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Laboratory Director

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Problem Title - The Separation of Actinium from Radium by Ion-Exchange
Report By - P. M. Engle
Work Done By - P. M. Engle

INTRODUCTION

As a preliminary phase of the actinium separation project, it was decided to investigate the ion-exchange method for the separation of lanthanum and barium, because of the similarity in the properties of these elements with those of actinium and radium respectively. It was felt that this work would yield information that would apply to the separation of the latter elements. An addition objective was to gain familiarity with ion exchange techniques in general. The ease with which ion exchange methods lend themselves to remote controlled operations makes them particularly attractive as a means of separating actinium and radium.

The general method employed was that developed at Clinton Laboratory during the early years of the Manhattan Project.¹ This method involves adsorbing completely the ions to be separated and then eluting them selectively with an ammonium citrate solution of predetermined acidity.

Since lanthanum and barium show a marked difference in their tendency to be complexed and thus eluted by citrate solutions, it was found that complete separations could be made in relatively short ion-exchange columns. Time did not permit the investigation of the optimum value for all the variable affecting this separation.

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DETAILED REPORT

Analytical

The analytical procedures used to determine the barium and lanthanum concentrations in the various solutions resulting from this work were compromises between speed and precision. Because of the large number of fractions taken from a column elution, a rapid method of analysis is essential.

The method employed for barium was the determination in a colorimeter of the turbidity resulting from a precipitation with sulfuric acid. The turbidity was compared with a plot of the turbidity obtained with known concentrations of barium. Ten drops of twelve normal sulfuric acid were added to ten milliliters of the sample in a fifty milliliter beaker on a magnetic agitator. A 25-millimeter colorimeter cell was rinsed twice with this solution before filling. It was necessary to clean the colorimeter cell after each test with concentrated sulfuric acid to remove traces of the barium sulfate precipitate. The minimum per cent transmission was determined in a Lumetron Model 402E colorimeter with a 430-millimicron filter in place. The plot of per cent transmission versus barium content, obtained with standard barium solutions, is shown in Figure 1. Samples were accurately diluted to the range between 10^{-4} and 10^{-3} normal before analyzing.

This procedure is subject to rather large errors due principally to variations in the particle size of the barium sulfate formed and extreme care must be observed in order to reproduce results. The presence of citrates reduces the rate at which the precipitate is formed but does not appear to affect the final turbidity of the solution.

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Volumetric determinations of lanthanum were made by precipitating lanthanum oxalate and then titrating the washed precipitate against standard potassium permanganate solution in the presence of sulfuric acid. The precipitate was separated and washed by centrifuging and losses were possible during this operation. The presence of citrates interferes with the oxalate precipitation above about pH 3, so the solutions were first acidified. The lowest concentration of lanthanum at which essentially quantitative precipitation may be obtained is about 10^{-3} normal.

The specific procedure was to pipette five or ten milliliters of sample into a fifteen-milliliter centrifuge tube. To this sample was added ten drops of four normal hydrochloric acid and ten drops of saturated oxalic acid solution. After stirring, the tube was centrifuged for five minutes, the supernatant was decanted, and the precipitate of lanthanum oxalate was washed twice by mixing with five milliliters of water, centrifuged, and decanted. To the final precipitate was added three drops of twelve normal sulfuric acid and one milliliter of water. This partially dissolves the precipitate and when heated it may readily be titrated against standard potassium permanganate solution. Typical results obtained with known samples of lanthanum are shown in Table I.

Equilibrium Studies

Because column operations inherently consume large amounts of time for the many analyses required, as much information as possible was obtained by equilibrium studies. The procedure used was to place the cation exchange resin and solution in a large stoppered test tube and agitate by tumbling for several hours.

Most of the equilibrium tests were made during the initial phases of this work in order to ascertain the optimum pH at which to elute selectively the lanthanum from the barium. The procedure ordinarily used was to adsorb 0.25 milliequivalents of the barium or lanthanum or mixture of the two on five grams of the resin. The resin was then eluted with five per cent citric acid solution, containing one tenth per cent phenol as a preservative, whose pH had been carefully adjusted to a predetermined value by the addition of concentrated ammonium hydroxide. The results of these runs in terms of eluted ion concentration versus pH are shown in Figure 3.

