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REPORT
for

GENERAL RESEARCH

SEPTEMBER 18 TO DECEMBER 11, 1950
(Actinium Volume)

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TABLE OF CONTENTS AND MAN POWER ANALYSIS

(Actinium Volume)

	Man Months	Page
SUMMARY		4
Construction of Facilities for the Actinium Separation Process - P. M. Engle	3 0	6
Actinium Extraction with Phenyltrifluoroacetone, W. S. Stringham	2 5	7
Chemical Apparatus for the Actinium Separation Process, W. T. Brown, W. S. Stringham	1 0	10
Dense Concrete for Cave Shielding P. M. Engle	1 0	11
A Surface Protective System to Assist in Decontamination, W. T. Brown	1 0	12
Reduction of Lanthanum from Liquid Ammonia - J. B. Otto	2 0	16
Fused Salt Polarography of Lanthanum - W. H. Power	2 0	20
Preparation of Lanthanum Metal by the DeBoer Process, G. Fish	3 5	25
The Separation of Lanthanum from Lanthanum Chloride with an Ion Gun with Variable Geometry. - D. L. Haas, D. B. Wehmeyer	2 0	33
The Separation of Lanthanum from Lanthanum Chloride with an Ion Gun with Fixed Geometry - L. G. Fauble	1 0	34
The Separation of Lanthanum from Lanthanum Chloride with Modified Calutron - D. B. Wehmeyer	1 5	38
Actinium Counting - R. W. Moshier	1 0	41
Preparation of Actinium-228 (Quantitative Data), J. B. Otto	1 0	44
Total	22 5	

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SUMMARY

The purpose of the research work presented in this volume is to develop a process for the separation and purification of actinium-227 produced by neutron bombardment of radium-226 and to develop methods by which uniform films of actinium metal may be deposited on metallic surfaces.

The design work on the cave structure and mechanical equipment used in the actinium separation is proceeding on schedule (p. 6). As the mechanical design phase is nearing completion the emphasis is being directed toward processing equipment.

The process as well as the mechanical equipment has been adapted from the research work of P. T. Hagemann and the Remote Control Group at Argonne National Laboratory. Consequently, one of the first objectives is to become familiar with the chemistry of the process and the operation of the mechanical equipment.

Cold runs have been made on the T.T.A. benzene extraction using lanthanum and barium in place of actinium and radium. No difficulty with the operation was observed. The formation of precipitates was one of the difficulties encountered with the process as the precipitates carry radium. It has been found that metals such as nickel cause these precipitates to form and should, therefore, be avoided in the construction of equipment. It was also found that a T.T.A. solution exposed to 0.5 curie of polonium over a period of days develops a precipitate (p. 7).

Some new mechanical features have shown promise. The use of copper-coated glassware which will hold together even though the glass is cracked has made it possible to replace custom-built heaters with standard heating mantles. A new graphite, silicone grease mixture appears to hold up in stopcocks handling benzene and, as a result, may eliminate the necessity of entering the cave for regreasing (p. 10).

Tests on the preparation of dense concrete have given results which meet the shielding requirements for the cave (p. 11). A strippable paint and tape combination has been studied and specified to provide for decontamination of the interior of the cave (p. 12).

A number of different methods for the preparation of actinium metal are being tested with lanthanum compounds. It has not been found possible to reduce lanthanum from liquid ammonia with metallic sodium. Electrolytic methods are being investigated (p. 16). Preliminary work has been started in an effort to determine polarographically the reduction potential of lanthanum from various fused salts (p. 20). An attempt to obtain lanthanum metal from the iodide by the DeBoer process is also under way. Lanthanum iodide vapor is thermally decomposed at a tungsten filament and the iodine vapor pumped from the system (p. 25).

Other pieces of apparatus have been constructed on the general principle of breaking molecular bonds by means of electron bombardment and withdrawing the positive ions with a suitable field (p.33). Electron currents of about one ampere and positive ion currents of about 10 milliamperes are required together with a high purity deposit of good yield at the desired location. A second instrument is being tested which provides for adjustment of the geometrical and electrical variables (p.34). Both instruments will bombard solid lanthanum chloride. A third instrument, which will bombard lanthanum chloride vapor, is expected to provide a higher yield of positive ions by having electrons oscillate through the vapor. The positive ions are to be withdrawn through a slot by an electric field and the lanthanum and chlorine ions separated by a magnetic field (p.38).

