

The distribution of lead in the process solutions is given in Table IE. In Experiment 21, a total of 93.3 per cent of the lead was eliminated in the basic waste solutions, and 6.7 per cent was found in the crude barium-radium nitrate solution. In Experiment 22, 97.9 per cent of the lead was eliminated, and 2.1 per cent remained with the crude barium-radium solution. The remaining lead was precipitated as sulfate along with the barium and radium on addition of sulfuric acid to the nitrate solution. After carbonation and re-solution in nitric acid, the lead was finally separated as lead sulfide by the addition of hydrogen sulfide. This amount of lead can be handled without trouble by this procedure; however, the formation of colloidal sulfur from the oxidation of hydrogen sulfide by the nitric acid present in solution has been observed on heating the filtrate from the lead sulfide. The same problem was not encountered when hydrochloric acid was used in dissolving the carbonated residues.

The possibility of simplifying the purification process by eliminating the lead sulfide precipitation was considered in order to avoid the use of hydrogen sulfide and the possible formation of colloidal sulfur. The precipitation of iron, aluminum, actinium, and other members of the ammonia group with ammonium hydroxide was already a part of the procedure. Lead is also precipitated by ammonia, although not completely under ordinary conditions. A test was made to determine the completeness of lead removal from actual

process solutions. A portion of the nitric acid solution of crude barium-radium nitrates from Experiment 22 containing 2 per cent of the original lead was treated with ammonium hydroxide. The insoluble hydroxides were filtered out and lead was determined in the precipitate and solution. It was found that 89.8 per cent of the lead present was removed in the precipitate. The 10.2 per cent remaining in solution represents 0.2 per cent of the total lead in the original K-65. Lead was also precipitated from duplicate aliquots of the crude nitrate solution by addition of hydrogen sulfide and sodium sulfide, respectively. Essentially 100 per cent of the lead was precipitated with either reagent. Spectroscopic tests on the barium-radium carbonate recovered from solutions purified by hydrogen sulfide showed the presence of about 0.01 per cent lead.

A fourth alternative method for lead removal consisting of an ammonium hydroxide precipitation in the presence of chromic ion, Cr^{+++} , to act as a carrier for the lead was also tested. Complete removal of the lead by this procedure was shown by testing the filtrate with hydrogen sulfide. Under the same conditions ferric ion also will act as a carrier for lead.

Table II summarizes the separation of lead achieved at each step of the process. The analysis of the original K-65 for lead and barium shows 17.38 per cent and 6.78 per cent, respectively, which gives an initial ratio of lead:barium of 2.56 on the metal basis. The per cent of the total lead removal at each step and the resulting lead:barium ratio is given in the table. The separation of barium and radium can be started by the chromate fractionation procedure with solutions purified by any of the alternate procedures. Qualitative tests on the behavior of lead during the fractionation indicate that some lead is dissolved at each extraction with concentrated nitric acid during the conversion of chromates to nitrates, but that most of the lead follows along with the radium in the radium-rich fractions. At some intermediate point in the fractionation scheme, it will be necessary to repeat the precipitation of lead to remove the last traces. The removal of lead at this point might well be done by adding chromic ion to the solution of barium radium nitrates (any chromate present must be reduced) and neutralizing with ammonia.

Radium Losses

Although it has been established that the overall recovery of radium in the purified barium-radium concentrate is high, an accurate estimate of the amount and distribution of losses can only be determined by direct measurement of the radium content of the various waste products. It was recognized that radon counting offered the best method of analysis for radium in these products but, unfortunately, it was necessary to use the alternative methods of gamma counting against a suitable standard or of isolation of the radium from other alpha emitters and counting by the alpha-slide technique. The determined radium losses are given in Table III. The highest solution losses occurred in the sodium hydroxide-sodium carbonate filtrate and in the sulfate solution from the precipitation of the crude barium sulfate. The radium in the latter solution can be readily recovered by the addition of a little barium to act as carrier. About 0.34 per cent of the radium was not extracted and remained in the final residue. The loss of radium by carrying with the lead separated in the final purification step was small, about 0.07 per cent. No significant difference in the loss with lead was noted by the alternative procedures of precipitation as sulfide or hydroxide. The total radium extracted was 99.66 per cent, and the radium recovered, calculated by difference from summation of the losses was better than 98 per cent.

Filtration Data

The filtration of the solutions obtained at various steps of the process was accomplished satisfactorily on Buchner funnels with paper as the filter medium. Some data were obtained on filtration rates and cake characteristics, which may be useful in extrapolation to larger scale operations. The filtration of the sodium hydroxide extract, which presented some problems because of the high content of sodium silicate and sodium plumbite in the solution, is described in detail.

The filtration of solution 21-B, extraction conditions given in Table IB, was taken as a typical example. The hot solution, 90°C. containing about 12 per cent solids, was filtered on a 15-centimeter Whatman No. 2 paper in a No. 5 Buchner funnel. Vacuum was maintained in the filter flask limited by the vapor pressure of the hot filtrate but was not measured. The filtrate came through clear from the start. The volume of filtrate collected, including wash water, was determined at various time intervals.

TIME, MIN.	5	10	15	20	25	30	35	40	50
VOLUME, ML.	470	685	865	1,010	1,150	1,285	1,380	1,470	1,830

The solution was completely filtered in 28 minutes at which time washing with hot water was started. The total wash water was about 600 milliliters. The filtrate remained clear on cooling to 45°C. Further cooling or dilution of the filtrate with water causes precipitation of lead sulfate. The resulting filter cake was 8 millimeters thick and contained about 30 per cent moisture.

The filtration of the sodium hydroxide-sodium carbonate solution was carried out in the same manner. The filtration time for equal volumes of filtrate was about 1.5 times that of the sodium hydroxide solution. Filtration of the solutions obtained in the remaining steps presented no problem. Filtration rates were relatively high, and clear filtrates were obtained. As an example, filtration after the second carbonation required 8 minutes on a 15-centimeter funnel for the total volume of 1,660 milliliters giving an average rate of over 200 milliliters per minute.

SUMMARY

A workable process for the extraction and purification of a barium-radium concentrate from K-65 residue has been developed and tested on a bench scale. Data have been obtained from which the economics of a larger scale operation can be estimated. A flow sheet for the process is given in Figure 1. It follows the procedure used in the final experiment, 22, with minor changes which have been discussed in connection with the experimental results. Alternative procedures have been considered and might be used at several points in the process. At the present time, they do not appear to offer any advantage over the procedure as outlined.

Outline of the Recommended Process

A. Extraction

1. The first step of the extraction stage consists of heating the K-65 residue with a 15 per cent sodium hydroxide solution for 1½ hours at 95°C. to 100°C.

The amount of sodium hydroxide used is one-half the weight of K-65. By this treatment, 85 per cent of the lead can be dissolved as sodium plumbite and 40 per cent of the silica converted to soluble sodium silicate. The residue, containing the barium and radium as sulfates, is reduced in bulk to one-half its original weight.

2. In the second step, the residue is heated in an autoclave with a solution of sodium hydroxide and sodium carbonate to 170°C. for 2 hours. This step converts about 90 per cent of the barium and radium to carbonate, at the same time dissolving an additional 13 per cent of the lead and 45 per cent of the silica.

3. The carbonated residue is treated with dilute nitric acid to dissolve barium and radium carbonates along with any other acid soluble constituents. Filtration gives the desired barium-radium nitrate solution which is purified in Part B of the process. The residue, now reduced to 15 per cent of its initial weight and containing about 10 per cent of the radium, is accumulated and after several runs is recarbonated and extracted with nitric acid. The barium-radium nitrate solutions are combined as indicated in the flow sheet.

B. Purification

1. The crude barium-radium nitrate solution is treated with dilute sulfuric acid to precipitate the insoluble sulfates. A clean-up of radium left in the filtrate is desirable, and this is done by addition of barium ion to carry down radium sulfate.

2. The sulfates of barium, radium, and lead are converted to carbonates by pressure carbonation with 3 moles of sodium carbonate per mole of barium sulfate.

3. The carbonates are dissolved in nitric acid and any unconverted barium-radium sulfate is recycled for carbonation in the previous step.

4. The nitrate solution is purified by neutralizing with ammonium hydroxide to precipitate insoluble hydroxides. If desired, the complete removal of lead can be accomplished at this point by the addition of ferric or chromic ion to act as a carrier. The filtrate containing the barium and radium as nitrates serves as feed for the final separation of radium by the chromate-urea procedure.

TABLE IA
RECOVERY OF BARIUM AND RADIUM FROM K-65
STARTING MATERIALS AND REAGENTS
EXPERIMENTS 21 AND 22

K-65 TAKEN		2,000 G.			
FROM ANALYSIS OF K-65					
SiO ₂		918. G.			
PB		347.6 G.			
BA AS BaSO ₄		230.6 G.			
RA		1498. μ G.			
REAGENTS USED	NaOH (g.)	Na ₂ CO ₃ (g.)	H ₂ O (ml.)	HNO ₃ (ml.)	H ₂ SO ₄ .98% (ml.)
A. FOR EXTRACTION OF BA AND RA					
1. NaOH LEACH	1,000		5,666		
2. COMBINED NaOH-Na ₂ CO ₃	500	264	2,560		
3. ACID EXTRACTION			3,800	260	
4. SECOND CARBONATION		264	1,056		
5. ACID EXTRACTION				<100	
B. FOR PURIFICATION OF BA-RA					
1. PRECIPITATION AS SULFATES					50
2. CARBONATION		264	2,560		
3. ACID EXTRACTION				<260	
4. NH ₄ OH-H ₂ S PRECIPITATION		AMOUNTS SMALL - NOT DETERMINED			
5. PRECIPITATION AS CARBONATES		90			
TOTALS	1,500	882		<620	50

TABLE 1B

EXTRACTION OF LEAD AND SILICA FROM K-65 BY 15 PER CENT
NAOH SOLUTION. TEMPERATURE 95°C. - 100°C.

EXPERIMENT	K-65 GRAMS	NAOH GRAMS	PB EXTRACTED		SiO ₂ EXTRACTED	
			GRAMS	PER CENT OF ORIGINAL PB	GRAMS	PER CENT OF ORIGINAL SiO ₂
21A	1,000	500	114.6	65.94	172.2	37.52
21B	1,000	500	138.0	79.40	169.3	36.88
21C (WASH)			5.6		19.1	
21 TOTAL	2,000	1,000	258.2	73.95	360.6	39.27
22A	500	250	73.26	84.30	94.3	41.09
22B	500	250	73.93	85.07	93.6	40.78
22C	500	250	73.09	84.11	91.5	39.87
22D	500	250	71.95	82.80	93.2	40.61
22 TOTAL	2,000	1,000	292.26	84.07	362.6	40.60

TABLE 1C

DISTRIBUTION OF SILICA IN PROCESS SOLUTIONS

SOLUTION	EXPERIMENT 21			EXPERIMENT 22		
	WEIGHT (G.)	SiO ₂ PER CENT OF TOTAL EXTRACTED	PER CENT OF ORIGINAL SiO ₂	WEIGHT (G.)	SiO ₂ PER CENT OF TOTAL EXTRACTED	PER CENT OF ORIGINAL SiO ₂
NAOH	360.5	88.71	39.27	372.7	45.01	40.60
NAOH-NA ₂ CO ₃	35.2	8.66	3.83	435.2	52.56	47.41
1ST HNO ₃	NIL	-	-	NIL	-	-
NA ₂ CO ₃	10.7	2.63	1.17	20.1	2.43	2.19
2ND HNO ₃	NIL	-	-	NIL	-	-
TOTAL	406.4	100.00	44.27	828.0	100.00	90.20
FINAL RESIDUE (grams)		665.5			238.0	
(per cent. of K-65)		33.28			11.9	

TABLE 1D

RECOVERY OF BARIUM AND RADIUM IN PURIFIED BARIUM CARBONATE

BARIUM RECOVERED	EXPERIMENT 21		EXPERIMENT 22	
	(g.)	(per cent)	(g.)	(per cent)
FROM 1ST HNO_3 (CALC'D AS BaSO_4)	102.2	44.3	207.1	89.8
FROM 2ND HNO_3 (CALC'D AS BaSO_4)	122.7	53.2	28.5	12.4
TOTAL (CALC'D AS BaSO_4)	224.9	97.5	235.6	102.2
RADIUM RECOVERED	EXPERIMENT 21		EXPERIMENT 22	
	(mg.)	(per cent)	(mg.)	(per cent)
FROM 1ST HNO_3	0.736	49.1	1.33	88.8
FROM 2ND HNO_3	0.778	51.9	0.20	13.3
TOTAL	1.514	101.0	1.53	102.1

TABLE 1E

DISTRIBUTION OF LEAD IN PROCESS SOLUTIONS

SOLUTION	EXPERIMENT 21		EXPERIMENT 22	
	(g.)	(per cent)	(g.)	(per cent)
NaOH	258.2	73.95	292.26	85.47
NaOH- Na_2CO_3	67.2	19.25	41.29	12.07
1ST HNO_3	20.06	5.74	6.38	1.87
Na_2CO_3	0.44	0.13	1.22	0.36
2ND HNO_3	3.27	0.94	0.80	0.23
SUMMARY				
PB ELIMINATED IN BASIC SOLUTIONS	325.84	93.33	334.77	97.90
PB WITH BA IN HNO_3 SOLUTIONS	23.33	6.68	7.18	2.10
TOTAL	349.17	100.0	341.95	100.0

TABLE II

SEPARATION OF LEAD FROM BARIUM AT VARIOUS STAGES OF THE PROCESS

	PB REMOVED PER CENT OF TOTAL PB	WEIGHT RATIO PB/BA
1. INITIAL IN K-65 RESIDUE	-	2.56
2. AFTER NaOH EXTRACTION	85.	0.38
3. AFTER PRECIPITATION OF CRUDE BaSO_4	98.	0.051
4. AFTER PURIFICATION (ALTERNATE PROCEDURES)		
(A) BY NH_4OH	99.84	0.004
(B) BY NH_4OH WITH CARRIER	99.996	0.0001 CA.
(C) BY NH_4OH AND H_2S	99.996	0.0001 *

* BASED ON SPECTROSCOPIC ANALYSIS OF THE FINAL BaCO_3

TABLE III

RADIUM LOSSES - EXPERIMENT 22

	RADIUM	
EXTRACTION	$\mu\text{g.}$	PER CENT OF TOTAL
NaOH FILTRATE	2.7	0.18
$\text{NaOH} \cdot \text{Na}_2\text{CO}_3$	4.24	0.28
FINAL RESIDUE	5.20	0.35
PURIFICATION		
BaSO_4 FILTRATE	7.2	0.48
Na_2CO_3 FILTRATE	3.3	0.22
CARRIED BY LEAD	1.11	0.07

FLOW SHEET RADIUM SEPARATION
AND RECOVERY PROCESS

Problem Title - The Concentration of Radium from Barium-Radium Mixtures

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INTRODUCTION

Radium was first separated from barium by fractional crystallization. Today, more than 50 years since its discovery, radium is still obtained primarily by fractional crystallization of its halides. To the chemist who is familiar with fractional crystallization procedures (such as those used for the separation of the rare earths and of radium from barium), they represent tremendously laborious and time and space consuming operations.

