REF: LAB-CMR-10-20
THIS DOCUMENT CONSISTS OF 25 PAGE(S)
NO 1 OF 2 COPIES, SERIES A

PROJECT AUTHORIZATION NO. CMR-10-10

UNCLASSIFIED

RaLa PROCESS RESEARCH

Date
August, 1948

Work Done By
Franklin Barker
R. P. Hammond
J. A. Leary
John Schulte
John Suttle
[illegible] Zeltmann

UNCLASSIFIED

PART I

RALA PROCESS RESEARCH
CMR-10-10

SUMMARY:

Seven major processes have been investigated for the chemical preparation of RaLa sources. These investigations have found five methods satisfactory and two methods unsatisfactory, as follows:

1. Processes satisfactory on a tracer scale.

   a. Precipitation of $Ba(NO_3)_2 \cdot 2H_2O$ with fuming HNO_3, leaving La in solution; followed by dilution of the solution and pptn. as fluoride.

   b. Precipitation of LaF_3 in a solution about 1.5 N in HNO_3 and 4 M in HF, leaving Ba in solution.

   c. Precipitation of $La(OH)_3$ twice with NH_4OH, leaving Ba in solution, followed by conversion of the $La(OH)_3$ precipitate to LaF_3 by metathesis.

   d. Extraction of La with 0.5 molar TTA-in benzene solution, leaving Ba in the aqueous phase, followed by precipitation of the La as fluoride.

   e. Elution of La from a resin column with ammonium citrate at pH 3, so that Ba is retained on the column, followed by precipitation of LaF_3.

2. Processes unsatisfactory on a tracer scale.

   a. Precipitation of $LaPO_4$ from a buffered ammonium phosphate solution was abandoned because of excessive barium carry and bulk of precipitate.

   b. Exchange of La with a suspension of SrF_2 to give a precipitate of LaF_3 was unsatisfactory because of the colloidal nature of the precipitate, which could neither be filtered nor precipitated.

Preparations are under way for testing the satisfactory methods at radiation levels up to 100 curies.

A. STUDY OF PHOSPHATE AND STRONTIUM FLUORIDE METHODS - Zeltmann

1. Strontium Fluoride Method

In previous research it appeared that it would be feasible to separate lanthanum from barium by stirring an acid solution of the two ions with a sparingly soluble salt such as strontium fluoride. The choice of strontium fluoride is not completely arbitrary. It is chosen because in the solution used the solubility of strontium fluoride is intermediate between the solubilities of barium fluoride and lanthanum fluoride. The dissolved strontium fluoride supplies sufficient fluoride ions to precipitate the more insoluble lanthanum fluoride while leaving the barium in solution.

At the time the process appeared promising it was expected that only 2500 curies (4.5 mg. La^{+++}) would be involved. However, present plans are for 10,000 curies (18 mg. La^{+++}). This alteration in capacity has changed conditions sufficiently so that the process no longer appears worthwhile.

It was previously planned that separation would be accomplished by filtration and with only 4.5 mgs. of La^{+++} as LaF_3 it was possible to filter within about a half hour. With the larger amount of LaF_3 however, the filter clogs and filtration times are sometimes infinite. No amount of filter aid appears to speed up the filtration. As an alternative, centrifugation was tried as a means of separation. This too was ineffective as the particles of LaF_3 appear to be almost colloidal in size so that they remain suspended and will

not centrifuge down. This fact appears to be the cause of the clogging of the filters also.

Attempts were made to coagulate or scavenge the LaF_3 but without success. At present this method of precipitation of LaF_3 is not usable. This does not obviate other methods of precipitating LaF_3 as it is known that filterable and centrificable precipitates of LaF_3 can be formed in other ways.

2. Lanthanum Phosphate Method

A method which was at one time used in Bayo Canyon to separate lanthanum and barium was to precipitate lantnanum as $LaPO_4$ from a buffered phosphate solution.

Experiments made recently to determine whether it would be feasible to use the phosphate method as a portion of the process did not disclose any advantages, while two disadvantages were discovered, namely, high barium carriage and excessive bulk of precipitate. The yields attained in the process were all over 90% so that this did not offer serious difficulty.

A 1 M solution of $NH_4H_2PO_4$ also 1 M in H_3PO_4 was used as a buffer; the pH was adjusted to desired values with NH_4OH.

Preliminary experiments to determine the optimum molarity of buffer solution showed that the yields observed were almost completely independent of the molarity of buffer.