The problem of counting samples of actinium-227 is a difficult one because of the low energy of its beta radiation and its complex decay scheme. Some preliminary work has been directed toward the isolation and alpha counting of thorium-227, the first daughter of actinium, as a method of actinium assay. (p. 41)

The procedure for the isolation of actinium-228 from thorium for use in tracer experiments is completed in this report (p.44).

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Problem Title **Construction of Facilities for the Actinium Separation Process**
Report By **P. M. Engle**
Work Done By **W. T. Brown, P. M. Engle**

INTRODUCTION

As the design of the cave and other facilities is completed emphasis is shifting to the selection of processing equipment.

DETAILED REPORT

The drawings and specifications for the cave structure have been completed in cooperation with the Engineering Division. This material is now being employed by the Atomic Energy Commission in negotiating a prime contract for the construction of the cave.

Plans and specifications for the architectural, mechanical and electrical facilities to be installed in the portion of that Semi-Works Building and used by this project are nearly complete.

The construction and ordering of processing and miscellaneous equipment is proceeding satisfactorily, and several types of remote-control devices were completed by the shops.

Subject Title Actinium Extraction with Thionyltrifluoroacetone
Report by W. S. Stringham
Work Done by W. S. Stringham

INTRODUCTION

An investigation of use of thionyltrifluoroacetone (TTA) in the extraction of actinium from radium was made with lanthanum and barium as substitutes. Although the feasibility of this process has been demonstrated,¹ it was felt that experience in the operations involved would be valuable. Efficiency of separation was determined by checking the amount of cross-contamination.

An attempt was made to determine the origin of the precipitate that formed in the extractor and caused considerable difficulty during the actinium processing at Argonne National Laboratory.²

DETAILED REPORT

Lanthanum bromide, for use in simulated separations, was prepared by the addition of hydrobromic acid to lanthanum oxide. The oxide was prepared by the ignition of lanthanum nitrate at 800° for six hours. The barium bromide was prepared by adding hydrobromic acid to barium carbonate and purified by recrystallizing from methyl alcohol. Five grams of barium bromide was used in each cold run plus 77 milligrams of lanthanum oxide (as lanthanum bromide).

To determine the extent of cross-contamination the following methods of analysis were used

Barium in the nitric acid extraction of the TTA solution was determined colorimetrically as the chromate with a Coleman Spectrophotometer. The optimum wave length of the light source was determined to be 3800A. When ammonium chromate was added to barium ion, a yellow precipitate of barium chromate formed which, when dissolved in hydrochloric acid, afforded a means of estimating barium in low concentrations colorimetrically. A careful control of pH was necessary. The method involved is as follows:

- 1 The sample is neutralized with glacial acetic acid
- 2 Ten milliliters of 30 per cent ammonium acetate is added.
- 3 The barium chromate is precipitated, filtered, and dissolved in dilute hydrochloric acid.
- 4 The solution is diluted to 100 milliliters.
- 5 The transmittance of the sample is then read.

The color obtained followed Beers Law very well in the range 0.01-0.10 milligrams of barium per milliliter.

The methods given in the literature for determining lanthanum are too involved for application to this problem. A semiquantitative method was devised which would give a rapid indication of the lanthanum content of the aqueous barium bromide phase. Capillary centrifuge tubes were constructed by sealing a one inch length of 2 millimeter inside diameter capillary tubing sealed at one end to a 3 inch length of 10 millimeter inside diameter tubing. The sample was placed in the centrifuge tube. 2 drops of cresol red were added and the solution was then neutralized with ammonium hydroxide. The hydroxide was added with a 200-lambda pipet to insert the hydroxide into the capillary tube in order to insure complete precipitation. The sample was centrifuged for five minutes and the height of the precipitate compared with a standard precipitate. Fresh standards were made up each day. It was found that barium did not interfere with the lanthanum precipitation. This procedure is sufficiently sensitive to detect as little as 0.5 milligram of lanthanum per milliliter.