Various methods have been suggested for the separation of barium and radium by fractional precipitation, none of which could compete with fractional crystallization until the development of the fractional chromate precipitation method given in this report. The fractional precipitation of barium-radium chromates gives better enrichments of radium per fractionation step than any of the other fractional procedures.¹ However, no systematic fractionation scheme has previously been developed which utilizes the chromates.

Three procedures for the concentration of radium from barium-rich mixtures obtained from K-65 residues were described in the previous quarterly report:¹ (1) chromate precipitation by the hydrolysis of urea at 100°C., (2) chromate precipitation by the hydrolysis of cyanate at 25°C., and (3) chromate precipitation by the hydrolysis of cyanate at 0°C. If the chromates are precipitated homogeneously, the coefficients of radium enrichment per fractionation step were found to be 3.00, 3.55, and 4.26 at temperatures of 100°, 25°, and 0°C. respectively.¹ In each of these cases the condition required for the simplest fractionation scheme involving no loss in efficiency was fulfilled; namely, that the sum of the per cent of total radium and the per cent of total barium precipitated is equal to 100. (Loss in efficiency results from mixing fractions of unequal concentration.)

This study shows that the radium enrichments found for single fractionation steps can be applied to a system in which the fractional precipitation of the chromates is repeated many times. This fact is used as the basis for the development of a systematic process for the concentration of radium.

The chromate-cyanate procedure at 25°C. was used in the following experiments since manipulation is less difficult than with either of the other two procedures.

DETAILED REPORT

In setting up a repeating fractional precipitation scheme, it is desirable to combine solids and solutions of the same composition, in order to avoid loss of efficiency in the separation. To operate such a scheme on a continuous basis, it is also necessary that fractions of the same composition (intermediate fractions) recur at regular intervals, so that addition of starting material can be made at the proper point.²

In order to obtain these intermediate fractions for recycling, it was necessary to prepare them from the original material. A schematic diagram of the barium distribution

for the preparation of the intermediate fractions from the original sample, A_0 , is presented in Figure 1. These intermediate fractions are represented by A with a positive subscript for samples richer in radium than the original sample, and by A with a negative subscript for samples poorer in radium than the original sample. The process data given in Figure 1 are based on 100 parts of starting material (column under A_0), the repeated precipitation of 22 per cent of the barium at each step in the process, and three fractionation steps on both the enrichment and depletion sides. The numerical values given in Figure 1 represent the amount of material in each intermediate fraction. Five fractionation series, I to V, were required before the intermediate fractions were built up to constant weight.

Arrows pointing or sloping to the right indicate the flow of the filtrate in the process, while the arrows pointing or sloping to the left indicate that of the precipitate. In every series fractions are obtained as follows:

- A_3 , the radium-rich fraction, is the precipitate obtained from A_2 ;
- A_2 is the precipitate obtained from A_1 ;
- A_1 is composed of precipitate from A_0 and filtrate from A_2 ;
- A_0 is composed of the precipitate from A_{-1} , the filtrate from A_1 and original material (feed);
- A_{-1} is composed of the precipitate from A_{-2} and the filtrate from A_0 ;
- A_{-2} is the filtrate obtained from A_{-1} ;
- A_{-3} , the radium-poor fraction, is the filtrate obtained from A_{-2} .

Starting with 100 parts of original material (A_0) (Fractionation Series I, Figure 1), intermediate fraction A_1 is prepared by the precipitation of 22 per cent of the barium, and A_{-1} is composed of the 78 per cent of the barium remaining in the filtrate. If 22 per cent of A_1 is precipitated in a second fractionation step, A_2 will contain 4.840 parts of the original 100 parts, while the filtrate from A_1 would contain 17.16 parts of the original. In a similar fashion A_3 , the radium-rich fraction, is obtained by the precipitation of 22 per cent of A_2 and contains 1.065 parts; the filtrate from this step contains 3.775 parts and has the same composition as A_1 .

Precipitation of 22 per cent of A_{-1} would yield 17.16 parts of a sample having the same composition as the original and a filtrate (A_{-2}) containing 60.84 parts of the original 100 parts. Intermediate fraction A_{-2} would yield 13.38 parts of a sample equal in composition to A_{-1} and a filtrate (A_{-3}) containing 47.46 parts of radium-poor material.

In all cases, Products A_3 and A_{-3} were removed from the fractionation series. For Fractionation Series II, 100 parts of A_0 was composed of 17.16 parts obtained from the filtrate of A_1 , 17.16 parts of precipitate of A_{-1} , and 65.68 parts as a feed from original material. A_1 for Series II would be composed of 3.775 parts obtained from the filtrate of A_2 (Series I) and 22 parts from the precipitate of A_0 (II). Fraction A_2 (II) is obtained from the precipitate of A_1 (II) and contains 5.672 parts; while A_3 (II) contains 1.248 parts obtained from the precipitate of A_2 (II).

In the second series, A_{-1} is composed of 13.38 parts obtained from the precipitate of A_{-2} (I) and 78 parts obtained from the filtrate of A_0 (II); A_{-2} (II), 71.28 parts, is obtained from the filtrate of A_1 (II), while A_{-3} (II), 55.60 parts, is obtained from A_{-2} (II).

In similar fashion intermediate fractions for each fractionation series can be obtained. It can be observed that after five series of fractionations the intermediate fractions have reached approximately constant values.

In each step of the process approximately 22 per cent of the barium was precipitated homogeneously (20 per cent was precipitated as barium chromate and about 2 per cent was coprecipitated as barium nitrate¹). The chromate was added (as potassium dichromate) to a solution which was 0.06 normal in nitric acid. The acidity was high enough to prevent the precipitation of the barium chromate. The solution contained one per cent of glacial acetic acid, which was added as a buffer to prevent the precipitation of barium carbonate during the subsequent neutralization. The internal reactant used to neutralize the acid was potassium cyanate (5 grams per liter). The barium concentration in each step was 10 grams per liter (as metal).

The specific amounts of reagents for each step are listed in Table I. The table is based on 100 parts of barium as the A_0 fraction; for any process the amounts of reagents can be calculated from these tabulated values.

Since the fraction of barium precipitated in each case was fixed by the amount of potassium dichromate added, chromate precipitates, richer in radium than the original material, were converted to nitrates by extraction with hot concentrated nitric acid. This conversion was necessary since the amount of chromate present was more than enough to precipitate 22 per cent of the barium in the subsequent step. It is to be stressed that although the amount of chromate added at each step is sufficient to precipitate 20 per cent of the barium present, actually 22 per cent of the barium does precipitate because of coprecipitation of barium nitrate.

Chromate precipitates which are equal to or poorer in radium than the original material are first dissolved in nitric acid before addition to their respective reaction mixtures. Since this amount of chromate is insufficient for the precipitation of 20 per cent of the barium, the addition of more chromate (as water-soluble chromate or dichromate) is required.

PROCEDURE

The general procedure follows; for specific data see Table I and Figure 1.

Each fractionation series consists of seven fractions, A_3 , A_2 , A_1 , A_0 , A_{-1} , A_{-2} , and A_{-3} . For each of these fractions the procedure is essentially the same, although there are some modifications.

A_0 Original barium-radium nitrate is added at A_0 , along with the barium filtrate from A_1 , and the chromate precipitate from A_{-1} in the previous fractionation series (in the initial fractionation series 100 parts of original barium-radium mixture was used). To this mixture is added enough nitric acid to dissolve completely the barium chromate and to make the final solution 0.06 normal with nitric acid. Enough water is added to make the solution one per cent with respect to barium, and likewise, sufficient glacial acetic acid is added to make the final solution one per cent with respect to this acid. Then enough potassium dichromate is added so that the total chromate present will be sufficient to precipitate 20 per cent of the total barium present. (Because of coprecipitation there is actually 22 per cent of the barium precipitated.)

To the solution which is at room temperature potassium cyanate (5 grams per liter) is added with stirring. The reaction is allowed to continue until the supernatant liquid is colorless -- which indicates that all of the chromate has precipitated. The mixture is then filtered. The precipitate is saved for A_1 and the filtrate for A_{-1} .

A_1 Fraction A_1 is composed of the filtrate from A_2 from the previous fractionation series and the precipitate from A_0 . Since the precipitate from A_0 is barium-radium chromate, the total amount of chromate present is more than enough to precipitate 20 per cent of the total barium and thus must be removed. The barium-radium chromate from A_0 , as a consequence, is extracted with hot concentrated nitric acid to convert it to the nitrate. This barium nitrate is then combined with the filtrate from A_2 . To this mixture is then added sufficient nitric acid to make the final solution 0.06 normal with respect to the acid and sufficient water to make the solution one per cent in barium.

Then acetic acid is added to make the solution one per cent in this acid, and enough potassium dichromate is added to precipitate 20 per cent of the total barium present. Finally the potassium cyanate (5 grams per liter) is added. When the reaction is complete, as evidenced by the colorless supernatant, the mixture is filtered. The precipitate is saved for A_2 , and the filtrate is saved to be added to the subsequent fractionation series at A_0 .

A_2 Fraction A_2 consists of the precipitate from A_1 only. This precipitate, consisting of barium-radium chromate, must be extracted with hot concentrated nitric acid to convert the barium chromate to barium nitrate, since the amount of chromate present is more than enough to precipitate 20 per cent of the barium. This barium nitrate is dissolved in water (sufficient water was used to make the final solution one per cent in barium). Enough nitric acid is added to make the final solution 0.06 normal with respect to this acid, and enough glacial acetic acid is added so that the final solution is one per cent acetic acid. Then potassium dichromate is added -- enough to precipitate 20 per cent of the barium. Finally the potassium cyanate (5 grams per liter) is added and the reaction mixture stirred. After completion of the reaction, the mixture is filtered. The precipitate designated as A_3 is saved for further concentration, and the filtrate is saved for addition to A_1 in the next fractionation series.

A_3 The precipitate from A_2 is extracted with hot concentrated nitric acid. The barium nitrate so formed is dissolved in water and stored. These fractions are collected and serve as starting material for further radium concentration.

A_{-1} Fraction A_{-1} is composed of filtrate from A_0 and the precipitate from A_{-2} from the previous fractionation series. The precipitate from A_{-2} , being barium-radium chromate, is treated with sufficient hot nitric acid (one part acid to three parts of water) to convert it to the dichromate. Sufficient excess nitric acid is added to make the final reaction mixture 0.06 normal with respect to the nitric acid.

The filtrate from A_0 is added to this chromate mixture. Then sufficient potassium dichromate is added so that the total chromate present is sufficient

to precipitate 20 per cent of the barium present. The filtrate from A_0 contains the acetic acid from that fractionation, so that it is not necessary to add any additional acid. It is to be noted that the concentration of barium in this step is less than 10 grams per liter; however the dilution does not effect the enrichment. To the reaction mixture finally is added potassium cyanate (5 grams per liter). The reaction is allowed to continue with stirring until the supernatant liquid is colorless. The mixture is then filtered. The precipitate is saved for A_0 in the subsequent series, and the filtrate is saved for A_{-2} .

A_{-2} Fraction A_{-2} is composed of the filtrate from A_{-1} only. Sufficient nitric acid is added to make this filtrate 0.06 normal with respect to the nitric acid. Potassium dichromate, to precipitate 20 per cent of the barium present, is then added. No additional acetic acid is required, since this filtrate from A_{-1} is already one per cent with respect to the acid. As before, the concentration of barium is less than 10 grams per liter, but the enrichment is not affected. Potassium cyanate (5 grams per liter) is finally added to the reaction mixture. The reaction is allowed to continue with stirring until the supernatant liquid is colorless. The mixture is then filtered. The precipitate is saved for A_{-1} in the subsequent series, and the filtrate for A_{-3} .

A_{-3} The filtrate from A_{-2} is heated to boiling, and the alkaline earths are precipitated as the carbonates. These carbonates are filtered, dried, and saved as starting material for subsequent treatment, if a greater radium recovery is required.