In the presence of impurities such as exist in the Ra-La soup (e.g. Pb, Cr, Fe, Sr, Ni), the pH required is higher than if the lanthanum is precipitated from a pure lanthanum solution. Lanthanum precipitates quantitatively as phosphate from a buffered phosphate solution at a pH of 1.85. Results obtained with solutions containing

a typical amount of impurities are as follows:

pH	% La Precipitated as $LaPO_4$
1.5	50%
1.8	65%
2.1	88%
2.4	98%

It was evident from the above results that in a solution containing impurities the pH must be maintained at 2.4 or higher.

An experiment performed to determine barium carriage gave the following results:

pH	% La Yield	% Ba carried
2.4	98.	2.40
2.7	97.5	2.84
2.8	100.	1.62
3.0	96.8	14.1
3.1	97.1	21.5
3.2	94.1	43.0

In order to cut down barium carriage an experiment was performed in which La_3PO_4 was precipitated and the supernate decanted. The precipitation was then repeated twice more. The results obtained were as follows:

pH	% La Yield	% Barium Carried
2.4	90.6	0.95%
2.6	92.1	1.54%
2.8	96.0	1.54%
3.0	92.4	2.22%

Conclusions which may be drawn from the previous experiment are that:

1. It is unlikely that the barium carriage may be reduced far below 1% whereas it is desired that barium carriage be held to 0.1%.

2. With successive precipitations the actual percentage yield of lanthanum decreases.

3. With a typical amount of impurities the bulk of precipitate did not pack down beyond a volume of 1.5 cm^3, whereas 0.1 cm^3 is a more desirable volume.

It is interesting to note that while this process was once a feasible method it no longer can be considered as such. Previously the difficulty with this method was filtration times. This has since been eliminated by use of centrifugation. Now the fact that more active sources will be used required the barium carriage to be lower in order that firing site contamination will at worst be no higher. Further, while the bulk of lanthanum and impurities must be increased by a larger source the specification for volume limits us to 0.1 cm^3.

B. STUDY OF NITRIC ACID AND HCl METHODS AND DETERMINATION OF EXTRACTION COEFFICIENTS WITH TTA-BENZENE - Suttle

Three methods of separating Ba from La were studied:

(1) The fuming nitric acid method

(2) The concentrated hydrochloric acid method

(3) The complexing method using TTA (thenoyltrifluoracetone)

1. The Fuming Nitric Acid Method

The following general procedure was used: One ml. of tracer (Ba-La mixture) was placed in a 15-ml. centrifuge tube. To this was added varying amounts of barium carrier and lanthanum carrier. Fuming nitric acid either chilled or at room temperature was added to

make the final volume about 12-13 ml. The mixture was stirred at high speeds for approximately one minute using an Eastern Model 1 variable speed motor and a platinum spiral stirrer. The addition of the nitric acid immediately produced a white precipitate. After stirring, the mixture was centrifuged for approximately one minute. When the centrifuge came to rest 2.3 mg. Ba^{++}(1 drop) was added and the mixture centrifuged again for about one minute. The liquid above the precipitate was decanted into a counting bottle and 10 ml. of fresh fuming nitric acid added to the centrifuge tube. The precipitate was mixed with the nitric acid by means of the stirrer previously mentioned. After approximately one minute the mixture was centrifuged and then the supernatant liquid was poured into the same counting bottle. The liquid in the counting bottle was made up to 35 ml. by the addition of distilled water.

The variables that were changed from run to run were as follows:

(a) Amount of barium carrier

(b) Amount of lanthanum carrier

(c) Temperature of all solutions used

(d) The addition of impurities that might be found at one time or another in the active mixture

(e) Increase in volume of operation

On some runs the barium nitrate precipitate was dissolved in distilled water and the solution counted. Usually, the precipitate was discarded. A standard was always counted with the sample. The standard consisted of 1 ml. of activity added to the counting bottle and made up to 35 ml. The calculation of the lanthanum extracted involved dividing the count from the standard into the count obtained from the sample.

UNCLASSIFIED

In the accompanying tables the yields of lanthanum reported are not corrected for the effect of radio barium. One millicurie of Ba^{140} will remain in equilibrium with 1.155 millicuries of La^{140} $\left(\frac{\lambda_2}{\lambda_2-\lambda_1}\right)$. The weak gamma rays from Ba^{140} will count in the apparatus used with 5.19% of the efficiency of those from La^{140}, (as described elsewhere in this report). Hence 95.7% of the counts recorded from an equilibrium mixture will be due to La. In the results reported, an apparent yield of 95.7% would represent complete recovery of the lanthanum, provided the barium present was small.