A complete extraction was made with the steps and quantities of reagents employed by Dr. Hagemann in the actinium processing.² No important difficulties with apparatus were observed. Analytical results gave 0.003 milligram of barium per milliliter in the lanthanum phase. No lanthanum could be detected in the barium phase after concentration and testing by the above procedure.

The principal difficulty encountered in the extraction operation at Argonne was the formation of a dark, flocculent precipitate which rapidly clogged the sintered bottom of the extraction flask and retained appreciable amounts of radium. Since no precipitate was observed in the simulated extraction described above, it was felt that this precipitate was caused by the action of the activity on the TTA. To test this theory an apparatus was set up to irradiate TTA under controlled conditions. At first a solid alpha source was used, but this was discontinued when it was found that metals seemed to catalyze the breakdown of TTA. A heavy precipitate occurs when nickel is used as a stirrer. Other metals such as iron and silver give a smaller amount of precipitate.

A mixture containing 25 milliliters of 0.25 molar TTA in benzene solution and 25 milliliters of nitric acid solution containing 0.5 curie of polonium was agitated in a glass stirring apparatus. After 48 hours a small amount of precipitate was formed. After four days enough precipitate was formed to cause the aqueous phase to be opaque. A longer testing time was employed since the amount of activity was much less than that present in the actual actinium separation.

From these results it appears that alpha radiation has a definite detrimental effect on TTA which cannot be avoided if TTA is used as a complexing agent. Whether this effect could be reduced to an insignificant amount by reducing concentrations or by other means has not been determined. It appears likely that this difficulty will remain as long as TTA extraction step is employed in the separation of actinium from radium.

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REFERENCES

1. Hagemann, F. T., The Isolation of Actinium, J. Am. Chem. Soc., 72, p. 768 (1950).
2. Engle, P. M. Preliminary Report on the Actinium Separation Project MLM-454, March 21, 1950.

Problem title **Chemical Apparatus for the Actinium Separation Process**
Report by **W. T. Brown, W. S. Stringham**
Work done by **W. T. Brown, W. S. Stringham**

INTRODUCTION

While the apparatus planned for the actinium separation process will be essentially a copy of that used at Argonne National Laboratory by Dr. Hagemann certain modifications are desirable. Changes that will be made include a new method of heating evaporation flasks and an improved stopcock lubricant.

DETAILED REPORT

To avoid the use of the custom-built heaters originally employed on the evaporating flasks in this process, it was decided to adapt standard heating mantles for this purpose.

The principal additional feature built into the Argonne heaters was a provision for retaining the liquid from the flask in case of breakage. The method we used to obtain this result consisted of plating the outside of the flask with 0.01-inch of copper. Ordinary round-bottomed flasks were employed and with this arrangement standard Glas-Col mantles provided satisfactory heating sources.

The procedure for applying the copper layer which worked most satisfactorily was to coat the bottom half of the flask with silver current-conducting paint, Dupont No. 4817. With the silver coating as a primary conductor, the desired copper layer can then be built up by plating from an acid copper sulfate bath at room temperature. Tests showed that flasks prepared in this way gave excellent heat transfer and that a flask containing an acid solution could be cracked without perforation of the copper layer or loss of liquid.

No satisfactory method was developed at Argonne for lubrication of stopcocks in contact with benzene solutions. This resulted in the necessity of relubricating these stopcocks or installing substitute apparatus after each run.

In an attempt to eliminate this difficulty a stopcock was lubricated with a mixture of silicone stopcock grease and graphite. This stopcock has been in contact with benzene for over six weeks without showing signs of sticking or leaking. During the initial portion of this test it was noted that the graphite-grease mixture was removed in the area through which the bore of the stopcock rotates. The ends, however, retain a sufficient amount of grease to insure smooth operation. Since in the actinium process neither the graphite nor the silicone lubricant would follow the valuable products, a slight removal of the lubricant can be permitted. This material should therefore, provide a completely satisfactory solution to the stopcock lubrication problem.