Once the intermediates have been built up (Figure 1) the amount of reagents used per fractionation step remains constant (Line V, Table I).

RESULTS AND DISCUSSION

The radium enrichment process was divided into three scales of operations (S_1 , S_2 , and S_3) in which the initial samples had barium-to-radium ratios of approximately 100,000:1, 2,500:1, and 3,000,000:1, respectively. It was necessary to divide the process into the three scales of operation because of the rapid changes in fraction size. In the first scale of operation (S_1) the radium-rich fraction has a barium-to-radium ratio of approximately 2,500:1, and the radium-poor fraction, a ratio of about 3,000,000:1. The radium-rich fraction from S_1 serves as starting material for S_2 , and the radium-poor fraction, as starting material for S_3 .

The radium-rich fraction from S_2 has a barium:radium ratio of approximately 60:1, and the radium-poor fraction, approximately 100,000:1. The radium-rich fraction from S_3 has a barium-to-radium ratio of approximately 100,000:1, and the radium-poor end, approximately 150,000,000:1 (Figure 3).

The actual barium-to-radium ratio of the original material for the first scale of operation, S_1 , was 102,300:1. Intermediate fractions were built up from this starting material on a basis (A_0) of 30 grams of barium. The numerical values given in Figure 2 represent the grams of barium in each intermediate fraction. The amounts of reagents used in this scale of operation can be obtained by taking 30 per cent of the values listed in Table I. Approximately 1 kilogram of barium was processed by this procedure. Representative

samples from both the radium-rich end (A_3) and the radium-poor end (A_{-3}) of the fractionation series were analyzed for radium and barium content.³ The results of these analyses are listed in Table II for three representative experiments. Average results of these experiments are also given.

The average barium-radium ratio of three radium fractions (A_3) from S_1 was 2,530:1 (Table II), that for the barium fraction (A_{-3}), 3,016,000:1 compared to 102,300:1 for the initial material (A_0). The radium fraction contains on an average 93.9 per cent of the original radium and 2.3 per cent of the original barium and the barium fraction contains only 3.3 per cent of the original radium and 96.8 per cent of the original barium. The average enrichment factor for three 3-step fractionations is 40.4. For a single fractionation step the enrichment factor is $(40.4)^{\frac{1}{3}} = 3.43$. This enrichment factor is in agreement with the average value previously reported⁴ for single fractionation steps by the chromate-cyanate method at 25°C.

The radium fractions (A_3) from S_2 were collected and used as starting material (A_0) in the second scale of operations (S_2) for further radium concentration. Intermediate fractions were built up on a basis (A_0) of one gram of barium. The weight of barium in each intermediate fraction can be calculated by taking one per cent of the values given in Figure 1 and the amounts of reagents used for this second scale of operation can be calculated by taking one per cent of the values listed in Table I. Representative samples from both the radium rich end (A_3) and the radium poor end (A_{-3}) of the fractionation series were analyzed for radium and barium.

The results for three representative experiments are listed in Table III along with the average values of these experiments.

The average barium-radium ratio of the radium fraction (A_3) from S_2 was 61.9:1, that for the barium fraction (A_{-3}), 69,030:1 as compared to 2,695:1 for the initial samples (A_0). The radium fraction contains on an average 94.7 per cent of the original radium and 2.2 per cent of the original barium as compared to the barium fraction which contains only 3.8 per cent of the original radium and 98.3 per cent of the original barium. The average enrichment factor for three fractionation steps is 43.5. For a single fractionation step the enrichment factor is $(43.5)^{\frac{1}{3}} = 3.52$. This enrichment factor is in agreement with the value reported for the first scale of operation, namely 3.43.

The barium fractions (A_{-3}) from S_1 were collected and used as starting material in the third scale of operations (S_3) for further radium recovery. The average barium-radium ratio of this starting material was 3,016,000:1. Large volumes of solution were required to work this low-radium-content material by the procedure as outlined. These volumes were reduced to one-third of that previously used, since a series of concentration studies indicated that a barium concentration as high as 30 grams of barium (as metal) per liter could be used without reducing the radium enrichment per step. The purpose of this experiment was to determine the radium losses in the barium fraction (A_{-3}) for the third scale of operation (S_3). This barium fraction contained 3.3 per cent of the original radium in the S_3 operation and had a barium-radium ratio of approximately 150,000,000:1. The radium content of this final fraction was determined by gamma counting, since the conventional alpha-slide method³ is impractical for samples of such low radium content.

Losses in the Radium Enrichment Process

A study was made of radium losses in the radium enrichment process. In addition to the radium losses in the radium-poor end of the fractionation series, the only other possible losses occur in the nitric acid from the chromate extractions.

The radium loss in the barium fraction obtained after three fractionation steps in the first scale of operation was 3.3 per cent of the total radium. This loss can be reduced to approximately 0.1 per cent by continuing the process through three additional fractionation steps, the final product in this latter case having a barium-radium ratio of 150,000,000:1 (Figure 3).

The radium losses in the hot, concentrated nitric acid extract of a three step fractionation process amounted to 3.30 per cent of the total radium. Of this amount, 3.17 per cent of the total radium can be recovered by filtering the crystallized barium nitrate from the nitric acid extract after it has cooled (Table IV). The remaining 0.13 per cent can be recovered also, since the nitric acid extract is distilled to recover both the nitric acid and chromic oxide for reuse. This 0.13 per cent of the original radium would be recycled with the chromic acid in the fractionation process.

It is obvious from the foregoing discussion and from Table IV that the radium losses in this process are negligibly small, amounting to a few tenths of one per cent of the total radium at most.

ALTERNATE PROCEDURES

Three methods, (1) the chromate-urea method at 100°C, (2) the chromate-cyanate method at 25°C, and (3) the chromate-cyanate method at 0°C, have been suggested¹ for the concentration of radium from barium-rich mixtures. The process described in detail in this report utilizes the second of these methods; however, a countercurrent batch process for the enrichment of radium can be devised which utilizes any of the three methods or a combination of these methods.

The chromate-cyanate method at 0°C, gives the best enrichment factor. However, in spite of a lower enrichment factor the chromate-cyanate method at 25°C has the advantage that no heating or cooling of the reaction is necessary. The chromate-urea method gives the poorest enrichment per fractionation step, but has the advantage of lower cost of reagents.

It seems that a combination of these methods might be desirable. It is suggested that the chromate-urea method be used for the recovery of radium from radium-poor samples, the chromate cyanate method at 25°C for the recovery of radium from the intermediate samples, and the chromate-cyanate method at 0°C for the recovery of radium from the radium-rich samples. This last method would be useful on a laboratory scale for the purification of radium from small samples.

The amounts of reagents required for each fractionation step in a four-step series are given for each of the three methods in Table V. The amounts of the reagents listed in Table V have been calculated, assuming that the intermediates have been built up to constant value. The distribution of barium in the intermediate fractions was calculated by the method reported in the previous quarterly report.²

In four steps the final product enriched by the chromate-urea method at 100°C. is 787 times richer in radium than the original barium-radium material; that from the chromate-cyanate method at 25°C. is 1,587 times richer than the original, and that product from the chromate-cyanate method at 0°C. is 3,333 times richer than the original.

Before any definite statement can be made in defense of one method, or a combination, a careful cost estimate is required.

The quantities of reagents listed in Table V are volume dependent. If the concentration of barium could be increased, then there would be a corresponding decrease in the amounts of reagents required.

The concentration of alkaline earth ions in solution was studied to determine its effect on the degree of separation of radium from barium by homogeneous precipitation. The concentration used for most of the work reported previously¹ was 10 grams of barium (as metal) per liter of solution. Experiments were performed with 5, 10, 20, and 30 grams of barium (as metal) per liter of solution. The largest of these amounts (30 grams per liter) approaches the limit of solubility of barium nitrate at 25°C. and, thus, no higher concentrations were studied.

The procedure used for this work was essentially the same as that used in previous studies.¹ In general, the method consisted of dissolving barium carbonate (containing radium) in nitric acid (sufficient excess nitric acid was used to make the final solution about 0.06 normal with respect to the acid). To the barium nitrate mixture was added 450 milliliters of water, 5 milliliters of glacial acetic acid, sufficient potassium dichromate to precipitate 20 per cent of the total barium in solution (approximately two per cent of additional barium nitrate was coprecipitated with barium chromate), and finally 4 grams of potassium cyanate dissolved in water. The total volume was in each case approximately 500 milliliters. The reaction was allowed to continue until the supernatant liquid was colorless.

Table VI shows the results of the series of experiments. From examination of this data it is evident that there is little if any effect of concentration on the efficiency of separation.

The significance of these experiments lies in the fact that concentrations up to three times those previously used can be employed in the separation of radium from barium. Smaller quantities of nitric acid, potassium cyanate, and acetic acid are also required (Table VII) at each step in the fractionation series. The amount of these materials used in the experiments, where 30 grams of barium ion per liter was studied, is essentially the same as that required where 10 grams of barium ion per liter was used.

The separation of radium from barium in radium-rich mixtures necessitates the handling of small quantities of materials. This handling would be facilitated if dilute solutions could be employed. From examination of the data in Table VI it is evident that the enrichment factor is constant even in the more dilute solutions (5 grams of barium per liter), so that this method of separation is applicable for the fractionation of radium-rich materials.

The procedures given in this report have utilized potassium cyanate as an internal reactant for the neutralization of nitric acid. However, sodium cyanate may be substituted for the potassium salt. The cost of sodium cyanate is less than half the cost of potassium

cyanate; hence, the usage of the sodium salt would decrease the cost of the process considerably. Approximately 4/5 as much sodium cyanate by weight is required per fractionation step, because of the lower formula weight of the sodium salt as compared to the potassium salt.

SUMMARY AND CONCLUSIONS

When a barium and radium bromide mixture (Ba:Ra = 400,000:1) is subjected to fractionation crystallization, the crystals in the head fraction show a barium to radium ratio of 1:9 after 23 fractionations.⁴ Only 8 to 12 fractional chromate precipitations (depending on the procedure used) are required for a comparable enrichment. An example of the rapid radium enrichment obtained by the chromate-cyanate method at 25°C. is given in Figure 3; after six precipitation steps the final chromate mixture (Ba:Ra = 61.9:1) is 1,650 times more concentrated in radium than the original material (Ba:Ra = 102,300:1). If the intermediate fractions have previously been prepared, the radium recovery is equal to or better than 99 per cent. It must be emphasized that fewer fractionation steps in a radium recovery process means less operating cost, time, equipment, and space, and a smaller retention of radium in intermediate fractions.

The chromate procedure presented in this report is a repeated fractional precipitation scheme which operated on a countercurrent batch basis by mixing solid and liquid fractions of the same composition which recur at regular intervals and by the addition of original material (feed) at the proper point. These regularly recurring fractions (intermediate fractions) are prepared from the original barium-radium mixture. The fraction of barium precipitated in each fractionation step depends on the quantity of chromate ions added to the reaction mixture. The barium-radium chromate fraction is precipitated at each step by neutralizing a 0.06 normal nitric acid solution. The acid is neutralized as a result of the hydrolysis of internal reactants, such as urea or a cyanate. Essentially, ammonia is added internally and homogeneously throughout the solution, thus eliminating localized precipitations which occur when reagents are added from an external source. The chromates precipitated in this manner are very granular and easily filtered.

Chromates richer in radium than the original material are converted to nitrates by extraction with hot concentrated nitric acid. The nitrates are dissolved in water, and the solution is used in the subsequent fractional precipitation. The nitric acid treatment serves several purposes, (1) it eliminates the excess chromate so that the proper quantity can be added in the subsequent fractionation step, (2) it removes the highly active radium daughters, greatly reducing the radiation hazard, and (3) it serves as a purification step, since practically all nitrates except barium and radium (and lead if present) are soluble in hot 70 per cent nitric acid.⁵

The alkaline earth halides are more soluble than the nitrates (the salt which limits the alkaline earth concentration used in the chromate methods). Hence, the volumes of solution required by fractional crystallization are smaller than those required by the chromate methods. For radium-poor mixtures the concentration of alkaline earth salts can be greatly increased with the chromate-urea method at 100°C., since the nitrates are considerably more soluble in hot solutions than in cold solutions. For radium-rich mixtures the high salt concentration used in fractional crystallization works to a disadvantage. A decrease in enrichment factor per fractionation step has been reported for the fractional crystallization of radium-rich mixtures because of the formation of double salts of barium and radium halides,⁶ such as $\text{RaBr}_2 \cdot 2 \text{BaBr}_2 \cdot 6 \text{H}_2\text{O}$.

No such double salt formation has been found for chromate mixtures. Actually it appears that the enrichment per fractionation step increases slightly for radium-rich samples.

The only reagent required for the fractional crystallization of barium-radium bromides is hydrobromic acid; most of which can be recovered for reuse. For the chromate precipitation methods the reagents which cannot be recovered for reuse are small amounts of nitric acid and the internal reagent, urea or cyanate, and, in some cases, acetic acid. The reagents in both fractional crystallization and precipitation are relatively inexpensive. An evaluation of the recovery of the reagents is required before a true evaluation of the process as a whole can be made.

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TABLE I

REAGENT DATA FOR THE CHROMATE-CYANATE METHOD AT 25°C.

