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RaLa PROCESS RESEARCH

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Work Done By
Franklin Barker
R. Philip Hammond
Joseph Leary

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PART I

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SUMMARY:

A study of previous work and consideration of chemical properties has led to the proposal of nine possible methods for seperation of lanthanum from barium. Some of these methods are modifications of previously tried processes. Four methods have been given preliminary testing and one is under full investigation. This process of liquid-liquid extraction has already given better yields than the present method and is ideally suited for remote control operations. A carrier-free chloride solution of active lanthanum and barium at pH 3.8-4.5 is agitated ten minutes with a larger volume of .1 M solution of thenoyltrifluoroacetone in benzene. The layers are separated automatically and quantitatively by means of a fritted glass plate. The lanthanum passes into the benzene phase and is recovered by re-extraction with .1 N hydrochloric acid. Exposure to 1000 R units of radiation did not effect the properties of the chelating compound. A 25 curies run will be attempted soon.

I. INTRODUCTION.

The design of a new laboratory for the production of RaLa sources of 10 kilocuries intensity has necessitated a renewed study of processes for the separation of lanthanum 140 from its parent, barium. Although the equipment in the new laboratory will be flexible enough to accommodate a variety of process changes, it is deemed wise to [illegible] first for one specific process.

The method at present in use at Bayo Canyon has not proved completely satisfactory, and it is believed that a more efficient and reliable process can be developed in time for tooling deadlines of the new laboratory.

II. Previous Work.

Several methods have been studied during the course of the ReLa project. Among these were the phosphate method, the calcium fluoride method, the strontium fluoride method, plating method, ion exchange methods, and the present hydroxide-oxalate method. These methods may be briefly described as follows:

A. Phosphate method: This is a one-step process depending upon the solubility of barium orthophosphate and the insolubility of lanthanum orthophosphate under proper conditions of acidity. In practice this method worked well, but required excessive filtration times. Centrifugation facilities for active materials were not available at the time.

B. Calcium or strontium fluoride method: This method is based on precipitation of lanthanum on an excess of calcium or strontium fluoride by metathesis in a solution in which the CaF_2 or SrF_2 is slightly soluble (pH=2). This method suffered from difficulties with impurities, yield, temperature control, and filtration or agitation time.

C. Plating method: A long series of attempts to electroplate, or co-plate as a mixture, the lanthanum from aqueous solution resulted in failure. The work of other investigators has shown that lanthanum metal may be produced satisfactorily only by electrolysis of the fused anhydrous chloride or as amalgam by electrolysis of the solution of the anhydrous chloride in absolute ethanol. None of these methods gives satisfactory yields except on a very large scale.

D. Ion exchange methods: The attempt was made to separate barium and lanthanum by selective ion-exchange on Amberlite resins without success. It is now known that this can be done, but high yields are not easy to obtain and it is necessary to use salted solutions.

E. Hydroxide-oxalate method: The presently used method is a two step process involving the precipitation and filtration of gelatinous lanthanum hydroxide, barium hydroxide remaining in solution, followed by solution of the precipitate in nitric acid and reprecipitation as crystalline lanthanum oxalate. This precipitate can then be filtered on a small-area filter. Since the oxalate precipitate is gradually peptized or decomposed under radiation, scavenging with HF is required. The final precipitate is probably nearly all lanthanum fluoride, retaining, however, the granular structure of the oxalate. A similar procedure is used in the industrial preparation of rare-earth fluorides. That the conversion to fluoride is almost complete is evident from the fact that nearly all of the oxalic acid used can be recovered and reused.

Difficulties of the present method are uncertain yield, trouble with impurities, mechanical losses, and necessity for two steps.

F. Minor methods: Many other methods have been proposed and some have been studied. Among these are the silicofluoride method, ferrocyanide method, sulfate method, ferrioxalate method, tartrate method, oxalate method, etc. Other methods considered may be found in an outline by Friedlander of October 29, 1945.

III. Processes Now Under Consideration.

A study of previous work and of the chemistry involved has led to several proposed processes, some of which are modifications of known methods. Since the process chamber in the new Bayo[illegible]tory will be

equipped for centrifugation, several previous methods condemned for slow filtration can be re-investigated. Following is the present program of processes to be studied:

A. Calcium fluoride method: This method, or its corollary, using strontium fluoride, was abandoned principally because of erratic results caused by iron contamination. It is proposed to re-investigate this method using various complexing agents to control iron and fluoride concentrations at constant levels. The use of FeF_3 in excess will be tried.