The acid form of the resin was used initially in these tests. This form has the disadvantage that the excess acid resin, remaining after the adsorption, exchanges with the ammonium ions during the elution and materially reduces the effective pH. Since this objection also applies to column operations it was decided to try the ammonium form of the resin. This form does not alter the pH and appears to be ideal for any work in which an ammonium salt is to be used as the eluent.

Column Experiments

The first column constructed consisted of a 60-inch length of one inch (inside diameter) Pyrex pipe. This column was filled to a height of 130 centimeters with 40-mesh Amberlite IR-120 cation exchange resin in the sodium form. It was used for some preliminary work in which an attempt was made to determine the strength of hydrochloric acid necessary to remove Ba^{++} from the column. This work was discontinued, and when regenerating this resin in the acid form it was found to contain an appreciable amount

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of iron contamination. At this time a quantity of Nalcite HCR (Dowex 50) resin became available and has been employed for all subsequent work. This resin is similar to IR-120 in that both are based on sulfonic acid substituted styrene polymers. This general type of resin was chosen because its exchange capacity is greater, and it is reported to be more chemically inert than the other common types. The Nalcite HCR does not contain iron and is also more uniform in appearance than the IR-120.

In order to reduce the volume necessary for a column run, the second column constructed was somewhat smaller. A diagram of the simple apparatus used in this work is shown in Figure 2. This column was filled with 40-mesh Nalcite HCR resin to a depth of 79 centimeters and was employed to obtain all the column data reported here. The capacity of this column calculated from the manufacturer's data is 450 milliequivalents.

Eight column runs were started, but the first three were not completed for various reasons. The fourth run gave a lanthanum fraction eluted at pH 3.7 which was contaminated with about one per cent barium. In attempting to remove the barium which remained after all the lanthanum had been removed, it was found that the ten per cent ammonium chloride solution used for this purpose removed the barium too slowly. Making the solution basic with ammonium hydroxide, and increasing its concentration to 15 per cent ammonium chloride increased the regeneration rate slightly. When, however, 15 per cent ammonium citrate solution containing 10 per cent by volume of concentrated ammonium hydroxide was employed as a regenerant, the rate was increased by a factor of 20. This solution was used for all subsequent regenerations.

For the fifth run elution was started at a pH of 3.4 in order to avoid the complexing of any barium. However, at this pH neither Ba^{++} nor La^{+++} was eluted, and the pH was increased to 3.9. Lanthanum was then eluted rapidly entirely free from barium, and the Ba^{++} did not commence to be removed until the flow of regenerant was started. Recovery of both ions was essentially complete.

The sixth column run was the last run made using approximately equivalent quantities of barium and lanthanum and the complete results obtained are included here. This run was made to confirm the favorable results of run number five and to determine the effect of increasing the eluent pH slightly. The feed-solution volume was 300 milliliters containing 9.8 milliequivalents of barium chloride and 10.4 milliequivalents of lanthanum chloride. The feed rate was 1.3 milliliters per minute per square centimeter and no lanthanum or barium was found in the effluent. The feed was followed by 200 milliliters of water rinse at the same rate. The eluent used was five per cent citric acid adjusted to pH 4.1 with ammonium hydroxide. The regenerant employed was basic 15 per cent ammonium citrate and was started after 725 milliliters of eluent had been used. After 400 milliliters of regenerant were through a water rinse was begun.

The results of qualitative tests made during the elution and regeneration are listed in Table II.

Quantitative analysis of the effluent fractions collected gave the results shown in Table III. Figure 4 is a plot of fraction analyses versus volume through the column. The smooth curves are approximations of the true elution rates.

In order to duplicate more closely the conditions that would prevail in an actinium-radium separation, the seventh and eighth column runs were made using lanthanum and barium in the ratio of one to 330. The actual amounts adsorbed were 0.4 milliequivalents of lanthanum and 133 milliequivalents of barium. This amount of material employed about 30 per cent of the total capacity of the resin.

