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A-85-012

REF: LAB-CMR-10-26

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PROJECT AUTHORIZATION NO. CMR-10-10

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RaLa PROCESS RESEARCH

Date
November, 1948

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PART I

RALA PROCESS RESEARCH
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SUMMARY:

In the preparation of RaLa sources several one-step processes have been studied, since their simplicity would give an easier engineering problem. Of those tried, only one still shows promise -- the precipitation of LaF_3 in the presence of sufficient acidity to hold BaF_2 in solution. Studies of $HF-HNO_3$ and $HF-HClO_4$ systems are reported.

One of the most satisfactory separations of lanthanum from barium remains the precipitation of the hydroxide. This process leaves nothing to be desired with pure solutions, but the addition of impurities causes the occlusion of Ba in the precipitate. Studies of double precipitation are reported here, showing very promising results.

Engineering work has been begun for tooling the fuming nitric acid process, since it has remained the most satisfactory from the standpoint of yield and tolerance of impurities. (But it is the most difficult to engineer for remote control.) Extensive work is reported on the determination of optimum acidities, dilutions, and volumes to be used at various points of this process.

Other radiochemistry research is reported on equilibrium sources, cobalt sources, and evaluation of present process.

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A. ONE-STEP PROCESSES

These processes consist mainly of precipitating La from a La-Ba solution containing enough fluoride ion for complete La removal and at the same time sufficient acidity to prevent the formation of insoluble BaF_2.

Three systems were tried, namely, HF-HNO_3, HF-$HClO_4$, HF-HCl. In the latter system an insoluble compound (probably $BaCl_2$ BaF_2) was formed which rendered this process useless. However, the first two systems appeared promising and were subsequently studied in detail.

1. HF-HNO_3 System

One of the chief objections to this process is that one is confined to narrow limits of acid concentration. A minimum of acid is necessary to dissolve BaF_2 and yet an excess of acid causes the formation of $Ba(NO_3)_2$ $2H_2O$. Nevertheless the process could still be satisfactory within these limits.

To the equilibrium solution were added the following reagents respectively: 5 mg. La, 60 mg. Ba, HNO_3 and HF. The final solution was 1.9 N in HNO_3 and 4 N in HF. After agitation the solution, 15 cc. total, was centrifuged. The La yield was 84% and 1.8% of the original Ba was found in with the La.

2. HF-$HClO_4$ System

Since one does not encounter a precipitate of barium with perchloric acid, there is no upper limit in using this reagent.

To the equilibrium solution were added the following reagents respectively: 5 mg. La, 80 mg. Ba, $HClO_4$ and HF. The La

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yield here was 97%, and the per cent Ba carriage was 4.0.

It is concluded that in these one-step processes, as carried out, the Ba carriage is too high to be satisfactory for the preparation of La sources.

B. DOUBLE HYDROXIDE PRECIPITATION

A re-study of precipitating La as the hydroxide from solutions containing typical impurities has been made. Precipitations were made with NH_4OH and KOH. In all cases the La recovery was virtually complete.

It has been shown that in the absence of impurities one precipitation gives a product containing less than 0.1% Ba.

To an equilibrium solution containing 5 mg. La, 200 mg. Ba and typical impurities was added enough KOH and NH_4OH to render the solutions 1 N in the respective bases. After agitating and centrifuging, the $La(OH)_3$ was dissolved in a minimum of dilute HCl and reprecipitated with 1 N KOH and NH_4OH. The following results were obtained:

Precipitating Reagent	Per Cent Ba Carriage
KOH	0.7, 0.2
NH_4OH	4.7, 2.2

It is concluded that even with a double precipitation, considerable Ba is found in the La product. This stresses the need for obtaining shipments of Ba relatively free of interfering contaminants.

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C. EXPERIMENTAL WORK ON PREPARATION OF EQUILIBRIUM SOURCES

Occasional demands for equilibrium sources of high intensity are met by precipitating the La + Ba as the molybdates. This is a time-consuming operation since the fine precipitate is very difficult to filter.

The following studies were made in the search for a better precipitant:

To a solution containing 10 mg. La, 100 mg. Ba and equilibrium solution was added 2 cc. of saturated precipitating reagents. The precipitates formed were then centrifuged and the supernatant decanted; the precipitates were dissolved and counted.