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Problem Title Dense Concrete for Cave Shielding
 Report by P. M. Engle
 Work Done By W. T. Brown, P. M. Engle

INTRODUCTION

Dense concrete will be used for certain portions of the cave structure to provide compact shielding at low cost. The composition and effectiveness of several experimental samples have been determined.

DETAILED REPORT

Considerable work was done on developing a dense concrete formulation that would meet the characteristics desired for the shielding panels of the cave front. It is desired that this material will have sufficient density so that a nine inch thick panel will be at least equivalent in shielding effectiveness to the six inch thick steel used in other portions of the cave. Data on several of the sample blocks cast are given in Table I. The dimensions of these blocks are approximately 7 by 7 by 4 inches. Shielding effectiveness was determined with an equilibrium radium source of gamma radiation and an ionization type meter.

TABLE I
 SHIELDING TESTS ON DENSE CONCRETE

SAMPLE NUMBER	2	3	5
COMPOSITION IN PER CENT			
CAST IRON SLUGS, 1 1/2" NCH	63.8		
STEEL PUNCH NGS, 1 1/2" TO 1 1/4" N.		64.5	39.1
STEEL SHOT, 1/8" NCH			29.9
FINE IRON*	22.8	25.8	21.8
CEMENT	9.4	6.7	6.0
WATER	4.0	3.0	3.3
SPECIFIC GRAVITY OF SAMPLE	5.25	5.61	5.63
SHIELDING EFFECTIVENESS** λ	0.243	0.254	0.255
MECHANICAL PROPERTIES	VERY GOOD	FAIR	GOOD

* THIS MATERIAL WAS FURNISHED BY MASTER BUILDERS COMPANY, CLEVELAND, OHIO AND IS KNOWN AS DIA. IT IS MILLED, CAST IRON OF KNOWN, GRADUATED PARTICLES AND CONTAINS A DISPERSING AGENT TO REDUCE THE AMOUNT OF WATER REQUIRED IN THE BATCH.

** THE ABSORPTION COEFFICIENT λ IS OBTAINED BY DIVIDING THE DIFFERENCE OF THE NATURAL LOGARITHMS OF THE RADIATION INTENSITY WITH AND WITHOUT THE SHIELD IN FEET BY THE THICKNESS OF THE SHIELD IN CENTIMETERS.

Samples 3 and 5 meet the shielding requirements of the cave and the formula chosen for construction will probably be similar to one of these two. Final selection will depend upon comparative price and delivery of the various components.

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Problem Title - A Surface Protective System to Assist in Decontamination

Report By - W. T. Brown

Work Done By - W. T. Brown

INTRODUCTION

Great difficulty was experienced at Argonne National Laboratory in decontaminating the cave interior at the completion of the actinium separation project. To avoid this difficulty, a surface protective system has been developed which appears to be superior to the Argonne system.

DETAILED REPORT

The protective coating schedule at Argonne was a system of refrigerator enamel, industrial tape, and additional refrigerator enamel. After operations had proceeded for a short time, they found it impossible to decontaminate the working surface by washing, and had to resort to removal of their tape layer for decontamination. Removing the tape was a procedure intended to be used only as a last resort.

Thinking the Argonne plan was basically acceptable, we conducted our investigations along a similar line. The requirements which we set out to meet were perhaps of a more severe nature than Argonne's. For instance, future uses of the development section of the cave were uncertain, and it was decided to make the cave capable of being dismantled as far as possible.

To satisfy these requirements, the basic materials must be kept as "cold" as is physically and economically feasible. In addition, we were looking for a solution to the periodic surface decontamination problem without disturbing the final protective covering. The main problem evolved into one of finding a strippable coating which could be placed over layers of industrial tape and paint to give primary protection against contamination. Resistance to corrosive agents was deemed of secondary importance in the outer and tape coatings.