The pH of the eluent at the start of run seven was reduced to 3.8 to avoid elution of any of the large amount of barium present. As the elution progressed without obtaining positive qualitative tests for either lanthanum or barium in the eluate, the pH of the eluent was increased at approximately 350-milliliter intervals to 4.1, 4.35, 4.7, and finally 5.0. Still no lanthanum and, more significantly, no barium tests were obtained. By spectrographic and improved precipitation methods all the lanthanum was later located in the original pH 3.8 eluate.

The barium was removed as before by the regeneration, with the concentration of barium in the effluent reaching a maximum of over 0.5 normal. While still eluting at a pH of 5.0 a white deposit was noticed forming near the center of the column. This deposit was dissolved out by the more basic regeneration, but a similar appearing deposit formed on standing in the most concentrated of the fractions obtained. This precipitate was readily soluble in hydrochloric acid and is believed to be barium hydroxide. Its formation did not adversely affect the separation in any way.

The eighth run was a repetition of the seventh that was made in order to improve the precision of the lanthanum elution and to confirm the previous

results. The feed solution (one liter) was added at the rate of 0.8 milliliters per minute per square centimeter, and was followed by 100 milliliters of water at the same rate. Barium and lanthanum tests on the feed effluent were negative. The eluent used was five per cent citric acid solution raised to pH 4.1 with ammonium hydroxide and was added at the rate of one milliliter per minute per square centimeter.

The analyses of the elution and regeneration fractions that were collected are listed in Table IV.

Figure 5 is a plot of fraction analyses versus volume through the column. Note that the lanthanum curve has been magnified by a factor of 10.

Discussion of Data

The data obtained from the equilibrium studies as shown in Figure 3 indicate that with a five per cent citric acid eluent in the pH range above 3.0, a pronounced difference exists in the tendency of these elements to be eluted. The ratio of elution of lanthanum to barium at equilibrium under the conditions employed is about 25 to 1, and this factor is relatively constant over the range of pH for which data were obtained. With this equilibrium enrichment the length of column needed for a complete separation could not be great. The concentrations of the ions shown by these curves should not be construed to be the maxima for a given pH, as these concentrations were limited by the small amount of material originally deposited on the resin.

As shown in Figure 3 a few tests were made by adding the Ba^{++} and La^{+++} directly to the eluent and bringing this to equilibrium with the resin.

The data obtained does not differ appreciably from that produced when the ions are first adsorbed completely on the resin. This fact suggests that in certain column operations it would be possible to separate materials by mixing them with the proper eluent and passing this solution through the column. This procedure has the advantage that all of the more easily eluted ions need not be deposited on the column. For example, in the case of the barium-radium separation a smaller column would be required because the majority of the barium present should pass through the column with the eluent.

The column runs confirmed the ease with which these elements may be separated. In all of the last four runs quantitative separations were attained to the extent that cross-contamination could not be detected by the analytical procedures employed. The minimum concentrations detectable were below 10^{-4} normal for barium and less than 10^{-3} normal for lanthanum.

An interesting phenomenon, which can be explained by the theoretical analysis of Mayer and Tompkins,² is the wide separation of the lanthanum and barium fractions at eluent pH values at which it would seem both ions should elute successively. For example, in the seventh column run 1700 milliliters of eluent were used without any barium being eluted. In the first 600 milliliters the pH of this eluent was increased in steps from 3.8 to 5.0 as previously described, and the lanthanum was removed. The failure of barium to be eluted at pH 5.0 at a time when no lanthanum was being removed appears to contradict the equilibrium data shown in Figure 3. However, calculating the equilibrium constant, C^2 , at pH 5.0 for barium from the equilibrium data gives a value of 28.4. Since C is equal to the amount of eluent in column

volumes required to reach the maximum eluate concentration, the volume required is 4.27 liters (the column volume used here is the liquid volume only and is assumed to be one-half of the total). The exact concentration of barium in the eluate when elution was stopped cannot readily be calculated because of the changes made in pH, but it would doubtless not have increased to the minimum detectable amount.

The presence of barium contamination in the lanthanum fractions of the fourth column run can probably be explained by the fact that, accidentally, only a partial regeneration preceded this run. Thus, the barium from the third run was no doubt distributed through the lower portion of the column, from where a small portion was eluted during the initial portion of the fourth run.