FRACTIONATIONS	REAGENT	UNITS	A ₃	A ₂	A ₁	A ₀	A ₋₁	A ₋₂	A ₋₃
I	BA ⁺⁺	G.	1.065	4.840	22.00	100.00	78.00	60.84	47.46
	K ₂ Cr ₂ O ₇	G.	-	1.036	4.711	21.41	16.70	13.03	-
	HNO ₃	ML.	-	1.936	8.800	40.00	40.00	40.00	-
	HOAC	ML.	-	4.84	22.0	100.	-	-	-
	KCNO	G.	-	2.42	11.0	50.	50.	50.	-
	TOTAL VOLUME	ML.	-	484.0	2,200.	10,000.	>10,000.	>10,000.	>10,000.
	BA ⁺⁺	G.	1.248	5.672	25.78	100.0	91.38	71.28	55.60
II	K ₂ Cr ₂ O ₇	G.	-	1.214	5.520	4.711	6.539	15.26	-
	HNO ₃	ML.	-	2.269	10.31	47.32	45.71	40.00	-
	HOAC	ML.	-	5.67	25.78	100.	-	-	-
	KCNO	G.	-	2.84	12.89	50.	50.	50.	-
	TOTAL VOLUME	ML.	-	567.2	2,578.	10,000.	>10,000.	>10,000.	>10,000.
	BA ⁺⁺	G.	1.278	5.812	26.42	100.0	93.68	73.07	57.00
	K ₂ Cr ₂ O ₇	G.	-	1.244	5.657	1.846	4.796	15.65	-
III	HNO ₃	ML.	-	2.325	10.57	42.87	46.69	40.00	-
	HOAC	ML.	-	5.81	26.42	100.	-	-	-
	KCNO	G.	-	2.91	13.21	50.	50.	50.	-
	TOTAL VOLUME	ML.	-	581.2	2,642.	10,000.	>10,000.	>10,000.	>10,000.
	BA ⁺⁺	G.	1.284	5.837	26.53	100.0	94.08	73.38	57.24
	K ₂ Cr ₂ O ₇	G.	-	1.250	5.681	1.353	4.499	15.71	-
	HNO ₃	ML.	-	2.335	10.61	42.10	46.86	40.00	-
IV	HOAC	ML.	-	5.84	26.53	100.	-	-	-
	KCNO	G.	-	2.92	13.27	50.	50.	50.	-
	TOTAL VOLUME	ML.	-	583.7	2,653.	10,000.	>10,000.	>10,000.	>10,000.
	BA ⁺⁺	G.	1.285	5.841	26.55	100.0	94.14	73.43	57.28
	K ₂ Cr ₂ O ₇	G.	-	1.251	5.685	1.268	4.445	15.72	-
	HNO ₃	ML.	-	2.336	10.62	41.97	46.89	40.00	-
	HOAC	ML.	-	5.84	26.55	100.	-	-	-
V	KCNO	G.	-	2.92	13.28	50.	50.	50.	-
	TOTAL VOLUME	ML.	-	584.1	2,655.	10,000.	>10,000.	>10,000.	>10,000.

TABLE II
CONCENTRATION OF RADIUM BY THE CHROMATE-CYANATE METHOD

SCALE OF OPERATION, S_1

ANALYSIS EXPERIMENT NO. 1	RADIUM FRACTION	BARIUM FRACTION	ORIGINAL SAMPLE
	A_3	A_{-3}	A_0
BARIUM (G.)	0.3998	17.27	17.58
RADIUM (μ G.)	163.1	6.00	171.8
BA:RA RATIO	2,451:1	2,878,000:1	102,300:1
% TOTAL BARIUM	2.3	98.2	100.0
% TOTAL RADIUM	94.9	3.5	100.0

ENRICHMENT FACTOR 41.7 PER 3 STEPS

ANALYSIS EXPERIMENT NO. 2

BARIUM (G.)	0.4127	16.91	17.58
RADIUM (μ G.)	160.6	5.42	171.8
BA:RA RATIO	2,570:1	3,120,000:1	102,300:1
% TOTAL BARIUM	2.3	96.2	100.0
% TOTAL RADIUM	93.5	3.2	100.0

ENRICHMENT FACTOR 39.8 PER 3 STEPS

ANALYSIS EXPERIMENT NO. 3

BARIUM (G.)	0.4123	16.84	17.58
RADIUM (μ G.)	160.4	5.51	171.8
BA:RA RATIO	2,570:1	3,056,000:1	102,300:1
% TOTAL BARIUM	2.3	95.8	100.0
% TOTAL RADIUM	93.4	3.2	100.0

ENRICHMENT FACTOR 39.8 PER 3 STEPS

AVERAGES OF EXPERIMENTS
(NO. 1, 2, AND 3)

BARIUM (G.)	0.4083	17.01	17.58
RADIUM (μ G.)	161.4	5.64	171.8
BA:RA RATIO	2,530:1	3,016,000:1	102,300:1
% TOTAL BARIUM	2.3	96.8	100.0
% TOTAL RADIUM	93.9	3.3	100.0

ENRICHMENT FACTOR 40.4 PER 3 STEPS OR 3.43 PER STEP

TABLE III

CONCENTRATION OF RADIUM BY THE CHROMATE-CYANATE METHOD

SCALE OF OPERATION, S₂

ANALYSIS RUN No. 7	RADIUM FRACTION	BARIUM FRACTION	ORIGINAL SAMPLE
	A ₃	A _{0.3}	A ₀
BARIUM (G.)	0.01285	0.5764	0.5858
RADIUM (μG.)	206.6	9.77	218.2
BA:RA RATIO	62.2:1	59,000:1	2,685:1
% TOTAL BARIUM	2.2	98.4	100.0
% TOTAL RADIUM	94.7	4.5	100.0

ENRICHMENT FACTOR 43.2 PER 3 STEPS

ANALYSIS RUN No. 13

BARIUM (G.)	0.01272	0.5763	0.5858
RADIUM (μG.)	208.8	7.48	209.5
BA:RA RATIO	60.9:1	77,096:1	2,796:1
% TOTAL BARIUM	2.1	98.4	100.0
% TOTAL RADIUM	99.7	3.6	100.0

ENRICHMENT FACTOR 45.9 PER 3 STEPS

ANALYSIS RUN No. 21

BARIUM (G.)	0.01267	0.5750	0.5858
RADIUM (μG.)	202.2	7.68	224.3
BA:RA RATIO	62.7:1	74,870:1	2,612:1
% TOTAL BARIUM	2.2	98.2	100.0
% TOTAL RADIUM	90.0	3.4	100.0

ENRICHMENT FACTOR 41.6 PER 3 STEPS

AVERAGES OF RUNS
(No. 7, 13, AND 21)

BARIUM (G.)	0.01275	0.5759	0.5858
RADIUM (μG.)	205.9	8.31	217.3
BA:RA RATIO	61.9:1	69,032:1	2,695:1
% TOTAL BARIUM	2.2	98.3	100.0
% TOTAL RADIUM	94.7	3.8	100.0

ENRICHMENT FACTOR 43.5 PER 3 STEPS OR 3.52 PER STEP

TABLE IV
RADIUM RETENTION IN THE NITRIC ACID EXTRACT AND INTERMEDIATE FRACTIONS

SCALE OF OPERATION, S₂

	RADIUM (μg.)	PER CENT TOTAL RADIUM
ORIGINAL SAMPLE (RUN NO. 1 THROUGH 21)	4,270.	100.0
RADIUM-RICH FRACTIONS (A ₃)	4,030.	94.3
NITRATES*	137.6	3.17
FILTERED NITRIC ACID EXTRACTS	5.4	0.13
NITRIC ACID DISTILLATE	0.0	0.0
INTERMEDIATE AND BARIUM FRACTIONS	145.0	3.4**

* NITRATES CRYSTALLIZED FROM THE NITRIC ACID EXTRACT.

** PER CENT RETENTION OF RADIUM DECREASES WITH INCREASING AMOUNT OF ORIGINAL MATERIAL WORKED.

TOTAL VOLUME NITRIC ACID EXTRACT = 586 ML.

VOLUME NITRIC ACID EXTRACT TAKEN FOR DISTILLATION = 550 ML.

VOLUME NITRIC ACID COLLECTED AT $118 \pm 3^\circ\text{C}$. = 513 ML.

NITRATES = 58.89 MG.

BA (ASSUMING NITRATES AS $\text{Ba}(\text{NO}_3)_2$) = 30.95 MG.

TABLE V

COMPARISON OF REAGENT DATA FOR THREE CHROMATE METHODS

CHROMATE-UREA METHOD AT 100°C.

FRACTIONATION	REAGENT	UNITS	A ₄	A ₃	A ₂	A ₁	A ₀	A ₋₁	A ₋₂	A ₋₃	A ₋₄
I	BA ++	G.	0.625	2.5	10.	32.5	100.	97.5	90.0	67.5	50.63
	K ₂ Cr ₂ O ₇	G.	-	0.6695	2.678	8.704	0.67	2.01	6.02	18.08	-
	HNO ₃	ML.	-	1.	4.	13.	51.75	51.45	50.5	40.00	-
	UREA	G.	-	15.0	60.0	195.	600.0	300.0	-	-	-
	TOTAL	ML.	-	250.	1,000.	3,250.	10,000.	>10,000.	>10,000.	>10,000.	>10,000.
	VOLUME										

CHROMATE-CYANATE METHOD AT 25°C.

II	BA ++	G.	0.357	1.623	7.369	27.85	100.	98.86	94.81	73.95	57.68
	K ₂ Cr ₂ O ₇	G.	-	0.347	1.577	5.960	0.25	0.87	4.46	15.83	-
	HNO ₃	ML.	-	0.649	2.947	11.14	49.28	48.90	46.94	40.00	-
	HOAC	ML.	-	1.62	7.369	27.85	100.	-	-	-	-
	KCNO	G.	-	0.812	3.685	13.93	50.0	50.0	50.0	50.0	-
	TOTAL										
	VOLUME	ML.	-	162.3	736.9	2,785.	10,000.	>10,000.	>10,000.	>10,000.	>10,000.

CHROMATE-CYANATE METHOD AT 0°C.

III	BA ++	G.	0.189	0.995	5.236	23.27	100.	99.0	95.8	77.60	62.86
	K ₂ Cr ₂ O ₇	G.	-	0.1812	0.9535	4.237	0.18	0.58	3.32	14.13	-
	HNO ₃	ML.	-	0.398	2.094	9.31	47.90	47.65	46.20	40.00	-
	HOAC	ML.	-	0.995	5.236	23.27	100.	-	-	-	-
	KCNO	G.	-	0.498	2.618	11.63	50.0	50.0	50.0	50.0	-
	TOTAL										
	VOLUME	ML.	-	99.5	523.6	2,327	10,000.	>10,000.	>10,000.	>10,000.	>10,000.

TABLE VI
EFFECT OF BARIUM CONCENTRATION ON RADIUM ENRICHMENT
BY THE CHROMATE-CYANATE METHOD AT 25°C.

BA ⁺⁺ CONC. (G./L.)	BAO ₃ (G.)	HNO ₃ (ML.)	HOAc (ML.)	KCNO (G.)	K ₂ CR ₂ O ₇ (G.)	PER CENT BA PRECIPITATED	PER CENT RA CARRIED	ENRICHMENT *
5	3.7	4.5	5	4	0.552	21.6	77.2	3.57
5	3.7	4.5	5	4	0.552	21.4	78.8	3.68
10	7.4	7.0	5	4	1.103	22.1	75.7	3.43
10	7.4	7.0	5	4	1.103	21.9	79.6	3.63
20	14.8	12.0	5	4	2.206	22.5	76.5	3.40
20	14.8	12.0	5	4	2.206	22.8	79.7	3.50
30	22.2	17.0	5	4	3.309	22.9	82.7	3.61
30	22.2	17.0	5	4	3.309	22.2	79.9	3.61

* ENRICHMENT CALCULATED AS $E = \frac{\text{PER CENT RADIUM CARRIED}}{\text{PER CENT BARIUM PRECIPITATED}}$

TABLE VII

REAGENT DATA FOR THE CHROMATE-CYANATE METHOD
AT 25°C. FOR SEVERAL BARIUM CONCENTRATIONS

FRACTIONATION	REAGENT	UNITS	A ₄	A ₃	A ₂	A ₁	A ₀	A ₋₁	A ₋₂	A ₋₃	A ₋₄
5	BA ⁺⁺	G.	0.357	1.623	7.369	27.85	100.0	98.86	94.81	73.95	57.68
	K ₂ Cr ₂ O ₇	G.	-	0.347	1.577	5.960	0.25	0.87	4.46	15.83	-
	HNO ₃	ML.	-	1.298	5.894	22.28	89.25	88.90	86.94	80.	-
	HOAC	ML.	-	3.24	14.738	55.70	200.	-	-	-	-
	KCNO	G.	-	1.624	7.370	27.86	100.0	100.0	100.0	100.0	-
	TOTAL VOLUME	ML.	-	324.6	1,473.8	5,570.	20,000.	>20,000.	>20,000.	>20,000.	>20,000.
10	BA ⁺⁺	G.	0.357	1.623	7.369	27.85	100.0	98.86	94.81	73.95	57.68
	K ₂ Cr ₂ O ₇	G.	-	0.347	1.577	5.960	0.25	0.87	4.46	15.83	-
	HNO ₃	ML.	-	0.649	2.947	11.14	49.28	48.90	46.94	40.00	-
	HOAC	ML.	-	1.62	7.369	27.85	100.	-	-	-	-
	KCNO	G.	-	0.812	3.685	13.93	50.0	50.0	50.0	50.0	-
	TOTAL VOLUME	ML.	-	162.3	736.9	2,785.	10,000.	>10,000.	>10,000.	>10,000.	>10,000.
20	BA ⁺⁺	G.	0.357	1.623	7.369	27.85	100.0	98.86	94.81	73.95	57.68
	K ₂ Cr ₂ O ₇	G.	-	0.347	1.577	5.960	0.25	0.87	4.46	15.83	-
	HNO ₃	ML.	-	0.325	1.473	5.57	29.28	28.90	26.94	20.00	-
	HOAC	ML.	-	0.81	3.685	13.93	50.	-	-	-	-
	KCNO	G.	-	0.41	1.843	6.97	25.0	25.0	25.0	25.0	-
	TOTAL VOLUME	ML.	-	81.2	368.5	1,393.0	5,000.	>5,000.	>5,000.	>5,000.	>5,000.
30	BA ⁺⁺	G.	0.357	1.623	7.369	27.85	100.0	98.86	94.81	73.95	57.68
	K ₂ Cr ₂ O ₇	G.	-	0.347	1.577	5.960	0.25	0.87	4.46	15.83	-
	HNO ₃	ML.	-	0.216	0.982	3.71	22.61	23.23	20.27	13.33	-
	HOAC	ML.	-	0.54	2.456	9.28	33.3	-	-	-	-
	KCNO	G.	-	0.237	1.228	4.64	16.67	16.67	16.67	16.67	-
	TOTAL VOLUME	ML.	-	54.1	245.6	928.	3,333.	>3,333.	>3,333.	>3,333.	>3,333.