B. Phosphate method: This process was described above and would probably be suitable if centrifugation were used. Several modifications are possible.

C. Nitric acid method: This method consists of precipitation of $Ba(NO_3)_2 .2 H_2O$ with an excess of chilled fuming nitric acid, lanthanum being poured off with the supernate after centrifugation and precipitated, after dilution, as fluoride or sulfato-fluoride. The first step is part of the standard radiochemical method for barium as used for determining fission yield. Preliminary tests have shown this method to be quite promising.

D. Sulfate method: This method consists of precipitating $BaSO_4$ under conditions where lanthanum sulfate is soluble or can be leached out. A new modification which may be tried is the use of pyrophosphoric or metaphosphoric acid as leaching agent. Another possible leaching solution is potassium carbonate.

E. Ion exchange method: Improved resins and new techniques indicate this method may be reinvestigated with greater promise. Nothing is known, however, about the effect of high radiation levels on the resins.

F. Carbonate method: Since it is known that lanthanum [illegible]

has some solubility in saturated potassium carbonate solution, whereas barium carbonate is insoluble, another possible method is indicated.

G. Chloride method: The method of ether-HCl precipitation of barium chloride is used at Clinton Laboratories. Ether, however, is easily polymerized by radiation to thick gums. (This is believed to be the cause of much trouble in some of the shipments received.) It is possible that the precipitation of barium chloride in the presence of an excess of anhydrous HCl gas may offer a suitable, if difficult, method. It is not presently proposed to study this method.

H. Fluoride method: This method, used by N. Sugarman in radiochemical separations of lanthanum, depends upon the solubility of barium fluoride in solutions which are 2 N in nitric and 4 N in hydrofluoric acid. Lanthanum fluoride is precipitated under these conditions, giving a simple one-step process. Preliminary tests show this method to be very promising.

I. Solvent extraction: Last, but perhaps of greatest interest, is the selective extraction of lanthanum from aqueous solution into a benzene solution of thenoyltrifluoroacetone, a beta-diketone having chelating powers for various ions which are a function of pH. This method was first suggested by A. Broido and P. Tompkins at Clinton Laboratories. Considerable work has been done here on the process, which is reported below.

IV. Solvent-Extraction Experiments.

A. Theory: The relation between the lanthanum concentrations in the aqueous and benzene phases may be represented as an equilibrium reaction as follows:

$La^{+++} + 3\,HT = LaT_3 + 3H^+$, where HT represents the enol form of the chelating agent. When equilibrium is established, a

constant may be set up as $K_{La} = \frac{[LaT_3] \cdot [H^+]^3}{[La^{+++}] \cdot [HT]^3}$. Assuming an excess of reagent the value of HT is fixed, and the proportion of the lanthanum in the benzene phase becomes a function of the relative volumes of the two phases and of the third power of hydrogen ion concentration. The K for a divalent element such as barium will be considerably different than that for lanthanum. Actually, trivalent elements are favorably extracted at pH values above 2.5 and divalent elements at values above 6. Thus it seems easily possible to secure quantitative separation.

Recovery of the lanthanum from the benzene layer may be accomplished by one of 3 methods:

1. Direct precipitation by an agent such as HF in water solution.

2. Re-extraction with acid into aqueous phase followed by precipitation.

3. Re-extraction as above followed by filtrature of the solution through a new very high capacity resin. Some resins are stated to have sufficient capacity that 0.1 gram can absorb about 20,000 curies of carrier-free radio-lanthanum. One such resin is Amberlite IRC-50. A sample of this has been ordered.

B. Experimental method: The apparatus used is illustrated in figure 1. The procedure followed was to agitate measured volumes of water containing known amounts of radio-barium and radio-lanthanum with known volumes of 0.1 M solution of T.T.A. in benzene. (T.T.A. is the abbreviation of thenoyltrifluoroacetone.)

The pH of the aqueous phase is carefully measured with a glass electrode before and after agitation. Separation of the phases is accomplished by venting the lower chamber of the apparatus whereupon the aqueous phase drains through the sintered plate but the benzene phase does

not. The solution is received in a counting bottle and, after rinsing and diluting to volume, the gamma ray counting rate is obtained and compared with that of the original solution.

The benzene layer is then agitated with 0.1 N HCl solution, and the phases separated as before. The acid solution, containing the recovered lanthanum, is drawn off into another counting bottle and counted. The T.T.A. solution is cleaned of all lanthanum by repeated acid washing, then restored to neutrality by distilled water washes. It may be re-used many times without apparent change.