2. The Concentrated Hydrochloric Acid Method

The procedure followed in this method was essentially the same as that followed in the nitric acid method with only the substitution of hydrochloric acid in place of nitric acid. All runs were chilled with an ice bath.

3. Extraction of Lanthanum with TTA

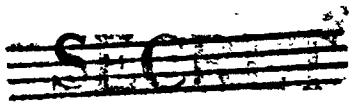
The activity was started in the aqueous phase. The aqueous phase was .1 M in KCl and very small amounts of KOH and HCl were used when it was desirable to vary the pH. The TTA was .2 M in benzene in all cases except one when it was .5 M. A ratio of 10 to 1 benzene phase over aqueous phase was used. Prolonged violent stirring action was found to be necessary.

The following table gives the results obtained up to this time. No correction for barium in either phase has been made yet.

$$3\,HT + La^{+++} \rightleftharpoons LaT_3 + 3H^+$$

$$K_{La} = \frac{[LaT_3]\,[H^+]^3}{[HT]^3\,[La^{+++}]}$$, where quantities in brackets are activities.

UNCLASSIFIED



TYPICAL EXPERIMENTS WITH SOLVENT EXTRACTION

(Figure I)

Sample No.	pH	$\frac{La_B}{La_A}$	K_{La}	Molarity TTA	Stirring Time
82	3.30	.046	3.80×10^{-10}	.5	30 min.
81	3.40	.0043	2.38×10^{-10}	.2	30 min.
83	3.51	.0056	1.43×10^{-10}	.2	30 min.
86	3.56	.0089	1.62×10^{-10}	.2	30 min.
80	3.79	.055	2.04×10^{-10}	.2	30 min.
69	3.82	.0705	2.12×10^{-10}	.2	15 min.
70	3.94	.0964	1.26×10^{-10}	.2	15 min.
72	4.02	.1783	1.35×10^{-10}	.2	15 min.
79	4.02	.1307	9.9×10^{-11}	.2	30 min.
87	4.18	.346	8.69×10^{-11}	.2	30 min.
71	4.19	.264	6.19×10^{-11}	.2	15 min.
75	4.62	1.191	1.43×10^{-11}	.2	30 min.
74	4.64	.9548	1.01×10^{-11}	.2	15 min.
73	4.66	1.124	1.02×10^{-11}	.2	15 min.
77	4.83	1.237	3.48×10^{-12}	.2	30 min.
76	5.05	1.278	7.86×10^{-13}	.2	30 min.
88	5.39	1.62	9.5×10^{-14}	.2	30 min.

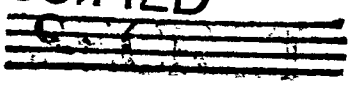


Figure II

TYPICAL EXPERIMENTS WITH NITRIC ACID PROCESS

Sample No.	Counts per minute	Standard c/m	Ba Carrier 2.3 mg. Ba^{++} scavenger	La Carrier	Temp. of HNO_3 and other sol. used	Impurities 1 ml. contains 5 mg. Cr^{+++}, 10 mg. Nc^{++}, 2 mg. Sr^{++}, 32 mg. Ce^{+++}, 5 mg. Fe^{+++}	Pb^{++}	% La in sample 95.7% is maximum possible	Calc. of Ba carriage by other methods I, II, or III
14	5748	6028	4.6 mg.	15 mg.	Chilled	----	-----	95.3	I 10.15%
24	6379	6989	90 mg.	10 mg.	Chilled	----	-----	91.2	I negligible
24A	398	6967	$Ba(NO_3)_2$ ppt dissolved and counted = 5.7%						
26	9386	10252	90 mg.	10 mg.	Chilled	1/2 ml.	-----	91.5	I negligible
28	9826	10211	90 mg.	10 mg.	Chilled	1 ml.	-----	96.2	I neg. II neg.-2.5
41	8427	8992	90 mg.	10 mg.	Chilled	1 ml.	60 mg.	93.7	II 1.91%, 1.08
46	7316	7903	90 mg.	10 mg.	Room temp.	1 ml.	60 mg.	92.6	II 2.2%, .98%
46A	500	7903	$Ba(NO_3)_2$ ppt dissolved and counted = 6.3						III .6%
47	7556	7868	90 mg.	10 mg.	Room temp.	1 ml.	----	96.0	II 1.02%, .39%
47A	467	7903	$Ba(NO_3)_2$ ppt dissolved and counted = 5.9						
Total volume increased to 75 ml. in this run									
48	7332	29473	500 mg.	20 mg.	Chilled	5 ml.	-----	92.7	II .405%
48A	852	29701	$Ba(NO_3)_2$ ppt dissolved and counted = 6.2%						
Total volume increased to 200 ml. in this run									
49	4074	12670	500 mg.	20 mg.	Chilled	5 ml.	-----	87.4	II .23%
	Difficulty	encountered	in removing ppt from solution						
49A	111	12299	$Ba(NO_3)_2$ ppt dissolved and counted = 9.3%						
61	1529	11260	90 mg.	10 mg.	Chilled	1 ml.	-----	93.5	I negligible II negligible III negligible