The tests were conducted on small metal plates and/or concrete blocks with the facilities at Mound Laboratory. Amercoat products were obtained from the American Pipe and Construction Company, Los Angeles, California; oil-based paint from the Benjamin Moore Company, New York City; Packaid No. 18 from Seal-Peel Incorporated, Van Dyke, Michigan; Unichrome XL-1826 from United Chromium Incorporated, Carteret, New Jersey; Plastrip materials from Protective Treatments Incorporated, Dayton, Ohio; and industrial tape from Bauer and Black, Chicago, Illinois.

For the requirements stated, the following painting schedule for the interior of the proposed cave structure is recommended:

In order of their application

1. Concrete and steel base-protective coating of Amercoat No 33. Three heavy coats.
2. Industrial tape, Bauer and Black No. 113. One layer.
3. Tape seal-coat of Amercoat No. 33. One medium coat.
4. Parting agent of Amercoat No. 1395. One coat.
5. Strippable coating of Amercoat No. 1133. To produce solid film showing no bleed-through of Amercoat No. 1395.

Recommended precautions and amplifications on the application of the above schedule

1. Application may be by brushing or spraying.
2. Compatible equivalents of the above products may be used.
3. Special precautions should be taken to assure good adherence of the base-protective coating by complying with the manufacturers recommendations for application.
4. The tape passes should be overlapped to assure maximum protection. Attention should be given to rolling or otherwise pressing of the tape into firm and continuous contact with the base material.
5. The tape-seal coat must cover all tape edges.

The detailed results of tests are given in Table I.

TABLE I
RESULTS OF PROTECTIVE COATING TESTS

TEST NUMBER	BLOCK SEAL COAT	TAPE LAYER	TAPE SEAL COAT	STRIPPABLE COATING	RESULTS AND OBSERVATIONS
A	AMERCOAT No. 33 3 SPRAY COATS EYE-REST GREEN	BAUER & BLACK INDUSTRIAL TAPE No 113	AMERCOAT No. 33 2 SPRAY COATS EYE-REST GREEN	PACKAID No. 18 (WHITE) BRUSH COAT	UNSATISFACTORY. NO STRIP PROPERTIES TO THE PACKAID. FUSION AT PAINT BOUNDARIES. GOOD TAPE REMOVAL. NO GUM LEFT ON BLOCK.
F	AMERCOAT No. 33 3 SPRAY COATS. EYE-REST GREEN	BAUER & BLACK INDUSTRIAL TAPE No 113	BENJAMINE MOORE DULAMEL (MON- SANTO No. 1-4 EYE-REST GREEN) 2 BRUSH COATS.	PACKAID No. 18 (WHITE) 2 BRUSH COATS	UNSATISFACTORY. FAIR STRIP PROPERTIES. SOLVENT FROM PACKAID DIFFUSED THROUGH TAPE-SEAL COAT AND TAPE TO SOFTEN GUM ON BACK OF TAPE. POOR TAPE REMOVAL. DULAMEL SOFTENED AND IN SPOTS WAS REMOVED WITH THE STRIP COATING. ONE WEEK LATER AFTER AIR EXPOSURE - NO CHANGE. HEAT LAMP AT 4 1/2 INCHES FOR 1/2 HOUR, BETTER STRIP PROPERTIES. DULAMEL DRIED TO SOME EXTENT. GUM ON TAPE STILL SOFT
C	OMITTED	BAUER & BLACK INDUSTRIAL TAPE No 113	AMERCOAT No. 33 2 SPRAY COATS. EYE-REST GREEN.	AQUA PLASTIP (CLEAR) BRUSH COAT	UNSATISFACTORY. WATER SOFTENED STRIP COAT. PLASTIP SEEMED TOUGHER THAN PACKAID. TAPE STUCK VERY WELL TO BARE BLOCK.
D	OMITTED	BAUER & BLACK INDUSTRIAL TAPE No 113	BENJAMINE MOORE DULAMEL (MON- SANTO No. 1-4 EYE-REST GREEN) 2 BRUSH COATS	AQUA PLASTIP (CLEAR) BRUSH COAT	UNSATISFACTORY. STRIP COAT PULLED OFF A LITTLE OF THE PAINT. STRIP SOLUBLE IN WATER
E	OMITTED	BAUER & BLACK INDUSTRIAL TAPE No 113	BENJAMINE MOORE DULAMEL (MON- SANTO No. 1-4 EYE-REST GREEN) CUT WITH 40 PER CENT THINNER. BRUSH COAT.	PACKAID No. 18 (WHITE) BRUSH COAT.	UNSATISFACTORY. FAIR STRIPPABILITY AFTER STRIP REMOVAL. PAINT LAYER DAMP. TAPE HAD A TENDENCY TO BE PULLED OFF TOO. GUM ATTACHED BY PACKAID SOLVENTS
F	OMITTED	BAUER & BLACK INDUSTRIAL TAPE No 113	AMERCOAT No. 33 (GREEN) 3 SPRAY COATS FOLLOWED BY BENJAMINE MOORE DULAMEL (MONSANTO No. 1-4 EYE-REST GREEN) BRUSH COAT.	PACKAID No. 18 (WHITE) SPRAY COAT	UNSATISFACTORY. DULAMEL DID NOT GIVE SATISFACTORY SEAL TO AMERCOAT. POOR STRIP PROPERTIES. DULAMEL REMOVED WITH STRIP COATING.
G	OMITTED	BAUER & BLACK POLYEN No 900 SERIES BLACK	AMERCOAT No. 33 EYE REST GREEN	OMITTED	UNSATISFACTORY. NO ADHESION OF AMERCOAT TO TAPE