C. Results: Among the process variables studied or to be studied are the effects of pH, time of agitation, concentration of solutions, carriers, impurities, temperature, salting of solutions, and radioactive bombardment. The work done so far has had extremely promising results, but the data have not been checked sufficiently for quantitative reporting.

The results so far may be summarized as follows:

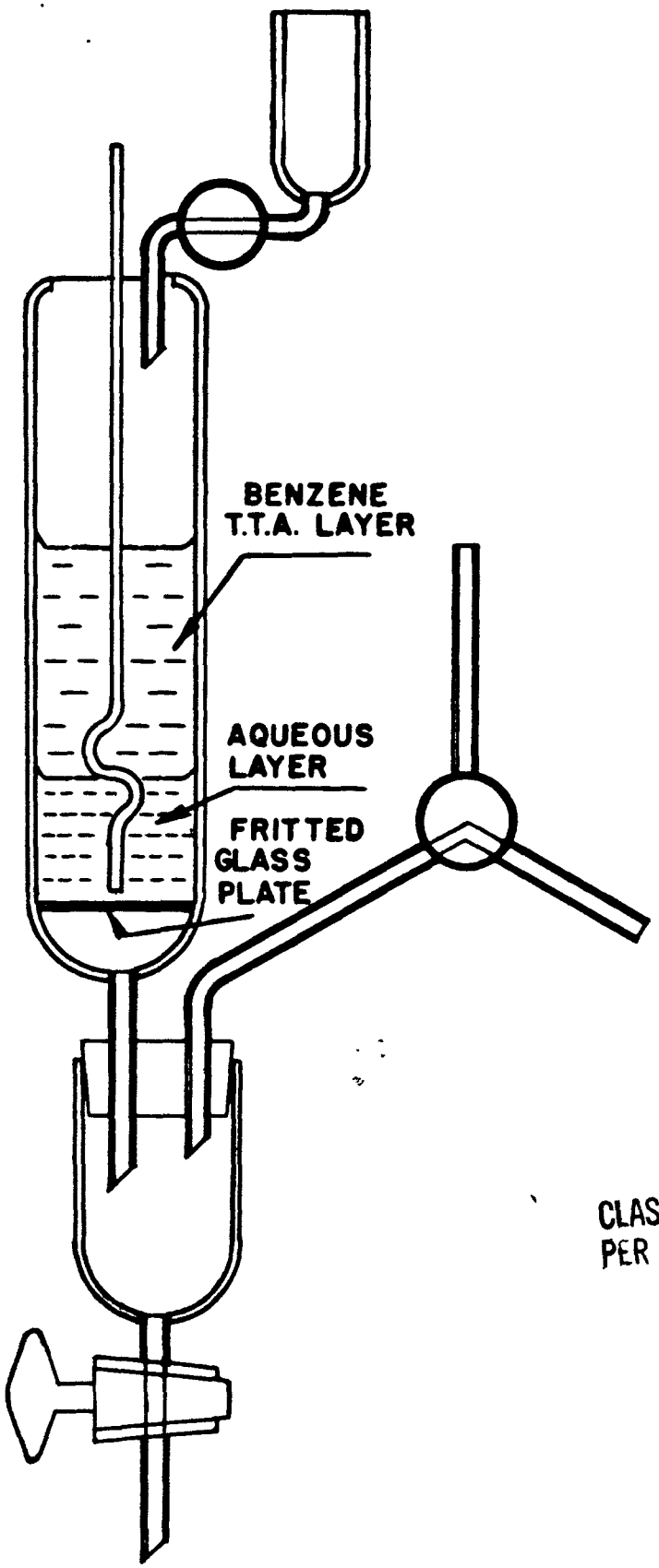
1. At least 98% of the lanthanum may be extracted into benzene-T.T.A. in carrier-free form by a ten-minute agitation period. There is some uncertainty in this yield figure because the proper correction for the gamma-ray counting efficiency of barium has not been accurately measured. This measurement is in progress.

2. The optimum pH range is 3.8 to 4.5.

3. The re-extraction of lanthanum from T.T.A.-benzene to HCl solution does not, at first study, appear to follow the theoretical relation.

4. A sample of T.T.A. in benzene suffered no change in properties or extraction efficiency after exposure to [illegible] units of gamma radiation.

5. Preparations are nearly ready for an actual milking of a



LIQUID
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Figure 1

25 curie source by this method.

R. P. Hammond