Figure III

TYPICAL EXPERIMENTS WITH HYDROCHLORIC ACID PROCESS

Sample No.	Counts per minute - sample	c/m standard	Ba carrier plus 2.3 mg. Ba^{++} scavenger	La Carrier	Impurities 1 cc.contains 5 mg.Cr^{+++};10 mg. Nc^{++};2 mg.Sr^{++};32 mg.Ce^{+++};5 mg.Fe^{+++}	% La in sample 95.7% is maximum possible	Calculation of Ba carriage by other methods I, II, or III
57 57A	19878 943	21032 21191	50 mg. $BaCl_2$ ppt dissolved and counted = 4.5%	10 mg.	1 ml.	94.5	II 13.02%, 14.82, 14.91 III 14.66%
58 58A	19238 1040	20405 20405	89 mg. $BaCl_2$ ppt dissolved and counted = 5.1%	10 mg.	1 ml.	94.3	II 7.01%, 6.91%
59 59A	19468 1030	20357 20357	128 mg. $BaCl_2$ ppt dissolved and counted = 5.1%	10 mg.	1 ml.	95.6	II 18.45%, 14.52% III 16.2%
62	16928	18027	90 mg. 5 to 1 HCl to ether	10 mg.	1 ml.	93.9	I negligible II negligible III 2.17%
63	17540	17917	90 mg. no ether	10 mg.	1 ml.	97.9	I negligible II 2.17% III 3.00%

Activity = (C_{HT}) (γ):

when C_{HT} .2 M, γ = .89

C_{HT} .5 M, γ = .82

when ionic strength = .1, γ for La^{+++} = .18

γ for LaT_3 assumed equal to γ for HT

$[H^+]$ taken from pH measurement

4. Determination of Barium Carry

Barium carriage was determined by three different methods furnished by Al Zeltmann. These will be referred to as method I, method II, and method III.

Method I

$$Co = Ba\ k_o\ (1-\lambda_1 t) + La(1-\lambda_2 t) + \frac{\lambda_2}{\lambda_2-\lambda_1} Ba(\lambda_2-\lambda_1)\ t$$

This equation can be set up to resemble the general expression for a straight line,

$y = b + mx$

$$Co = \left[k_o Ba + La\right] + \left[(\lambda_2-\lambda_1)\ k_o Ba - \lambda_2\ La\right] t$$

Co = counts of Ba after separation

k_o = efficiency of counting Ba

λ_2 = La decay constant — La = relative La activity

λ_1 = Ba decay constant — Ba = relative Ba activity

t = time in hours

A number of counts of the sample are made in a short period of time so that the approximation $(1-\lambda_1 t)$ can be used in place of $e^{-\lambda_1 t}$. These counts are plotted against time linearly. The calculation of Ba carriage on sample #14 is an example.

From plot

$$m = \frac{\Delta Y}{\Delta X} = \frac{-820}{9} = -91.5$$

ΔY = counts/min.

ΔX = hours

intercept b = 5820

$$\begin{cases} -91.5 = .01598C_{Ba} - .0172C_{La} \\ 5820 = .052C_{Ba} + C_{La} \end{cases}$$

solving simultaneously

$$8.6 = .01688\ C_{Ba}$$

$$C_{Ba} = \frac{8.6}{.01688} = 509 \text{ Ba counts/min.}$$

La counts/min. $= 1.151\ C_{Ba}$ (at equilibrium)

Count on standard = 6028

1.151 Ba + .052 Ba = 6028

1.203 Ba = 6028

Ba = 5010 in original

$$\% \text{ Ba carriage} = \frac{509}{5010} \times 100 = 10.15\%$$

Method II

$$\% \text{ Ba carriage} = \frac{C_2 - C_1 e^{-\lambda_2 t}}{C_o (e^{-\lambda_1 t_o})(e^{-\lambda_1 t} - e^{-\lambda_2 t})}$$

In this method successive counts are taken after separation. Usually a count on the sample was taken every day for a week or two. Only two counts on the sample are needed for the calculation. C_2 is the latest or smallest count and C_1 is earliest or largest count. C_o is the standard corrected to the time of C_2.