As previously mentioned, time did not permit the determination of the optimum and limiting values of such column variables as height, flow rate, temperature, and fineness of division of the resin employed. Other types of resin and different eluents might conceivably have advantages, although the ones used here seemed highly satisfactory. The maximum eluent pH appears to be at least 5.0, although it is doubtful whether such a value would appreciably increase the concentration of the lanthanum fractions when only very small amounts of this element are originally present.

Conclusions

The principal conclusion reached is, of course, that lanthanum and barium may be easily separated quantitatively in one cycle by the methods described above, even if the lanthanum present is only 0.3 per cent. The

column height required is less than 80 centimeter of 40 mesh Nalcite HCR resin and the close adjustment of eluent pH is not highly critical. No further work with barium and lanthanum is contemplated at the present time.

Whether this method of separation may be extended to the entire actinium-radium separation is difficult to predict. These elements exhibit great similarity in their chemical properties to lanthanum and barium, so that the difficulties encountered should be those associated with the radioactivity of actinium and radium. Since the control of column work is very simple, remote operations would present no great difficulty. The greatest threat to this process is the detrimental effect of radiation on the ion exchange resin employed. If the intense alpha, beta, and gamma radiation associated with actinium, radium, and their decay products should decompose appreciable quantities of the resin as certain data indicate,³ the use of ion exchange for the entire separation would not be practical. The decomposition of the sulfonic acid group in Nalcite HCR resin might yield sulfates which would precipitate the radium within the column. Such a precipitate would be difficult to recover under the remote control conditions imposed.

REFERENCES

1. Tompkins, E. R., Khym, J. X., and Cohn, W. E., JACS, 69, 2769-2881, (1947).
2. Mayer, S. W. and Tompkins, E. R., JACS, 69, 2866-2874, (1947).
3. Hagemann, F. T., Argonne National Laboratory, Verbal Communication.

Table IANALYSES WITH KNOWN LANTHANUM SAMPLES

<u>Sample Size ml.</u>	<u>La⁺⁺⁺ Concentrated Normal</u>	<u>Ml. 0.00985 Normal KMnO₄</u>	<u>Experimental La⁺⁺⁺ Concentrated Normal</u>	<u>Per Cent Recovery</u>
10	0.001	0.90	0.00090	88
10	0.001	1.20	0.00118	118
10	0.002	1.59	0.00157	79.5
10	0.005	4.90	0.00481	96.4

Table IIRESULTS OF QUALITATIVE TESTS ON THE SIXTH COLUMN RUN

<u>Volume Through Column in ml.</u>	<u>Effluent pH</u>	<u>La⁺⁺⁺ Test</u>	<u>Ba⁺⁺ Test</u>
100	5.8*	Negative	Negative
220	4.1	Strong	Negative
300	3.95	Strong	Negative
400	3.95	Strong	Negative
500	4.05	Medium	Negative
600	4.1	Light	Negative
700	4.1	Negative	Negative
850	4.6	Negative	Light
900	5.85	Negative	Strong
950	7.03	Negative	Very Strong
1050	9.65	Negative	Medium
1125	9.65	Negative	Light
1300	9.7	Negative	Negative

* The effluent at this point is still essentially rinse water.

Table IIIRESULTS OF QUANTITATIVE ANALYSES ON THE SIXTH COLUMN RUN

Fraction (ml.)	<u>Lanthanum</u>		<u>Barium</u>	
	Normality $\times 10^3$	Per Cent of Original La^{+++}	Normality $\times 10^3$	Per Cent of Original Ba^{++}
0-100	0	0	0	0
100-200	11.0	10.6	0	0
200-300	23.9	23.1	0	0
300-500	26.6	51.2	0	0
500-600	5.9	5.8	0	0
600-700	0.2	0.2	0	0
700-850	0	0	0	0
850-940	0	0	50	47.8
940-1050	0	0	44	48.8
1050-1125	0	0	7.5	6.1
1125-1300	0	0	0.5	1.0
1300-1500	0	0	0.1	0.2
Total		90.9		103.9