Reagent	Vol. of ppt. in cc.	Per Cent Yield
Potassium fluoride	0.21	99.6
Sodium oxalate(1)	0.41	97.1
Sodium sulfate(2)	0.24	99.9
Sodium carbonate	0.47	99.7
Sodium phosphate	0.60	99.7
Sodium molybdate	0.20	99.9

(1) Complete Ba precipitation was not obtained.

(2) The resultant precipitate is very insoluble which might make decontamination of equipment more difficult.

Studies with silicofluoride are in progress for comparison with the results above.

The need for a new precipitating agent was shown clearly by the following experiment: Solutions containing 800 mg. Ba and 20 mg. La in 60 cc. were treated with sodium molybdate in one case

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and with magnesium silicofluoride in the other.

Greater than five hours was required for filtering the molybdate precipitate through a spongy platinum pad; whereas only 25 minutes was required for the silicofluoride to filter.

D. EXPERIMENTAL STUDIES IN PRECIPITATING COBALT

This work was carried out to find a method for preparing a 100 millicurie source of Co^{60} for GMX-5. The solution available contains 12 mg. Co and 100 millicuries of radio cobalt in about 12 cc. of 0.1 N HCl.

Since Co^{60} has a 5.3 year half life, the preparation of this source will be carried out at Bayo Canyon where a slight contamination from this material will not cause serious interference.

A series of thirteen precipitations was made based on methods found in analytical texts. In each case 12 mg. of inert Co was used; the volume of precipitate after centrifuging was noted. Only two reagents gave precipitates that were easily centrifuged and dense enough to be acceptable. The cobalt will be precipitated as the hydroxide. This work will be completed as soon as the source holder has been prepared.

E. EXPERIMENTAL WORK ON TENTATIVE PROCESS

The tentative process submitted to the design group consists of separating the Ba and La by fuming HNO_3. In this method the La stays in the supernatant and is subsequently precipitated by HF. Several problems have arisen concerning optimum volumes for processing. In addition problems of corrosion exist when two such

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reagents are used. This work was therefore designed to ascertain conditions necessary for mitigating these problems.

1. <u>Precipitation of Ba</u>

The purpose of this experiment was to determine the minimum concentration of HNO_3 necessary to precipitate completely 1 g. of Ba. All operations were carried out in ice-water mixtures.

To a chilled aqueous solution of $BaCl_2$ containing 1 g. of Ba was added cold fuming HNO_3 to give the desired normality for 50 cc. of solution. The resulting solution (in stainless steel centrifuge cups) was agitated for 10 minutes. After centrifuging the supernatant was decanted, and the precipitate was dissolved in H_2O. The Ba was reprecipitated as $BaSO_4$ and determined gravimetrically. Listed below are the results obtained.

Normality of HNO_3 at which Ba was ppt'd	% Precipitated
17	100
15	99.97
12	99.45
9	98.19
6	93.67

It is apparent that the HNO_3 concentration must be kept above 12 N for complete precipitation at this temperature (0-3°C).

2. <u>Precipitation of LaF_3</u>

This experiment was run to ascertain the minimum fluoride ion requirement and the maximum allowable HNO_3 concentration consistent with complete La precipitation.

a. Maximum HNO_3 Determination. Pure active La tracer, 40 mg. La, HNO_3 and water were placed in a waxed stainless steel cup and agitated for two minutes in an ice-water bath. Potassium fluoride was added to render the 35 cc. of solution 4 N in KF, and agitation was continued for 5 minutes. After centrifuging, the supernatant was decanted and counted. The yields obtained were as follows:

HNO_3 Concentration	% Yield	Average % Yield
17 N	16.5, 6	11.2
13.1 N	39,20	30
9.3 N	65, 88	76
5.4 N	91.7, 79.4	86
3.9 N	98.9, 99	99
2.3 N	99.2, 99.8	99.5
1.2 N	99.3, 99.8	99.5
0.0 N	99.1, 98.4	98.8

b. Minimum KF. Information gained from the preceding experiment was used in this study; i.e., HNO_3 conc. was maintained at 4 N while the KF conc. was the variable.