λ_2 = La decay constant

λ_1 = Ba decay constant

SECRET

 UNCLASSIFIED

As an example, the calculation of Ba carriage on #28 is worked out.

#28

$$\% \text{ Ba carriage} = \frac{C_2 - C_1 e^{-\lambda_2 t}}{C_0 (e^{-\lambda_1 t_0})(e^{-\lambda_1 t} - e^{-\lambda_2 t})}$$

$t = [6/28 \quad 8:28] - [6/29 \quad 13:35]$

$= 29.11$ hours

$t_0 = [6/23 \quad 11:58] - [6/28 \quad 8:27]$

$= 117.15$

$C_2 = 888$

$C_1 = 1357$

$C_0 = 10211$

$e^{-\lambda_2 t} = .607$

$e^{-\lambda_1 t} = .936$

$e^{-\lambda_1 t_0} = .768$

% Ba carriage = 2.5%

As long as C_1 was taken a day or so after the separation the percent Ba carriage could be approached by taking other values of C_1 and C_2 but if C_1 was taken immediately after the separation, no verification could be made by taking other values of C_1 and C_2. The calculations on #46 showed a value of 10.86% Ba carriage when C_1 was taken immediately after separation and C_2 was only 27 hours later. If C_1 is taken 42 hours after separation and C_2 192 hours from the time of C_1 the percent carriage is only 2.2%. The actual plotting logarithmically shows less than 1% carriage. Calculation of the Ba carriage by both methods and by plotting logarithmically show the fuming nitric acid method to be a better method of separation than the concentrated hydrochloric acid method under the conditions studied.

SECRET

Method III

In this method the decay of the lanthanum sample is followed over a period of several weeks until equilibrium with the residual barium is reached. When plotted on semi-log paper the activity decreases with approximately the lanthanum half-life and then curves into another straight line having a slope for the barium half-life. Extrapolating this latter line to the time of the original count will give an activity proportional to the barium in the sample

$$\% \text{ Ba} = \frac{\text{extrapolated Ba activity} \times 100}{\text{original La activity}}$$

C. EXPERIMENTS ON COUNTING EFFICIENCY AND TESTS OF HYDROXIDE, FLUORIDE AND EXTRACTION METHODS - Schulte

1. Determination of Fraction of Ba Counted in an Equilibrium Solution

a. La Scavenged with $Fe(OH)_3$

To five cc. of equilibrium solution was added 10 mg. Fe . The solution was then made ammoniacal and centrifuged. Since the $Fe(OH)_3$ should remove all the La, only Ba would remain in the super-

[redacted]

a counting bottle and counted periodically for 4 weeks

$$\text{Count}_{\text{maximum}} = La_T + Ba_T \times K$$

$$= 0.73^{*}\ Ba_o + 0.73\ Ba_o \times K$$

$$= 0.73\ Ba_o\ (1+K)$$

*at maximum 73% of Ba_o remains

$$\text{Count}_{\text{initial}} = Ba_o\ K$$

$$\frac{\text{Count}_{\text{maximum}}}{\text{Count}_{\text{initial}}} = 0.73\ \frac{(1+K)}{K}$$

$$K = \frac{0.73\ \text{Count}_{\text{initial}}}{\text{Count}_{\text{max.}} - 0.73 \times \text{Count}_{\text{initial}}}$$

Substituting the results from this experiment a value of 5.19% is obtained for K, the percentage of Ba counted in an equilibrium solution.