Problem Title - Solubility of Barium Chromate in Nitric Acid

Report By - M. Economides

Work Done By - M. Economides

INTRODUCTION

In the chromate process for separating radium and barium, barium chromate is precipitated from a 0.06 molar nitric acid solution containing barium ions and chromate ions by neutralizing the acid as a result of the hydrolysis of an internal reactant, such as urea or potassium cyanate.¹ In concentrated nitric acid solutions barium chromate is converted into sparingly soluble barium nitrate and chromic acid. Solubility measurements of barium chromate in varying concentrations of nitric acid (0.1 to 5.0 molar) were made in order to ascertain the concentration of nitric acid which could be utilized in the precipitation of barium chromate from homogeneous solution. The concentration of barium ion as well as the concentration of chromate ion present in the saturated barium chromate-nitric acid solutions were determined. Comparison of these quantities indicates the amount of barium chromate going into the saturated solutions and the amount of barium ion which crystallizes out of these solutions in the formation of barium nitrate for the varying concentrations of nitric acid (0.1 to 5.0 molar).

In the previous quarterly report,² results reported were based on the amount of barium ion in the saturated nitric acid solutions. The data presented in this report are based on the amount of chromate ion contained in the saturated solutions of barium chromate in varying concentrations of nitric acid (0.1 to 5.0 molar). Determinations of the barium present in the saturated nitric acid solutions showed the maximum solubility of barium chromate to be in the neighborhood of 1.2 molar nitric acid with a decreasing amount of barium present in saturated solutions of higher acid concentration. The amount of barium present in a saturated solution of barium chromate in 5 molar nitric acid approximates the concentration of barium present in a saturated solution of barium nitrate in 5 molar nitric acid. To determine the effect on the solubility of barium chromate of an acid which contained no nitrate ion and the accompanying sparingly soluble barium nitrate, perchloric acid was substituted for nitric acid.

DETAILED REPORT

A centrifuge tube was constructed as previously described.² Into this were placed 220 milligrams of barium chromate and 3 milliliters of nitric acid. The tube was sealed off and agitated at 24°C. in a constant-temperature bath for 18 hours. After this interval, the ampoules were opened, and two samples of 1 milliliter each were pipetted into 250-milliliter Erlenmeyer flasks. These samples were analyzed for chromate with sodium thiosulfate according to the procedure described in Kolthoff and Sandell.³ The results obtained, in grams of chromate ion per liter of saturated solution, appear in Table I and Curve II, Figure 1.

The solubility of barium chromate in nitric acid at 24°C. was then approached from a higher temperature. Each sample was heated to boiling before it was sealed off and agitated in the constant temperature bath for the 18-hour interval. These results appear in Table II and Curve I, Figure 1.

To establish further the effect of the formation of barium nitrate on the solubility of barium chromate, perchloric acid was substituted for nitric acid in the procedure. Perchloric acid was chosen (1) because of the possibility of the limiting factor of barium nitrate formed with nitric acid, and (2) because the solubility of barium perchlorate is sufficiently high so as not to interfere with the solubility of barium chromate. Results of determinations appear in Tables III and IV and Curves III and IV, Figure 1.

CONCLUSIONS

It can be noticed in Figure 1 that Curves I and III are displaced to the left. This displacement indicated that there is either an increased activity of the heated acid solutions or that saturation equilibrium was not reached by the samples placed in the constant temperature bath within 18 hours.

It is also shown that the formation of barium nitrate does not influence the solubility of barium chromate as much as was anticipated. This is evidenced by the fact that the maximum solubility of barium chromate expressed as chromate ion is approximately 35 grams of chromate ion per liter of saturated solution.

Sufficient information has been observed in these studies on the solubility of barium chromate in various concentrations of nitric acid to indicate that a nitric acid concentration in the neighborhood of 1.0 molar may be used in the barium chromate precipitations from homogeneous solution. If higher concentrations of nitric acid are used, barium nitrate will crystallize out. In a saturated solution of barium chromate in 5.0 molar nitric acid, the amount of barium in the saturated solution approximated that of a saturated solution of barium nitrate in 5.0 molar nitric acid.

REFERENCES

1. Salutsky, M. L., Rpt. Gen. Res., MLM-475, p. 48, July 31, 1950.
2. Economides, M., Rpt. Gen. Res., MLM-518, p. 29, January 15, 1951.
3. Kolthoff and Sandell, Textbook of Quantitative Analysis, p. 594, (1936).

TABLE I

SOLUBILITY OF BARIUM CHROMATE IN NITRIC ACID, 24°C.

NITRIC ACID CONCENTRATION (normality)	CHROMATE ION (grams per liter of saturated solution)	BARIUM CHROMATE (grams per liter of saturated solution)
0.10	2.30	5.02
0.25	4.92	10.75
0.49	9.95	21.73
0.74	15.26	33.33
1.00	22.09	48.24
1.19	30.59	66.81
1.46	31.22	68.18
2.00	31.76	69.36
2.99	31.65	69.12
3.98	31.49	68.77
4.98	31.33	68.42

TABLE II

SOLUBILITY OF BARIUM CHROMATE IN NITRIC ACID, 24°C.

SATURATION EQUILIBRIUM FROM HEATED MIXTURE

NITRIC ACID CONCENTRATION (normality)	CHROMATE ION (grams per liter of saturated solution)	BARIUM CHROMATE (grams per liter of saturated solution)
0.10	2.46	5.37
0.25	5.07	11.07
0.49	11.71	25.57
0.74	25.44	55.56
1.00	33.08	72.25
1.19	32.31	70.57
1.46	33.21	72.53
2.00	32.89	71.83
2.99	32.39	70.74
3.98	32.19	70.30
4.98	31.61	69.04

TABLE III

SOLUBILITY OF BARIUM CHROMATE IN PERCHLORIC ACID, 24°C.

PERCHLORIC ACID CONCENTRATION (normality)	CHROMATE ION (grams per liter of saturated solution)	BARIUM CHROMATE (grams per liter of saturated solution)
0.05	1.37	2.99
0.10	2.03	4.43
0.25	4.06	8.87
0.50	6.95	15.18
0.76	9.52	20.79
1.01	11.71	25.57
1.48	15.14	33.07
1.99	18.30	39.97
3.01	23.80	51.98
4.05	30.36	66.31
5.07	32.70	71.42

TABLE IV

SOLUBILITY OF BARIUM CHROMATE IN PERCHLORIC ACID, 24°C.

SATURATION EQUILIBRIUM FROM HEATED MIXTURE

PERCHLORIC ACID CONCENTRATION (normality)	CHROMATE ION (grams per liter of saturated solution)	BARIUM CHROMATE (grams per liter of saturated solution)
0.05	1.25	2.73
0.10	2.07	4.52
0.25	4.10	8.95
0.50	7.49	16.36
0.76	11.28	24.64
1.01	15.18	33.15
1.48	25.48	55.65
1.99	30.44	66.48
3.01	32.46	70.89
4.05	32.54	71.07
5.07	31.76	69.36

Problem Title -- The Separation of Radium from Barium by Ion Exchange

Report By -- W. C. McCluggage and W. H. Power

Work Done By -- W. C. McCluggage and G. D. Nelson

INTRODUCTION

The first separation of radium and barium by use of Dowex-50 ion exchange resin was made on a microscale by E. R. Tompkins at Oak Ridge.¹ Work at this laboratory has been directed toward determining the best conditions for the separation of radium and barium by ion exchange and developing the process to serve either as a single method of separation and purification or as the purification step after the concentration of the radium by some other process.

Nearly total separation of 30,000 parts of barium to one of radium has been accomplished, but material cost and time consumption were prohibitive for large-scale operation.² A good separation of 2,000 parts of barium from one of radium has been made by the elution of radium and barium on a 25-centimeter bed of Dowex-50 with 0.5 molar ammonium citrate at pH 4.9.³ The process was limited chiefly by the occurrence of precipitates of barium citrate in citrate solution if more than a few per cent of the total column capacity was occupied by barium at the start of the elution. Solubility studies of barium citrate solutions have been made.⁴

Recent work has been directed toward increasing the amount of barium which can be eluted from a column without the formation of a barium citrate precipitate and toward lowering the citrate content of the elutriant for purposes of economy. The effects of citrate concentration, pH, and temperature upon the separation of barium and radium will be considered.

DETAILED REPORT

Five separations were carried out on an ion-exchange column whose design and operational data are given in Table I.

Elution With 0.24 Molar Citrate at pH 5.6

Studies of barium complexes in citrate solutions indicated that eluting solutions with 0.24 molar citrate at 75°C. and pH 5.6 were roughly optimum for economical operation.⁴ The first elution in this series therefore, was made with the above solution. Forty-one column volumes was required to remove the barium (Figure 1, Tables II-A, III). This slow removal was attributed to the low citrate ion concentration. The separation was good, but the elutriant volume was too great.

The consideration of some equilibrium calculations⁴ (Calculation 1) lead to the selection of 0.32 molar ammonium citrate at pH 5.6 as conditions most likely to remove barium in a reasonable number of column volumes, i.e., 8 to 12.

Elutions With 0.32 Molar Citrate at pH 5.6

Two separations, one at room temperature and one at 50°C. were made with 0.32 molar citrate solutions at pH 5.6. The drop rate of the elutriant for the elevated

temperature run was increased to 1 milliliter per square centimeter per minute, a rate three times that normally used. The barium was removed in 19 column volumes at room temperature and in 20 column volumes at 50°C. (Figures 2, 3, and Tables II-B, II-C, V, and VI).

For these separations the ratio of the column volumes at which the radium peaks occur is 3.3 at room temperature and 2.6 at 50°C. Separating conditions are less favorable at the higher temperature and elution rate.

High Barium Elution

With 0.32 molar ammonium citrate at pH 5.6 established as the best elutriant of those tried, a run was made to separate 49 micrograms of radium from the maximum quantity of barium which could be eluted from the 25-centimeter column without precipitation (10 per cent of the column capacity or 0.553 grams). (Figure 4, Tables II-D, and VII.) Because of the relatively large quantity of barium eluted, a well defined separation of barium and radium was not attained. Ninety-nine per cent of the radium was recovered in a fraction enriched to a barium-radium ratio of 68:1, according to extrapolation values for the barium concentrations beyond the lower limit of barium analysis.

Precipitation of Barium Citrate During Elution

In addition to the elutriant characteristics necessary to effect a good separation of barium and radium and to remove the barium from the column with a reasonable liquid volume, a second requirement is imposed on the elutriant in case it forms a slightly soluble compound with the barium. Precipitates in the column must be avoided. The formation of a barium citrate precipitate in an ion exchange column depends not only on its solubility but also upon the leaching rate of barium from the resin and the rate of removal of soluble barium to lower parts of the column. The physical conditions of a column, elution rate, and temperature, in addition to the chemical nature of the elutriant, therefore affect the formation of a precipitate.

To obtain practical information regarding column eluting conditions which would or would not form precipitates, a series of precipitation studies was made (Table IV). Citrate elutriants with different citrate contents, pH's, and temperatures were passed at a uniform rate through a thick resin bed of the barium form of Dowex-50. The elution was continued until a lightening of the resin color was noticed, indicating the formation of a slight precipitate. The resin was then "developed" by stopping the flow of elutriant for a period of about ½ hour, after which the precipitate band became pronounced. The depth of this precipitate band below the resin surface indicated the maximum barium content which could be tolerated at the top of a resin column under the specific eluting conditions. For example, the distance from the top of the resin to the precipitate was 22 millimeters for 0.32 molar citrate at 5.6 pH and 25°C. If the resin column were 25 centimeters high 22/250 or 9 per cent of the column capacity could be converted to the barium form without a precipitate forming upon elution. Increasing the temperature decreased the amount of barium which could be handled without a precipitate, probably because of the increased diffusion rate of barium out of the resin. Raising the pH of the citrate decreased the amount of barium which could be handled by more rapidly removing barium from the resin. It is fortuitous that the citrate conditions selected for elution (0.32 molar citrate and 5.6 pH) are also satisfactory from the standpoint of not readily causing a precipitate.