TABLE I (CONTINUED)
RESULTS OF PROTECTIVE COATING TESTS

TEST NUMBER	BLOCK SEAL COAT	TAPE LAYER	TAPE SEAL COAT	STRIPPABLE COATING		RESULTS AND OBSERVATIONS
H	OMITTED	BAUER & BLACK POLYKEN NO 800 SERIES - BLACK	PACKAID NO 18 (WHITE)	OMITTED		UNSATISFACTORY GUM ON TAPE SOFTENED GIVING POOR PULL OFF GOOD PACKAID STRIPPABILITY
I	OMITTED	BAUER & BLACK INDUSTRIAL NO 113	AMERCOAT NO 33	PLASTRIP C-179% BRUSH COAT		UNSATISFACTORY SIMILAR TO OBSERVATIONS UNDER "A" ABOVE
J	OMITTED	BAUER & BLACK INDUSTRIAL NO 113	AMERCOAT NO 33	UNICHROME XL-1826 BRUSH COAT		UNSATISFACTORY SIMILAR TO OBSERVATIONS UNDER "C" ABOVE
K	OMITTED	BAUER & BLACK INDUSTRIAL NO 113	AMERCOAT NO 33 FOLLOWED BY BENJAMINE MOORE DULAPIEL (MONSANTO NO 14 EYE-REST GREEN) 2 BRUSH COATS	PLASTRIP C-179% BRUSH COAT		UNSATISFACTORY SIMILAR TO OBSERVATIONS UNDER "F" ABOVE
PARTING AGENT						
L	OMITTED	BAUER & BLACK INDUSTRIAL NO 113	AMERCOAT NO 33 LIGHT SPRAY COAT	AMERCOAT NO. 1395	PACKAID NO. 18 (WHITE) OR AMERCOAT NO. 1133 (BLUE)	SATISFACTORY. GUM ON TAPE NOT AFFECTED VERY GOOD STRIP PROPERTIES PARTING AGENT STRIPPABLE WHEN FILM CUT OR BROKEN.
M	OMITTED	BAUER & BLACK INDUSTRIAL NO 113		AQUA-PLASTRIP 2 BRUSH COATS	AMERCOAT NO. 1133 (BLUE).	UNSATISFACTORY. JUST ENOUGH MIXING AT BOUNDARY TO PREVENT STRIPPING
N	OMITTED	BAUER & BLACK INDUSTRIAL NO 113		AMERCOAT NO. 1395		UNSATISFACTORY TAPE SHRINKAGE CAUSED TAPE TO CURL AND PULL OFF BASE

Problem Title **Reduction of Lanthanum from Liquid Ammonia**
Report by **J. B. Otto**
Work Done By **J. B. Otto**

INTRODUCTION

Exploratory work on the chemistry of lanthanum in liquid ammonium is in progress in order to determine if this solvent will prove a suitable medium for the reduction of lanthanum compounds to metallic lanthanum. It is hoped that any useful information in this regard can be carried over to actinium compounds. Attempts have been made to reduce the lanthanum ion in liquid ammonia both electrolytically and by the action of a solution of elemental sodium in the same solvent. The latter method was found not to work, the former is in the process of investigation.