In separating La from Ba in an equilibrium solution the maximum yield obtainable is derived from the following calculations:

$$\text{Maximum yield} = 1 - \frac{N \times .0519}{1.55 \times N + Nx\ .0519}$$

$$= 1 - \frac{.0519}{1.155 + .0519}$$

$$= 0.957 \text{ or } 95.7\%$$

b. Fuming HNO_3 Method for Removing La

Twenty-five ml. of equilibrium solution containing 10 mg. Ba and 5 mg. La was chilled and then added to 100 ml. of cold fuming HNO_3. After the $Ba(NO_3)_2 \cdot 2H_2O$ had precipitated, the reaction vessel was centrifuged. The supernatant containing the La was poured off. The barium nitrate was then dissolved in a minimum of warm distilled H_2O and reprecipitated with cold fuming HNO_3. After centrifuging and again decanting the supernatant the barium nitrate was dissolved in H_2O, diluted to 35 cc. and placed in a bottle

The sample was then counted periodically as described under "A".

A value of 5.64% was obtained by this separation method.

The lower value of 5.19% obtained under "A" is probably more accurate, and consequently has been used as the percent barium counted in an equilibrium solution.

2. Separation of Ba and La by Precipitation with NH_4OH

a. Single Precipitation Using Only La

Four runs were carried out using different Ba/La ratios to determine percent yield and Ba carriage.

To an aqueous solution of Ba and La containing one cc. of equilibrium mixture (9 cc. total) was added 3 cc. conc. NH_4OH. The reaction mixture was agitated thoroughly and centrifuged followed by two rinses with thorough agitation. All supernatants were combined and diluted to 35 cc. with HCl for counting. The final precipitate of La was dissolved in HCl, diluted for counting and saved for decay studies.

In these experiments the Ba/La ratios were as follows: 1; 4; 10 and 20. The percent La recovery varied from 95-100% by this method, and the Ba carriage was much less than 0.1%.

Barium carriage is determined by allowing the sample to decay for at least three weeks. The sample is counted once a day during this period. When the decay line levels off and assumes the slope of the Ba decay line, it is extrapolated back to "last separation time" on semi-log graph paper. Then:

$$\% \text{ Ba carriage} = \frac{\text{extrapolated count} \times 100}{\text{total counts at separation}}$$

b. Single Precipitation Using La and Impurities

Since the lanthanum hydroxide precipitate is too bulky to package as a source, several different reagents were tried after the separation step to reduce this volume. Typical impurities were added in these experiments to determine their effect on the volume of the final precipitate*. In this way several interesting points were brought to light. The Ba carriage was found to vary from 0.08% to 2.4% when the Ba/La ratio was 40 and when impurities were present. Whereas when only La was present, the Ba carriage was practically nil.

The reagents were added directly to the hydroxide precipitate except with the exceptions noted in the following table. (Figure IV).

Figure IV

Experiments on Metathesis of $La(OH)_3$ Ppts.

Reagent	Ba Carriage	Vol. of Final ppt.	La Yield (1st step)	La Yield (2nd step)	Remarks
5 cc. Na_3PO_4-H_3PO_4 (pH-2.0)	0.10%	0.2 cc.	95%	97%	
5 cc. 28 N HF	1.89%	0.1 cc.	94%	100%	
0.3 cc. 3 N HCl; then 5 cc. sat'd Na_2CO_3	2.4%	0.9 cc.	94%	88%	Necessary to dissolve ppt. in acid before adding reagent
5 cc. sat'd oxalic acid	1.8%	0.14 cc.	97%	97%	
0.3 cc. 2 N H_2SO_4; then 5 cc. sat'd Na_2SO_4	2.3%	0.07 cc.	97%	74%	Necessary to dissolve in acid and then apply heat
5 cc. 28% H_2SiF_6	0.08%	0.07 cc.	97%	92%	Necessary to heat before pptn. begins

*Appropriate 1/4 batch size contains the following in 12 cc. of solution:

5 mg. La	2.5 mg. Ni
200 mg. Ba	0.5 mg. Sr
8 mg. Ce	1.25 mg. Fe
1.25 mg. Cr	

Improvement in the present counting techniques might show that complete La recovery is possible by precipitation with NH_4OH. The values listed in the table above for Ba carriage merely show the variation encountered when impurities are present; standardization of washing techniques, etc., could conceivably lower some of these values.

3. Separation of Ba and La by Single Precipitation with KOH

A series of experiments similar to those carried out with NH_4OH (see "a") were carried out using 2 cc. of 1 N KOH and impurities representing 1/4 batch size operation with 5 mg. La present. No effort was made to use carbonate-free KOH. Data and results are listed in the following table:

Ba/La Ratio	La Yield	Ba Carriage
1	98%	41%
10	97.4%	7%
40	97.5%	3.7%
100	97.6%	0.8%

The results obtained here highlight the effect of hold back carrier on the percent of barium carried.