High Radium Elution

For the last run, 0.158 grams of barium was separated from 1.779 milligrams of radium by eluting with 0.32 molar citrate at 5.6 pH. This level of radium, the highest which could be handled without shielding, was selected to investigate possible deleterious effects caused by irradiation of the resin such as retention of radium by the resin because of sulfate formation. Particular attention was given in this run to the degree of separation of radium and barium. Extrapolation procedures and supplementary experiments with barium-140 were used to judge the best possible radium yield and purity.

If extrapolated values of barium concentration can be relied upon, 99.8 per cent of the radium can be separated with a purity of 99.8 per cent (Figure 5, Table II-E, and VIII). The method of extrapolation is explained later in this report.

Barium analyses by the use of barium-140 are believed to be high because of the presence of an impurity in the radioisotope. However, if these analyses are used for barium concentrations, 99.8 per cent of the radium was separated with a purity of 95.6 per cent.

All of the radium used for this run was recovered; no retention of radium by the resin was detected.

Barium Analysis by Use of Barium-140

Barium concentrations less than 10^{-4} normal cannot satisfactorily be determined turbidimetrically; therefore, in fractions of eluate whose barium concentrations were less than 10^{-4} normal, the 13-day barium-140 were used as a tracer. A slide was prepared from the barium chloride obtained by the cold hydrochloric acid-ether method of separation.⁵ The slide was then beta counted and corrected for barium-140 decay and lanthanum-140 growth.

Stable barium (158 milligrams) and barium-140 was eluted from a bed of Dowex-50 with 0.32 molar ammonium citrate at pH 5.6. Data from this run (Table IX) were used to obtain the circled points A, B, C, of Figure 7.

The presence of alpha particles in the elutriant indicated that an impurity was present in the original barium-140 sample. The alpha peak in the barium elution curve at a column volume of 31 was likely caused by radium impurity in the barium. The alpha activity likely increased the apparent beta count over the true beta count of barium-140.

A purification of barium-140 samples from alpha-active materials should precede future runs with this material.

Extrapolation Methods

The fitting of elution data to mathematical expressions is of interest in this work to provide a method of extrapolation to concentrations which are too low for chemical analysis (five parts per million in the case of barium). A comparison of elution data with calculations based on equilibrium conditions provides a comparison between the actual separation and the best possible separation for a given column.

Mayer and Tompkins⁸ have developed a simple elution theory based on the analogy of the ion exchange column to the fractional distillation column. Their general expression for the concentration of solute in the eluate is:

$$M = \frac{p}{\sqrt{2\pi}} \frac{(p+n-1)^{p+n-\frac{1}{2}} C^{n-1}}{(n-1)^{n-\frac{1}{2}} p^{p+\frac{1}{2}} (1+C)^{p+n}} \quad (1)$$

where: M = the fraction of solute per column volume, $V \approx Lp$

p = the number of theoretical plates

$$= \frac{2\pi C(C+1) M^2}{\text{Max.}}$$

L = the fraction of solute in any plate volume, v . (2)

C = the distribution constant of the solute between the solution and the resin.

$n = pF$ = the number of plate volumes which have passed through a column up to a given time.

The circled points on Figure 5 show the effluent concentrations calculated by Equation 1. The calculated points do not fit the data for the barium elution, possibly because barium was not being eluted under equilibrium conditions. Equation 1 assumes equilibrium prevailing between the solute in solution and solute on the resin. The system would depart from equilibrium conditions as the flow rate is increased, as the resin particle size is increased, or as the diffusion rate of the solute is lowered. As eluting conditions deviate from those of equilibrium, the elution curve becomes broader, and separation between two cations becomes poorer. The elution curve for radium fits the points of Equation 1 better than the barium curve, possibly because radium is present in much smaller quantities.

Under the conditions reported in Figure 5, Mayer and Tompkins' method for calculating the degree of separation between two elements is complicated by the apparent change of the number of column plates with change in concentration of the solute. For instance, 41 plates were calculated for the barium elution, while 118 plates were calculated for the radium elution. This discrepancy may be caused by different degrees of removal from equilibrium for the two cations or by the effect of ionic strength upon the distribution coefficient, C , point (A) on Figure 5, twice as high as the actual concentration at the barium maximum, illustrated the concentration of barium to be expected if the number of theoretical plates for the barium elution were the same as for the radium elution (118).

Martin and Synge⁷ have adapted the normal error curve to approximate the theoretical elution curve.

$$y = y_{\text{max}} e^{-\frac{t^2}{2}} \quad (3)$$

where:

y = the concentration of solute in any column volume of eluate.

Mayer and Tompkins show that " t " may be calculated as follows:

$$t = \frac{(F - F_{\text{max}}) p}{[pC(1+C)]^{\frac{1}{2}}} \quad (4)$$

where F = the number of column volumes which have passed through a column up to any given time (at the maximum of the elution curve $F_{\max.} = C$).

That Equations 1 and 3 describe practically the same elution curve is shown by Figure 5. From a mathematical standpoint, Equation 3 is much easier to use than Equation 1.

Since neither of the above treatments fit the data of Figure 5 well, an empirical expression based on Equation 3 was used.

$$y = y_{\max.} e^{-\frac{(RS)^2}{2}} \quad (5)$$

where:

$$S = (F - F_{\max.})$$

The constant, R , was introduced to control the width of the bell-shaped curve representing an elution. In the logarithmic form, Equation 5 becomes:

$$\log \frac{y}{y_{\max.}} = -\frac{(RS)^2}{4.6} \quad (6)$$

If the logarithm of the ratio $y/y_{\max.}$ is plotted against S^2 , the slope will be $-R^2/4.6$. The slope of the left hand side of the radium elution curve as shown by Figure 6 is 0.023. The linearity of this plot for radium ($E - F$) indicates that Equation 5 fits the radium elution curve well. The fit for barium elution was not as good, however. The slope of the logarithm plot varied from the left hand side of the curve ($A-B$) to the right hand side ($B-C$). When more than five columns had been eluted after the maximum, however, the curve was linear, and the slope was then the same as for the radium elution. This linear portion of the barium curve was extrapolated ($C-D$) to estimate barium contents in fractions where its concentrations were less than five parts per million. The extrapolated data is used in Table VII and Figure 7. The circled points A, B, and C are three points representing data from barium-140 analysis (Table IX). If the barium-140 analysis data were superimposed on Figure 7, the curve would pass through A, B, and C.

CONCLUSIONS

1. Ion exchange is a good method for separating barium from radium, particularly if the barium-radium ratio is less than 1,000 to 1.
2. The best elutriant found for the separation of barium and radium is 0.32 molar citrate solution at pH 5.6. This solution provides good separation of the cations and does not cause barium citrate precipitates if less than 0.43 grams of barium per square centimeter is adsorbed on top of a Dowex-50 column before elution.
3. A recovery of 99.8 per cent of the radium with a purity of 95.6 to 99.8 per cent was found when 1.799 milligrams of radium was separated from 0.158 grams of barium. The purity of 95.6 per cent, obtained as the result of a barium-140 analysis, is believed to be low because of the presence of considerable alpha active impurity in the radio-active barium. Future experiments with barium-140 should be preceded by removal of alpha active materials from the barium.

4. No retention of radium was detected when 1.799 milligrams of radium was eluted from a Dowex-50 column.

5. In general, elution data formed broader bell-shaped curves than calculated by the equations of Mayer and Tompkins or Martin and Synge. The theoretical equations assume that the column is operating under equilibrium conditions. Broadening of the elution curve is probably caused by nonequilibrium conditions prevailing during elution.

CALCULATION I

The ratio of total soluble barium in contact with barium resin for two solutions of different citrate concentrations, x and y, is given by:

$$\text{Ratio} = \frac{[\text{NH}_4^+]^2_x \left(1 + \frac{[\text{H Cit}^{--}]}{0.057} + \frac{[\text{Cit}^{--}]}{0.008} \right)_x}{[\text{NH}_4^+]^2_y \left(1 + \frac{[\text{H Cit}^{--}]}{0.057} + \frac{[\text{Cit}^{--}]}{0.008} \right)_y} = \frac{L_{\text{max. } y}}{L_{\text{max. } x}}$$

where:

$L_{\text{max.}}$ = column volume in which the barium peak occurs.

From Tables II-A, and III, $L_{\text{max. } x} = 24$, and $x = 0.24$ molar. $L_{\text{max. } y}$ is set equal to 10, and y is calculated to be 0.32 molar.

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TABLE I
COLUMN DESIGN AND OPERATION

ITEM	DATA
RESIN	DOWEX-50; 70 - 100 MESH AMMONIA FORM RESIN
BED DEPTH	25 CM.
BED DIAMETER	1.3 CM.
WEIGHT OF RESIN (OVEN DRIED)	16.3 G.
LIQUID ABOVE RESIN	10 CM.
BED VOLUME	33.2 ML.
COLUMN VOLUME	16.6 ML.
FEED SOLUTION DROP RATE	1 ML. $\pm$ 0.1 ML./CM. ² /MIN.
ELUTRIANT DROP RATE	0.3 ML. $\pm$ 0.03 ML./CM. ² /MIN.
CAPACITY OF OVEN-DRIED DOWEX-50 RESIN	5.1 M. EQ. OF BARIUM /G.

TABLE II
OPERATION SUMMARIES

A				
		CATION RETURN		
PROCESS STEPS	REAGENTS USED	VOLUME REQUIRED (ml.)	BARIUM (per cent)	RADIUM (per cent)
FEED SOLUTION	0.158 G. BARIUM AS THE ACETATE. 36.75 μ G. RADIUM SOLUTION 0.2 N HCL	500		
BARIUM ELUTION	0.24 M. CITRIC ACID PH 5.65 ADJUSTED WITH NH_4OH ; TEMP. 75°C.	680	99.6	
RADIUM ELUTION	SOLUTION 15 PER CENT (WEIGHT) AMMONIUM CITRATE 10 PER CENT (VOLUME) NH_4OH .			104
B				
FEED SOLUTION	0.158 G. BARIUM AS THE ACETATE. 35.6 μ G. RADIUM AS THE CITRATE. 0.2 N HCL	1,000		
BARIUM ELUTION	0.32 M. CITRIC ACID PH 5.6 ADJUSTED WITH NH_4OH ; TEMP. 25°C.	320	99.0	
RADIUM ELUTION	SAME AS BARIUM	640		98.4
C				
FEED SOLUTION	0.158 G. BARIUM AS THE ACETATE AND 33.0 μ G. RADIUM AS THE CITRATE. 0.2 N HCL.	1,000		
BARIUM ELUTION	0.32 M. CITRIC ACID PH 5.6 ADJUSTED WITH NH_4OH ; TEMP. 50°C.	323	95.0	
RADIUM ELUTION	SAME AS BARIUM.	600		100.5
D				
FEED SOLUTION	0.553 G. BARIUM AS THE ACETATE AND 49 μ C. OF RADIUM SOLUTION 0.2N HCL	1,000		
BARIUM ELUTION	0.32 M. CITRIC ACID PH 5.6 ADJUSTED WITH NH_4OH ; TEMP. 25°C.	340	102	
RADIUM ELUTION	SAME AS BARIUM	650		99.0
E				
FEED SOLUTION	0.158 G. BARIUM AS THE ACETATE AND 1,799 μ G. RADIUM SOLUTION 0.2N HCL.	1,000		
BARIUM ELUTION	0.32 M. CITRIC ACID PH 5.6 ADJUSTED WITH NH_4OH ; TEMP. 25°C.	366	100.7	
RADIUM ELUTION	SAME AS BARIUM	650		99.7

TABLE III

ELUTION OF BARIUM AND RADIUM WITH 0.24 MOLAR CITRATE PH 5.6 TEMPERATURE 75°C.

158 MILLIGRAMS BARIUM AND 36.7 MICROGRAMS RADIUM

FRACTION NUMBER	VOLUME (ml.)	COLUMN VOLUME	BARIUM PER FRACTION (mg.)	BARIUM PER FRACTION (per cent)	BARIUM PER COLUMN VOLUME (per cent)	RADIUM PER FRACTION (μ g.)	RADIUM PER FRACTION (per cent)	RADIUM PER COLUMN VOLUME (per cent)
1 - 35	357	21.5						
35 - 37	13	22.3	1.5	1.0	1.3			
38	7	22.7	3.8	2.4	5.7			
39	13	23.5	12.5	7.9	10.1			
40	19	24.6	23.8	15.1	13.2			
41	16	25.6	18.1	11.5	11.9			
42	13	26.4	12.5	7.9	10.1			
43	12	27.1	10.9	6.9	9.6			
44	11	27.8	9.7	6.1	9.2			
45	14	28.6	11.9	7.5	8.9			
46	17	29.6	11.3	7.1	6.9			
47	16	30.6	9.3	5.9	6.1			
48	15	31.5	7.0	4.4	4.9			
49 - 59	120	38.7	22.7	14.5	2.0			
60	11	39.4	0.6	0.38	0.57			
61	20	40.6	0.6	0.38	0.32			
62	18	41.7	0.2	0.13	0.12			
63 - 64	23	43.1						
65	15	44.0				15.8	43.0	52.5
66	20	45.2				20.4	55.5	46.0
67	23	46.6				1.7	4.6	3.3
68	16	47.5				0.3	0.82	0.85

TABLE IV
PRECIPITATION OF BARIUM CITRATE IN A DOWEX-50 COLUMN

PH	MOLAR CITRATE	TEMPERATURE (°C.)	DISTANCE BETWEEN RESIN SURFACE AND PRECIPITATE BAND (mm.)
5.63	0.32	25	22
5.63	0.32	75	8
5.63	0.32	25	20
5.63	0.32	75	8
5.0	0.5	25	16
5.0	0.5	75	11
7.0	0.32	25	5
7.0	0.32	75	3

DROP RATE 0.33 ML./MIN./CM.².