DETAILED REPORT

In order to determine if liquid ammonia reacted with metallic lanthanum, some freshly cut pieces of this metal were sealed up in a tube with liquid ammonia. The metallic luster of the freshly cut surfaces of the metal chips remained unchanged for several weeks. There was no indication of hydrogen formation. This evidence tends to indicate that lanthanum is unaffected by liquid ammonia. It should be pointed out that, even though precautions were taken to prevent it, there is a possibility that the lanthanum metal surfaces exposed to the liquid ammonia were covered with a protective oxide coating. This could be true despite the fact that the freshly cut surfaces had a bright metallic luster and appeared to be free of macroquantities of oxide.

Lanthanum iodide was chosen as a suitable compound from which to attempt reduction to the metal in liquid ammonia. This choice was made because iodides tend to be soluble in liquid ammonia and the iodide ion is non-reducible. Bergstrom¹ reports lanthanum iodide to be "moderately" soluble in liquid ammonia at room temperature. Lanthanum iodide is the only lanthanum compound whose solubility is reported in the literature. The anhydrous lanthanum iodide used in this work was prepared by a modification and combination of the methods of Young and Hastings² and that given in Inorganic Synthesis.³ These methods depend on the interaction at elevated temperature of lanthanum oxide and ammonium iodide and the final removal of the excess of the latter by sublimation *in vacuo* leaving almost pure anhydrous lanthanum iodide. Analysis of the product gave the following results. (calculated values based on the formula, LaI_3 , are given in parentheses) per cent lanthanum, 28.53 (26.73); per cent iodine, 69.29 (73.27). These results indicate the lanthanum iodide prepared contains around three per cent unconverted oxide.

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Attempts to reduce lanthanum from lanthanum iodide with sodium were carried out at the boiling point of liquid ammonia, about -33° . Small unsilvered Dewar flasks were used as reaction vessels. The light tan anhydrous lanthanum iodide turned reddish to dark brown immediately on contact with gaseous ammonia, on contact with liquid ammonia its color became white, and it appeared to be amorphous in character. When about 100 milliliters of liquid ammonia was added to about 0.5 gram of lanthanum iodide at -33° , the result was a white, amorphous suspension. Addition of an insufficient amount of sodium to reduce all the lanthanum to the metal only imparted the dark blue color to the suspension which is characteristic of a solution of sodium in liquid ammonia. The intensity of the blue color caused by excess sodium appeared to be undiminished after $1\frac{1}{2}$ hours, indicating that no reaction was taking place between the dissolved sodium and the precipitate. In order to see if any change had taken place in the precipitate, nearly all the blue color was discharged from the reaction mixture by addition of ammonium iodide which reacts with the excess of sodium with the evolution of hydrogen. The precipitate in the faintly blue (caused by an extremely small excess of sodium) solution was white and amorphous, and appeared to have been totally unaffected by the sodium solution. This confirmed the previous observation that no reaction had occurred between the insoluble lanthanum iodide precipitate and the sodium solution.

The insolubility of lanthanum iodide which may account for its unreactivity toward sodium in liquid ammonia has been shown to be due to ammonolysis. The first step of this reaction is shown in Equation 1

Ammonolysis products in ammonia, like hydrolysis products in water, are usually extremely insoluble in the cases of the heavy elements. According to Equation 1 the addition of ammonium iodide to the insoluble lanthanum iodide precipitate would shift the equilibrium to the left and tend to dissolve the ammonolysis product. In actual practice it was difficult to tell whether or not the presence of ammonium iodide increased the solubility of the lanthanum iodide used in this work because its impurities (presumably mainly La_2O_3) were also insoluble in liquid ammonia. This difficulty was overcome by dissolving lanthanum metal in a solution of ammonium iodide in liquid ammonia. This reaction had been previously carried out by Bergstrom¹ who first observed the solubility of lanthanum iodide in liquid ammonia. It proceeds according to Equation 2.