A study is currently in progress to determine the effect of making a double precipitation in the hydroxide separation step for both KOH and NH_4OH.

4. Reduction in Volume of Hydroxide Precipitates

It was believed that the volume of the hydroxide precipitate might be reduced by physical methods.

a. The hydrated oxides of La and impurities were heated with an infra red lamp. The product resulting from evaporation

was not restricted to a defined area and was therefore not satisfactory.

b. "Spin Dry"

Lanthanum and impurities in a typical solution were precipitated with ammonia and centrifuged; the supernatant was then decanted. The centrifuge tube used here had one-half inch of coarse sintered glass in the lower end; the bottom was open. It was hoped that the excess water would be forced out the bottom when the tube was centrifuged at high speeds. Unfortunately the gelatinous precipitate formed a tightly packed layer on the sintered glass, thus preventing any water from being forced out the bottom.

This method was not applicable with LaF_3, but a very compact dry product is possible when a granular precipitate such as lanthanum oxalate is used.

5. Solvent Extraction

a. Effect of NaCl Concentration on TTA

Since the hot run with TTA at Bayo and others obtained on tracer scale experiments have given poor yields, it was believed that this might be attributed to NaCl in the aqueous phase. This study was therefore carried out to determine the effect of salt concentration on TTA.

One hundred cc. of benzene, 0.1 M in TTA, was used to extract the La from 10 cc. Ba-La equilibrium solution. The separation was accomplished by agitating the two phases vigorously in a cylindrical chamber having a porous sintered disk in the bottom. At the end of the agitation period the aqueous phase was drained out the bottom and assayed for activity. Calculations were m

$$\% \text{ yield} = \frac{\text{Soup-Ba}}{\text{Soup}} \Big/ 0.957$$

Experiments were then carried out in which the salt concentration in the aqueous phase was varied. In the following table are found data and results pertinent to this series of runs.

NaCl Concentration	Percent Yield
$<$0.001 M	95.3 - 100
0.01 M	99.3
0.10 M	96.3
1.0 M	94.5
3.2 M	22, 50, 54, 55.8

From these results it is concluded that the efficacy of TTA in separating La from Ba is seriously impaired only at NaCl concentrations above one molar.

b. Effect of Radiation on TTA-Benzene

The TTA-benzene solution which had been used in the hot run at Bayo had turned dark red during the operation. This solution was treated repeatedly with 0.1 N HCl to remove the activity.

Two tracer scale runs were then made with this solvent to determine whether the irradiation received at Bayo had decomposed the TTA enough to render it ineffective in separating La from Ba.

The yields obtained in these experiments were both virtually 100%.

Subsequent preliminary experiments indicated that the red coloration of the TTA could be caused by a highly colored TTA-iron complex. There is usually a small quantity of iron remaining in the soup after several milkings. In view of these points the TTA was

probably not damaged by the irradiation received at Bayo.

6. Behavior of Ba in an $HF-HNO_3$ System

By maintaining the proper HF and HNO_3 concentrations, Leary found that the La could be precipitated as the fluoride leaving the BaF_2 in solution.

A more detailed study was then carried out to determine the limitations of this process.

Several runs were made in which the Ba was varied from 20-200 mg. in about 13 cc. Enough 14 N HF was added to give 15 cc. of solution 4 N in HF. These reactions were carried out in lusteroid tubes, and agitation was provided by a metal stirring rod coated with DeKhotinsky cement. Concentrated HNO_3 was added in small increments until the BaF_2 dissolved and continued until the formation of $Ba(NO_3)_2 \cdot 2H_2O$ was observed.

The data obtained in these experiments are found in the following table, and are plotted in Figure V.

Mg. of Ba Used	N of HNO_3 when BaF_2 dissolved	N of HNO_3 when $Ba(NO_3)_2 \cdot 2H_2O$ formed	N of HF when BaF_2 dissolved	N of HF when $Ba(NO_3)_2 \cdot 2H_2O$ formed
20	0.88	No ppt. visible at 4.93 N	5.2	No ppt visible at 3.8 N
40	0.89	3.26	5.7	4.8
60	0.96	2.64	5.7	5.0
80	0.92	2.01	4.8	4.4
100	0.88	1.96	4.7	4.4
140	1.05	1.54	4.7	4.6
160	1.16	1.25	4.7	4.6
170	1.21	1.27	4.8	4.8
200	Precipitate present at all times			