TABLE V

ELUTION OF BARIUM AND RADIUM WITH 0.32 MOLAR CITRATE PH 5.6 TEMPERATURE 25°C.

158 MILLIGRAMS BARIUM AND 35.6 MICROGRAMS RADIUM

FRACTION NUMBER	VOLUME (ml.)	COLUMN VOLUME	BARIUM PER FRACTION (mg.)	BARIUM PER FRACTION (per cent)	BARIUM PER COLUMN VOLUME (per cent)	RADIUM PER FRACTION (μg.)	RADIUM PER FRACTION (per cent)	RADIUM PER COLUMN VOLUME (per cent)
1 - 6	100.	6.0						
7	17.	7.0	0.1	0.10	0.098			
8	16.	8.0	14.5	9.20	9.55			
9	9.	8.5	24.7	15.63	28.8			
10	14.5	9.4	46.7	29.60	33.9			
11	20.5	10.7	32.9	20.80	16.8			
12	22.0	12.0	19.1	12.10	9.15			
13	22.2	13.3	11.1	7.03	5.26			
14	20.6	14.6	4.7	2.98	2.40			
15	17.4	15.6	1.6	1.01	0.96			
16	16.6	16.6	1.0	0.63	0.63			
17	16.0	17.6	0.2	0.13	0.12			
18	16.0	18.5						
19	15.6	19.5						
20	15.0	20.4						
21 - 22	29.4	22.1				0.12	0.34	0.192
23 - 24	29.0	23.9				0.46	1.29	0.74
25	14.0	24.7				0.61	1.71	2.03
26	12.5	25.5				0.80	2.24	2.98
27	11.0	26.1				1.09	3.06	4.62
28	9.0	26.7				1.15	3.23	5.96
29	8.5	27.2				1.42	4.00	7.82
30	8.5	27.7				1.54	4.33	8.46
31	25.0	29.2				7.15	20.00	13.3
32	20.6	30.4				6.25	17.50	14.1
33	27.0	32.1				8.15	23.00	14.1
34	27.5	33.7				4.63	13.00	7.85
35 - 36	45.0	36.4				1.57	2.96	1.09

TABLE VI

ELUTION OF BARIUM AND RADIUM WITH 0.32 MOLAR CITRATE PH 5.6 TEMPERATURE 50°C.
158 MILLIGRAMS BARIUM AND 33.0 MICROGRAMS RADIUM

FRACTION NUMBER	VOLUME (ml.)	COLUMN VOLUME	BARIUM PER FRACTION (mg.)	BARIUM PER FRACTION (per cent)	BARIUM PER COLUMN VOLUME (per cent)	RADIUM PER FRACTION (µg.)	RADIUM PER FRACTION (per cent)	RADIUM PER COLUMN VOLUME (per cent)
1 - 5	107	6.5						
6	26	8.0	0.4	0.25	0.16			
7	26	9.5	29.1	18.4	11.75			
8	29	11.2	58.8	37.2	21.26			
9	27.5	12.9	36.9	23.4	14.14			
10	27.0	14.5	16.7	10.6	6.52			
11	27.0	16.1	4.8	3.40	2.09			
12	26.6	17.7	2.1	1.33	0.83			
13	26.5	19.3	1.1	0.70	0.44	0.024	0.073	0.046
14	24.8	20.8				0.126	0.382	0.256
15	26.0	22.3				0.485	1.47	0.940
16	25.5	23.9				1.52	4.61	3.00
17	25.0	25.4				3.30	10.00	6.65
18	33.7	27.4				12.50	37.9	18.66
19	24.4	28.9				6.48	19.6	13.32
20	24.0	30.3				4.64	14.1	9.75
21	23.8	31.8				2.57	7.79	5.43
22	15.0	32.7				0.84	2.54	2.81
23	30.0	34.5				0.55	1.67	0.93
24	26.0	36.0				0.125	0.38	0.24
25	25.6	37.5						

TABLE VII

ELUTION OF BARIUM AND RADIUM WITH 0.32 MOLAR CITRATE PH 5.6 TEMPERATURE 25°C.

553 MILLIGRAMS BARIUM AND 49 MICROGRAMS RADIUM

FRACTION NUMBER	VOLUME (ml.)	COLUMN VOLUME	BARIUM PER FRACTION (mg.)	BARIUM PER FRACTION (per cent)	BARIUM PER COLUMN VOLUME (per cent)	RADIUM PER FRACTION (μg.)	RADIUM PER FRACTION (per cent)	RADIUM PER COLUMN VOLUME (per cent)
1 - 6	100	6.0						
7	22.0	7.4	32.2	5.83	4.30			
8	23.0	8.7	148.0	26.80	19.35			
9	29.0	10.5	215.0	38.85	22.25			
10	27.0	12.1	109.0	19.70	12.10			
11	26.0	13.7	39.0	7.05	4.50			
12	27.5	15.4	14.0	2.53	1.53			
13	24.0	16.8	7.0	1.26	0.87	0.157	0.32	0.22
14	24.0	18.3	1.0	0.18	0.12	0.370	0.75	0.52
15	20.4	19.5	0.4	0.07	0.06	0.605	1.23	1.00
16	20.6	20.7				1.08	2.22	1.79
17	21.6	22.0				1.89	3.86	2.96
18	19.3	23.2				2.06	4.21	3.62
19	25.0	24.7				4.70	9.60	6.37
20	23.5	26.1				5.12	10.45	7.38
21	21.0	27.4				4.60	9.40	7.43
22	18.5	28.5				4.72	9.65	8.66
23	17.8	29.6				4.05	8.26	7.71
24	17.3	30.6				3.86	7.87	7.55
25	15.3	31.5				2.98	6.09	6.61
26	13.0	32.2				2.35	4.80	6.13
27 - 28	23.0	33.6				3.74	7.63	5.51
29 - 30	22.8	35.0				2.70	5.50	4.00
31 - 32	22.2	36.3				1.71	3.49	2.66
33 - 34	22.2	37.7				0.855	1.75	1.31
35	50.0	40.7				0.980	2.00	0.66

TABLE VIII

ELUTION OF BARIUM AND RADIUM WITH 0.32 MOLAR CITRATE AT
PH 5.6 158 MILLIGRAMS BARIUM AND 1.799 MICROGRAMS RADIUM

TOTAL VOLUME COLUMN VOLUMES				BARIUM ANALYSES				RADIUM ANALYSES				RADIUM PURITY (per cent)
FRACTION MILLILITER	COLUMN VOLUME	N _{BA}	N _{RA}	PER FRACTION (mg.)	CUMULATIVE NOT ELUTED (mg.)	PER FRACTION (per cent)	CUMULATIVE NOT ELUTED (per cent)	PER FRACTION (μg.)	CUMULATIVE NOT ELUTED (μg.)	PER FRACTION (per cent)	CUMULATIVE ELUTED (per cent)	
11	129	7.78	2.3	500	160.764	0.31	99.97					
12	148	8.93	1.2	26.100	160.264	16.23	99.66					
13	167	10.1	0	45.800	134.164	28.48	83.43					
14	186	11.2	1.1	33.900	88.364	21.08	54.95					
15	205	12.36	2.3	26.400	54.464	16.42	33.87					
16	224	13.50	3.4	17.500	28.064	10.88	17.45					
17	243	14.65	4.6	6.400	10.564	3.98	6.57					
18	262	15.80	5.7	2.200	4.164	1.37	2.59					
19	281	16.93	6.8	1.300	1.964	0.81	1.22					
20	300	18.09	8.0	500	664	0.31	0.41					
21	319	19.21	9.1	100	164	0.06	0.1006					
22	338	20.40	10	50*	64*	0.03*	0.0406*	0.13	1793.77	0.01	0.01	97.6**
23	357	21.55	11	10*	14.0*	0.008*	0.0106*	0.54	1793.64	0.03	0.04	99.2**
24	376	22.65	12	3*	4.0*	0.002*	0.0026*	1.86	1793.10	0.10	0.14	99.8**
25	395	23.80	13	0.8*	1.0*	0.0005*	0.0006*	5.35	1791.24	0.30	0.44	99.9**
26	414	24.95	14	0.2*	0.2*	0.0001*	0.0001*	14.00	1785.89	0.78	1.22	99.9**
27	433	26.10						29.57	1771.89	1.65	2.87	
28	452	27.25						59.20	1742.32	3.30	6.17	
29	471	28.40						115.68	1683.12	6.45	12.62	
30	490	29.55						171.51	1567.44	9.56	22.18	
31	509	30.70						260.78	1395.93	14.54	36.72	
32	528	31.85						323.39	1135.15	18.03	54.75	
33	547	33.00						323.05	811.76	18.01	72.76	
34	566	34.10						262.98	488.71	14.66	87.42	
35	585	35.25						98.42	225.73	5.49	92.91	
36	604	36.40						75.49	127.31	4.21	97.12	
37	623	37.55						34.04	51.82	1.90	99.02	
38	651	39.20						11.59	17.78	0.64	99.66	
39	670	40.40						3.20	6.19	0.18	99.84	
40	689	41.60						1.99	2.99	0.11	99.95	
41	708	42.60						1.00	1.00	0.01	99.96	

* EXTRAPOLATED VALUES

** BASED ON EXTRAPOLATED VALUES

TABLE IX

ELUTION OF BARIUM AND BARIUM-140 WITH 0.32 MOLAR CITRATE AT PH 5.6
158 MILLIGRAMS OF BARIUM AND 4.9 MICROGRAMS OF BARIUM-140

FRACTION NUMBER	VOLUME (ml.)	COLUMN VOLUME	BETA COUNTS PER FRACTION (cts./min.)	ALPHA COUNTS PER FRACTION (cts./min.)	BARIUM PER FRACTION (per cent)
1 - 9	214	12.9			
10	22.8	14.3			
11	22.6	15.6			
12	23.0	17.0			
13	22.4	18.4			
14	22.4	19.7		224	
15	22.2	21.0		733	
16	22.0	22.5		1,120	
17	22.0	24.0	2,112	1,850	0.009
18	22.0	25.4	1,452	5,100	0.006
19	21.6	26.7	842	7,580	0.004
20	21.8	28.0	1,787	10,600	0.008
21	22.8	29.4	661	13,100	0.003
22	26.8	31.0	2,519	25,200	0.011
23	34.7	33.5	3,018	15,200	0.013
24	47.0	36.3	470	7,100	0.002
25	48.0	39.2	--	--	--

INITIAL BETA COUNT 2.18×10^7 (CORRECTED).

ELUTION CURVE FOR THE SEPARATION OF
RADIUM FROM BARIUM AT 75°

ELUTION CURVE FOR THE SEPARATION OF
RADIUM FROM BARIUM AT 25°

ELUTION CURVE FOR THE SEPARATION OF
RADIUM FROM BARIUM AT 50°

SPECIFICATIONS

RESIN: DOWEX 50; NH_4R
70-100 MESH

FEED: Ba-Ra ACETATE
SOLUTION IN 0.2N
HCl

ELUTRIANT: 0.32 MOLAR
CITRIC ACID
pH 5.6

COLUMN VOLUME: 16.6 ML.

----- RADIUM
————— BARIUM

ELUTION CURVE FOR THE SEPARATION OF
RADIUM FROM BARIUM AT 25°

ELUTION OF BARIUM AND RADIUM.

ELUTION OF BARIUM AND RADIUM.

Problem Title - The Decontamination of Liquid Wastes from the Radium Process

Report By - R. W. Moshier

Work Done By - D. Hale, J. Kochendorfer, and S. Barth

INTRODUCTION

Decontamination studies have been continued in order to find a satisfactory method which would bring the count on the waste solution from the radium process to a sufficiently low level for discharge into natural waters.

The first step used is the same as previously reported which precipitates the bulk of the activity with the lead sulfate. Since the ferrous ferrocyanide scavenging second step is of doubtful value for bringing the final count to a satisfactory low level, a better method has been sought.

DETAILED REPORT

The liquid wastes resulting from the bench-scale radium process, as finally worked out, are shown in Table I.

Approximately 12 liters of first-step filtrate, obtained after neutralizing the wastes with sulfuric acid and filtering the lead sulfate, was prepared for second-step study. Several variables governing the ferrous ferrocyanide scavenging were studied with no consistent improvement.

As a second-step process a metallic sulfide precipitation was found to give the best decontamination. Of the several metals tested, i.e., lead, bismuth, zinc, tin, and ferrous iron; the ferrous iron was found best not only for decontamination but for economy, since scrap iron dissolved in hydrochloric acid gave comparable results to analytical-grade ferrous ammonium sulfate. The results of these metallic sulfide tests are shown in Table II.

For a final check on the ferrous sulfide second-step process and of the over-all process, eleven 1-liter batches of wastes were processed. The mixtures were made up from the ratios of wastes produced, as given in Table I. The results from these 11 batches are given in Table III. From these results it can be concluded that, for the first step, the addition of the acidified material to the sodium hydroxide-containing waste gave a much lower solid waste. The first-step filtrate at times may be of sufficiently low count for direct disposal, but a second-step process always assures a disposable waste liquor.

The satisfactory decontamination process for the liquid wastes from the bench-scale radium process gives a disposable liquid waste counting less than 10 counts per minute per milliliter. The filter cake averaged 250 grams wet and 75 grams dry per liter of waste.