Pure active La, 40 mg. inert La, H_2O and HNO_3 were added to a stainless steel centrifuge cup stirred for 2 minutes and then the requisite amount of KF was added with continued stirring for 5 minutes. After centrifugation the supernatant was decanted and counted.

This study was repeated at lower temperatures (0-3°C); the results for both experiments are found below:

	% Yield					
Temp.	4 N KF	3N KF	2 N KF	1 N KF	0.5 N KF	0.1 N KF
0-3°C	99	96.5	94.9	91.3	60.5	0.0
23°C	96.8	94.4	94	74.2	64.9	44.4

3. Dissolving $Ba(NO_3)_2 \cdot 2H_2O$

In determining the volumes which will have to be treated in the present process it is necessary to know approximately the quantity of water (and temperature) necessary to dissolve 1 g. of Ba as $Ba(NO_3)_2 \cdot 2H_2O$. This precipitate will contain a certain amount of HNO_3 remaining from the precipitation step.

Ten cc. of solution containing 1 g. of Ba as the chloride was chilled in an ice-water mixture. The Ba was precipitated by adding cold fuming HNO_3. After 5 minutes' agitation the precipitate was centrifuged and as much of the supernatant as possible was poured off. The precipitate was then transferred to a glass centrifuge tube with a minimum of H_2O. A bath was placed around the tube and maintained at the desired temperature. Water was then added by increments until complete solution of the precipitate was obtained. A "turbo" stirrer was used to provide efficient agitation.

Temperature	H_2O Necessary for Complete Solution
0-3°C	78, 80 cc.
23°	48, 50 cc.
68°	*22 cc.
71°	*22 cc.

(*Supersaturated at 23°C)

It may be possible to decrease the volume of H_2O necessary by removing the HNO_3 which wets the precipitate with some reagent in which barium nitrate is insoluble. The following data were obtained from Siedell's "Solubilities of Inorganic and Metal

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Organic Compounds":

100 g. methyl alcohol dissolves	0.5 g. ($Ba(NO_3)_2$ at 25°C
100 g. acetone	0.005 g. $Ba(NO_3)_2$ at 25°C
100 g. ethyl alcohol (abs.)	0.0016-0.0020 g. $Ba(NO_3)_2$ at 25°C
100 g. isopropyl alcohol	0.0016-0.0020 g. $Ba(NO_3)_2$ at 25°C

F. REACTION OF TYGON AND ETHER

A sample of tygon tubing was exposed to diethyl ether for about 20 hours. At the end of this time the ether was evaporated to dryness. Several drops of yellow oily liquid remained; a blank for comparison showed no residue. The tubing exposed to the ether became considerably stiffer after drying and assumed a milky appearance. Apparently the plasticiser had been removed.

Tygon tubing is used to convey the ether in one of the processing steps at Oak Ridge and may be a source of impurity.

G. Ba CARRIAGE ON FUMING HNO_3 SEPARATION OF Ba

Approximately $2x10^7$ counts of equilibrium solution were treated by the fuming HNO_3 method to separate the Ba. The supernatant containing the La was then counted for about five weeks. The Ba extrapolated back to separation time gave a Ba count of 2850. The per cent Ba carriage was therefore $\frac{2850}{2x10^7} = 0.14\%$. This work was started by J. F. Suttle.

H. EVALUATION OF Ba CARRY IN PRESENT PROCESS

The amount of barium carried in a RaLa source fired on September 21 was determined by analyzing the soil [illegible] after the shot. Two samples of dirt and one of charred wood were taken and leached with hot 6 N HNO_3, and the leachings counted for about four weeks. The results are shown in the following table:

Sample	Ft. from Crater	Initial Count/m	Final Count/m extrapolated	% Ba Carriage
Dirt	15	4180	~ 7	<0.2
Dirt	0	58900	129	0.22
Wood	15	62900	129	0.21

$$\% \text{ Ba carriage} = \frac{\text{final count extrapolated} \times 100}{\text{initial count}}$$

Since this shot was the second milking of the shipment, a further attempt will be made to sample after a shot from a first milking, since impurities tend to increase the amount of barium carried.

John Schulte