Table IVRESULTS OF QUANTITATIVE ANALYSES ON THE EIGHTH COLUMN RUN

<u>Fraction (ml.)</u>	<u>Lanthanum</u>		<u>Barium</u>	
	<u>Normality x 10³</u>	<u>Per Cent of Original La⁺⁺⁺</u>	<u>Normality x 10³</u>	<u>Per Cent of Original Ba⁺⁺</u>
0-150	0	0	0	0
150-250	0.98	24.5	0	0
250-350	1.72	42.0	0	0
350-450	0.79	19.7	0	0
450-650	0	0	0.56	0.075
650-850	0	0	279.	41.9
850-1050	0	0	230.	34.6
1050-1250	0	0	102.5	15.3
1250-1450	0	0	22.0	3.3
1450-1550	0	0	2.0	0.15
1550-1650	0	0	0.46	0.037
1650-1750	0	0	0.01	0.0001
Total		86.2		95.4

Problem Title - Volatilization of Lanthanum Iodide
Report By - J. G. Stites
Work Done By - J. G. Stites

INTRODUCTION

The rare earth metals and probably actinium are very difficult to volatilize because of their high chemical activity and extremely high boiling points. Halides of lanthanum have been synthesized and attempts made to volatilize these compounds. Of the fluoride, chloride, bromide, and iodide prepared, the only one which was volatilized with any degree of ease was lanthanum iodide.

DETAILED REPORT

Anhydrous lanthanum iodide was synthesized by heating lanthanum oxide with an excess of ammonium iodide for four hours at 300°, four hours at 500°, and four hours at 600°, while passing dry nitrogen slowly through the system.

A small sample of the lanthanum iodide was placed in a quartz tube and evacuated to a pressure of 1×10^{-5} millimeters. A small amount of ammonium iodide was removed at this reduced pressure by heating with a Bunsen flame. An oxygen-gas flame was used to volatilize the lanthanum iodide. All but a small quantity of the lanthanum iodide volatilized and collected on the cool walls of the quartz tube. A temperature of approximately 1000° was necessary for the volatilization.

The volatilization of the lanthanum iodide was verified by analyzing the volatilized material both for rare earth and iodide.

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In an oxygen atmosphere the volatilization of lanthanum iodide was not possible because of the formation of the refractory lanthanum oxide.

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Problem Title - Analytical Counting of Actinium
Report By - P. E. Ohmart
Work Done By - I. B. Grafton, P. E. Ohmart, and A. J. Rogers

INTRODUCTION

The fact that actinium decays through eight daughter elements one of which is a gas tremendously complicates the problem of determining quantities of actinium by counting. In order to understand the problem better a study of the amounts of daughter elements present after any given time and of the number of disintegrations per minute resulting from each of the daughter elements is being made for both the 13.5 and 21.7 year half life values.

DETAILED REPORT

Using expressions developed by Chaplin, DeBrosse, and Eyles¹ the quantities present of actinium and each of the daughter elements were worked out for the first one hundred days of the life of the actinium of 13.5 years half-life. These are shown in curve form in Figure 1. The quantity of radiation given off by each one of these elements is shown in Figure 2.

These curves indicate that quantities of actinium can possibly be analytically determined by counting by three means:

1. The alpha particles emitted from the sample could be counted at two definite time intervals and the change of count could be used as a basis of computations to determine the quantity of actinium in the sample.

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2. The beta radiation alone could be counted by using a circuit so arranged that pulses exceeding a given amplitude would not count. If this system were used corrective data obtained from the rate of growth of beta emission curves could be applied to give fairly accurate results.

3. A system of electrostatic and electromagnetic focusing and electrostatic acceleration which would present low geometry to alpha particles and high geometry to beta particles could possibly be used to give the same type of results as those of the second method except that the resolution loss would be much lower.

These same computations are now being carried out based on the 21.7 half-life value for actinium.

REFERENCE

1. Chaplin, R. L., DeBrosse, K., and Eyles, T. E., Decay of Pure Radium-Beryllium Neutron Sources, Quarterly Report for General Research, MLM-379-2 (July - August - September, 1949).

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