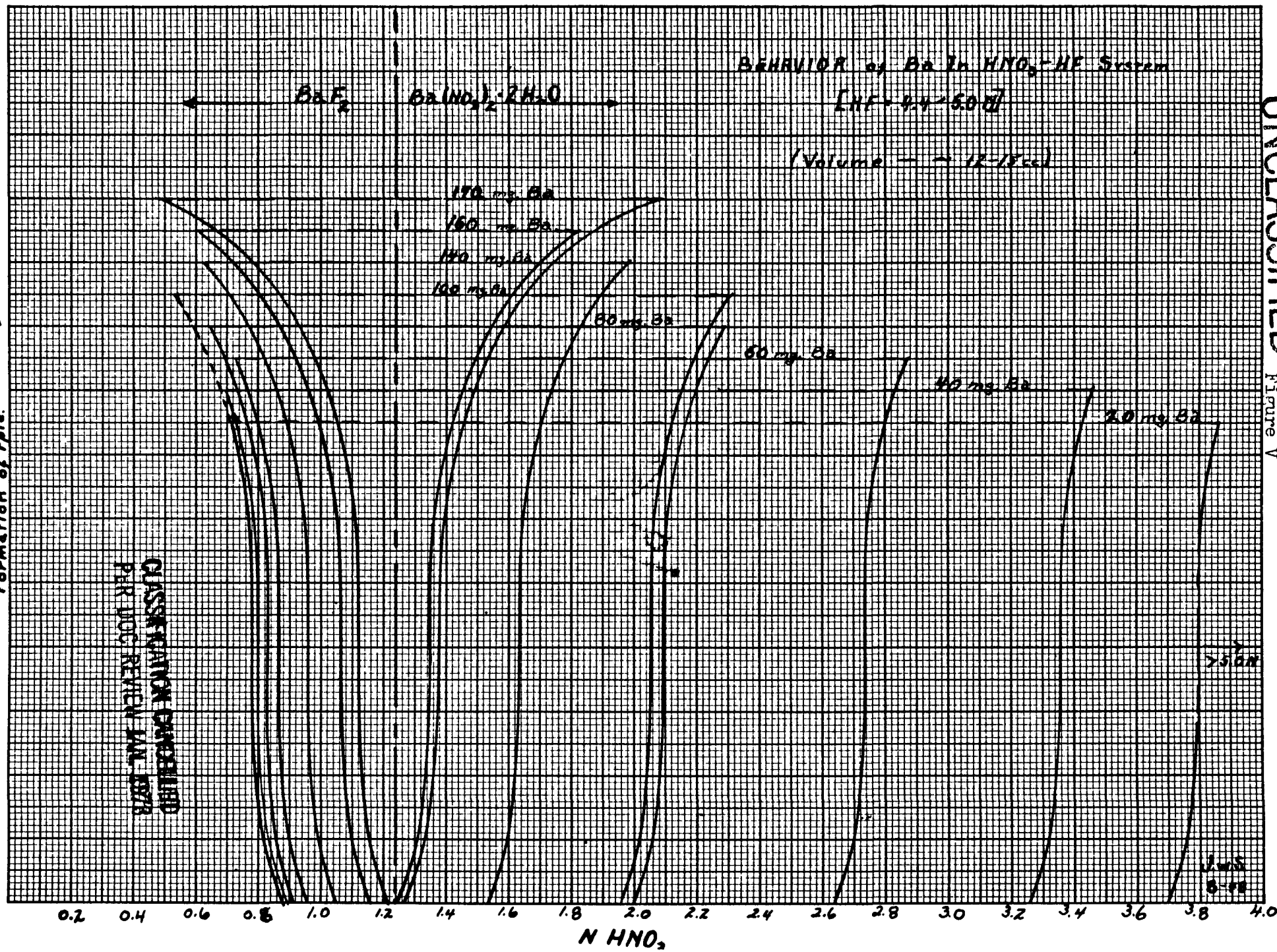


Figure V

A few runs will be made at optimum concentrations of HF and HNO_3 for a given amount of Ba. The Ba carriage will then be determined on the La precipitate.

Another problem posed by this process is that the La which grows between milkings will precipitate immediately. Now this is a decidedly different case than that where all the La is precipitated at once. It is not known whether the LaF_3 will cling to the walls or can be centrifuged to the bottom.

A run will be made in the millicurie scale to determine the feasibility of using this one step process.

It is obvious that in complexing the La after the first milking to prevent the formation of LaF_3 during the growing period it would be quite troublesome to precipitate the La in subsequent milkings.