TABLE I

CHARACTER OF THE LIQUID WASTES FROM THE RADIUM PROCESS

WASTE	VOLUME PER KILOGRAM OF K-65 (ML.)	HNO ₃ (N)	PER CENT FOUND							ACTIVITY CTS./MIN./ML.	
			NaNO ₃	Na ₂ CO ₃	ALKALI ACETATE	NaOH	Pb	SiO ₂	SO ₄	BETA + ALPHA	ALPHA
SODIUM HYDROXIDE LEACH	7,200			0.0		15.	4.1	5.2	1.46	16,032	390
SODIUM HYDROXIDE-SODIUM CARBONATE FILTRATE	3,300			12.		15.	1.25	13.2	2.92	55,784	2,324
SODIUM CARBONATE FILTRATE	2,200			20.		0.	0.06	0.9	0.42	329	31
BARIUM-RADIUM SULFATE FILTRATE	5,000	0.4								66,945	21,078
CHROMATE CRYSTALLIZATION FILTRATE	10,700		2.1	PH 8-9	1.07					25	8

TABLE II
SECOND STEP SCAVENGING WITH METALLIC SULFIDES TESTS
ON 100 MILLILITERS OF FIRST STEP FILTRATE

TEST NO.	METALLIC SULFIDE PRECIPITATED	METAL ADDED (MG.)	SODIUM SULFIDE (MG.)	COUNTS/MINUTE/MILLILITER ALPHA + BETA	ALPHA
1	ZINC	13	100	51	13
2	LEAD	41	100	158	14
3	BISMUTH	42	100	42	16
4	TIN (II)	24	100	229	15
5	IRON (II)	7	14	7	0
6	IRON (II)	7	14	21	2
7	IRON (II)	71	100	14	2
8	IRON (II)	35	50	7	3
9	IRON (II)	21	30	9	1
10	IRON (II)	7	10	0	0
11	IRON (II)	71	100	5	4
12	IRON (II)	7	10	9	5
TESTS 1 TO 6 ORIGINAL COUNT				167	68
TESTS 7 TO 12 ORIGINAL COUNT				102	50

TABLE III
DECONTAMINATION ON 1-LITER BATCHES OF MIXED WASTE

TEST No.	FILTER CAKE		FIRST STEP		SECOND STEP	
	(GRAMS) WET	(GRAMS) DRY-50°C.	(CTS./MIN./ML.) ALPHA + BETA	(CTS./MIN./ML.) ALPHA	(CTS./MIN./ML.) ALPHA + BETA	(CTS./MIN./ML.) ALPHA
1	850	299	84	10	74	6
2	225	121	102	50	7	0
3	730	410	13	6	6	0
4	646	205	82	14	11	4
5	426	110	64	10	22	9
6	486	110	29	14	7	4
7	308	78	23	5	4	4
8	350	82	12	2	5	5
9	256	69	31	13	28	0
10	211	60	69	9	11	9
11	278	78	14	5	1	4

TESTS 1 TO 3 BY ADDING ALKALI SOLUTION TO THE ACIDIFIED SOLUTION.

TESTS 4 TO 5 BY NEUTRALIZATION IN A SEPARATE BEAKER, HOLDING THE PH AT 8.

TESTS 6 TO 11 BY ADDING ACIDIFIED SOLUTION TO THE ALKALI SOLUTION.

Problem Title - Recovery of Nitric Acid from the Radium Process

Report By - R. W. Moshier

Work Done By - J. S. Kochendorfer

INTRODUCTION

One of the by-products of the radium process is a slightly diluted nitric acid containing chromic anhydride, small amounts of radium, and radium-decay products. This nitric acid is obtained in converting the radium-barium chromate, formed in the fractional precipitation, to nitrates.¹ Both the nitric acid and the chromic anhydride are of sufficient value to consider recovering and recycling in the process. On the other hand, if considered as a waste, its disposal presents difficulties not only because of its being a concentrated acid but also because it contains radioactive materials.

This recovery problem was undertaken to alleviate the waste disposal problem and to reduce the cost of the radium process.

DETAILED REPORT

Reagent grade nitric acid, constant-boiling, 70 per cent acid, has a specific gravity of 1.402 and a normality of 15.7. The by-product nitric acid from the radium process has a specific gravity of 1.389 and a normality of 14.3 or about 65 per cent acid.

Simple distillation does not concentrate the acid, but it does free it from non-volatile impurities, especially the chromium, and also from the radioactive materials which are present in the following amounts:

RADIOACTIVITY	COUNTS/MINUTE/MILLILITER	
	(ALPHA + BETA)	(ALPHA)
IN THE ORIGINAL	18,440	6,580
IN THE DISTILLATE (0.05-ML. MOUNT)	20	0 TO 80

In order to obtain sufficiently strong acid for reuse in the radium process, two alternatives are open.

1. The distilled acid can be fortified with 100 per cent acid. For fortifying purposes 100 per cent acid can be obtained from our distilled acid by a commercial dehydration process such as distillation from sulfuric acid dehydrating agent.
2. The acid can be fractionally distilled to obtain part of it at the desired concentration.

A fractional distillation of the by-product nitric acid was made with the apparatus illustrated in Figure 2. The assembly joined entirely by nonlubricated 24/40 standard taper joints consisted of a 500-milliliter round-bottom-flask still pot heated by an electric hot plate; an improved West-type condenser with indentations and vertically mounted for reflux service with no cooling or heating; a simple still head containing a thermometer well but

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uncooled and with no means of controlling the reflux ratio; and a Liebig condenser with adapter. The reflux ratio controlled only by the pot heater was about four to one of the drops returning from the tip of the condenser to the drops into the receiver.

The distillation characteristics are shown in Figure 1. It can be seen that less than half of the acid of the desired strength was obtained with the apparatus. However, it should be possible to obtain a suitable concentration with better fractionation.

Since nearly all the radioactivity remains with the small quantity of still residue, and this residue is essentially chromic anhydride, it is desirable to recover it for re-cycling in the radium process. Since the simpler distillation was conducted to give a maximum yield of nitric acid, the still pot was heated to a temperature which decomposed the anhydride to oxygen and green chromic oxide. If still residues are accumulated before the decomposition temperature is reached, most of the residual nitric acid can be removed from it as useful acid by controlled evaporation. By this means the chromic anhydride from 600 milliliters of by-product acid was recovered as a very thick syrup satisfactory for re-cycling. Analysis shows a negligible quantity of lower valent chromium present in this syrup.

REFERENCE

1. Salutsky, M. L., and Stites, J. G., this Volume, p. 18.

Problem Title -- Chemical Engineering Development of the Radium Process

Report By -- H. L. Rawlings

Work Done By -- W. T. Brown, P. M. Engle, and H. L. Rawlings

INTRODUCTION

Because laboratory research on the radium process has entered its final stages, more intensive engineering development of the process has been resumed. The scope of the engineering work has been rearranged to fall into three phases:

1. Preparation of a process flow sheet illustrating the projection of the laboratory scale process to a scale permitting the production of 500 grams of radium in 2 years. This level of production is defined as being "full-scale."
2. Preparation of a preliminary cost estimate for the full-scale installation.
3. Preparation of a cost estimate of a pilot plant to furnish the engineering data necessary to design the full-scale installation.

The research chemists have investigated several methods of separating radium from a crude radium-barium mixture. Four methods showed the greatest promise of being economically advantageous:

1. Fractional precipitation of radium-barium chromates from a dilute nitric acid solution at room temperature by the hydrolysis of sodium cyanate to neutralize the acid.¹
2. Fractional precipitation of radium-barium chromates from a nitric acid solution at 90°C. by the hydrolysis of urea to neutralize the acid.²
3. Fractional precipitation of radium-barium chromates from a dilute nitric acid solution at 0°C. by the hydrolysis of sodium cyanate to neutralize the acid.
4. Fractional crystallization of radium-barium bromides from a hydrobromic acid solution.³

As a necessary approach to phase 1 of the problem, a series of cost estimates were made to evaluate the above methods in terms of full-scale production.

The calculation of heat and material balances, time cycles, and radiation levels for the entire process of extracting radium from K-65 residues was of a preliminary nature.

DETAILED REPORT

As a basis for calculations prior to the preparation of a process flow sheet, a 265-day work year was assumed, at three 8-hour shifts per day. The process was visualized as strict scale-up of the laboratory process; i.e., a batch-type process for the residue treatment and waste disposal portions, and a batch-type process with constant recycle for the fractional precipitation portion. Rough calculation of time cycles indicated that the longest hold-up time in the process (the carbonation of radium-barium sulfates) was of the order of 6 hours. In consideration of the inaccuracies introduced

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by various assumptions, the batch time was set at 8 hours. Therefore, the equipment has been sized to produce one 320-milligram batch of radium per shift.

Comparative cost estimates of the four methods of radium-barium separation were made. These estimates were based upon the costs of installed equipment, piping, instruments, reagents, and power consumption for 2 years. Since the estimates were intended for comparison, factors that were assumed to be about equal were not estimated; i.e., labor, maintenance, shielding, and power consumption of agitators and pumps. The installed equipment costs were estimated with the cost data assembled by Chilton.⁴ The reagent costs were based upon experimental data⁶ and current chemical prices.⁵ The initial portion of Table 1 summarized the results of these estimates. The costs in this portion of the table were for chromate precipitation processes involving solutions of one per cent barium concentration. No provision was made for reclaiming the concentrated nitric acid used to extract the radium-barium chromates to obtain the soluble nitrates.¹ Stainless steel equipment was projected. The cost of the cyanate at room temperature method was based upon a 30 per cent faster time cycle to show the advantage accorded this process because of the elimination of heat-up or cooling time and the faster rate of neutralizing the nitric acid.

An analysis of the cost estimates shown in this portion of Table I for the chromate precipitation methods revealed:

1. In general, the costs of the methods were controlled by the barium concentration of the solutions used.
2. In particular, the controlling costs were those of the sodium cyanate used (at \$1.25 per pound), the wasted nitric acid, and the stainless steel reactor tanks.

The possibility of savings in the areas indicated in the above analysis was investigated. Further studies by the research chemists showed that the barium concentrations could readily be increased to 3 per cent. A poll of chemical manufacturers showed that sodium cyanate could be bought for \$0.90 per pound in 1-ton lots. An investigation of the recovery of the wasted nitric acid by distillation showed that at least 75 per cent of this waste could be recovered as 70 per cent acid. A cost estimate was made of an installation to effect this recovery in a full-scale plant. The estimate indicated that the cost of the nitric acid could be reduced by over 50 per cent. A test of Koroseal in 5 per cent nitric acid indicated that Koroseal lined tanks could be substituted for stainless steel reactors for room temperature reactions.

Application of the above savings to a method using cyanate at room temperature on the radium-rich side and urea on the barium-rich side showed a reduction in cost to about \$900.00 per gram of radium produced. This cost is listed in Table I for "Combined Cyanate at 25°-Urea, Improved." Comparative estimates of the other chromate precipitation methods at varied barium concentrations indicated that the combined cyanate at 25°-urea method would remain the cheapest at concentrations less than saturated.

The cost listed in Table I for the fractional crystallization method does not include possible savings resulting from the recovery of the hydrobromic acid. Inclusion of these savings would apparently restore economic advantage to this method. However, the assumptions of enrichment factor, mechanics, and constant recycle type of process made in arriving at this estimate have not been experimentally verified. Therefore, the present plan is that the combined cyanate-urea method will be included in the full-scale plant cost estimate.

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Additional cost estimation indicated that the cost of reagents of the entire process, exclusive of the radium-barium separation portion, would be of the order of \$600.00 per gram of radium produced. Calculation of radiation levels indicated that the radium-rich reactors in the radium-barium separation process will have to be shielded to a maximum of 4.5 half thicknesses of shield to attain the prescribed gamma tolerance at a distance of 1 meter from the vessels. The heat and material balances necessary to size the equipment in the residue treatment portion of the process were completed. A process flow sheet for this portion is about 25 per cent complete.

SUMMARY

Cost estimates were prepared to evaluate various methods of separating radium from barium by precipitation of the radium-barium chromate and by fractional crystallization. A combined cyanate-at-room-temperature and urea method was found to be the most economical of the chromate precipitation methods based upon equipment, piping, instrumentation, and reagent and power consumption for 2 years. The cost of this method for separating radium from barium was found to be of the order of \$900.00 per gram of radium at a production level of 500 grams in 2 years. Although the fractional crystallization method was shown to have a possible economic advantage, use of the combined cyanate and urea fractional precipitation method was assumed for use in a full-scale plant because experimental verification of the assumptions made in estimating the cost of the fractional crystallization method are not complete.

Calculation of radiation levels, heat and material balances, and reagent consumption of the entire radium process has been completed. Work has been initiated on a process flow sheet for this process.

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TABLE I

COMPARATIVE COST OF METHODS FOR THE SEPARATION
OF RADIUM FROM BARIUM-RADIUM MIXTURES*

PROCESS	COST				TOTAL
	EQUIPMENT	REAGENTS	STEAM	REFRIGERATION	
CYANATE AT 0°	\$1,150	\$2,257	\$	\$29	\$3,740
CYANATE AT 25°	526	2,991			3,520
UREA	1,260	2,282	39		3,580
COMBINED CYANATE AT 25°-UREA	995	2,073	28		3,100
FRACTIONAL CRYSTALLIZATION	256	658	4		920
COMBINED CYANATE AT 25°-UREA IMPROVED	276	592	9		880

* ALL COSTS ARE PER GRAM OF RADIUM PRODUCED FROM A 200,000 TO 1 BARIUM-RADIUM MIXTURE AT A PRODUCTION LEVEL OF 500 GRAMS OF RADIUM IN 2 YEARS OF 265 OPERATING DAYS PER YEAR.

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