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A number of small chips of lanthanum metal were treated with about two grams of ammonium iodide in about 100 milliliters of liquid ammonia at -33° . The rate of reaction between the lanthanum and ammonium iodide, as evidenced by the extremely fine stream of hydrogen bubbles evolved, was quite slow. For this reason the reaction was allowed to proceed over night to provide sufficient lanthanum iodide in solution to work with. About 90 milliliters of the clear supernatant liquid was then decanted from above the still-reacting lanthanum chips into another unsilvered Dewar flask. This clear solution of lanthanum iodide was then treated with small pieces of sodium metal in an attempt to reduce lanthanum to the metal. The sodium, however, only reacted with the excess ammonium iodide with the production of hydrogen. Just at the point where almost all the excess ammonium iodide had been used up by reaction with sodium, a precipitate began to form which would not react with excess sodium. The precipitate, which was white and appeared to be amorphous dissolved when about two grams of ammonium iodide was added. Rough quantitative analysis on the residue after the liquid ammonia had evaporated showed that about 230 milligrams of lanthanum iodide had been present in the 90 milliliters of liquid ammonia solution. These results show that lanthanum iodide ammonolyzes in neutral liquid ammonia to form a very insoluble precipitate which may be redissolved by addition of ammonium iodide which shifts the equilibrium back toward unammonolyzed lanthanum iodide (see Equation 1). These results also confirm the observation that lanthanum iodide is not reducible to lanthanum metal by sodium in liquid ammonia at -33° .

Attempts to reduce lanthanum iodide with sodium in liquid ammonia at room temperature in sealed tubes also failed. No change was noted in the extremely insoluble precipitate produced by lanthanum iodide after it had been subjected to the above conditions overnight.

Since lanthanum iodide was found to be soluble in a dilute liquid ammonia solution of ammonium iodide, this solution was considered to be suitable for studies directed toward reduction of lanthanum electrolytically. The first approach to this problem was made polarographically to determine if a lanthanum reduction wave could be obtained. These experiments were carried out at the boiling point of liquid ammonia, -33° , in an unsilvered Dewar flask equipped with a mercury pool anode and dropping mercury cathode. The agitation of the solution by slow boiling made the results only slightly erratic. The first polarographic electrolysis was carried out on the supporting electrolyte only which was 100 milliliters of 0.1 molar ammonium iodide. The current-voltage curve was almost perfectly horizontal until the potential reached -1.3 volts from which point the current began to increase until it reached an unlimited value at about -1.6 volts. Potentials were measured against the mercury pool anode. The above experiment was repeated under identical conditions

(supporting electrolyte, 0.1 molar ammonium iodide) except the solution was made about two millimolar in lanthanum iodide. The results were identical with those obtained in the previous experiment indicating that no lanthanum reduction wave could be obtained below -1.6 volts in liquid ammonia. The large reduction current obtained at -1.6 volts may be caused by the reduction of the ammonium ion. It has been shown that the ammonium ion produces a reduction wave at -1.69 volts measured against the mercury pool anode.^{4,5} In this case the solution was about 0.4 millimolar in ammonium ion, and the supporting electrolyte was saturated tetra-n-butylammonium iodide.⁴ It has been suggested that, in the present investigation, the ammonium ion concentration be lowered to such a point that a limiting current would occur for this ion. This would allow one to study the reduction of lanthanum ion above -1.6 volts. The work is to be continued along this line.

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Problem Title **Fused Salt Polarography of Lanthanum**

Report By **W. H. Power**

Work Done By - **W. H. Power**

INTRODUCTION

The strong basic nature of lanthanum makes reduction to the metal impossible in aqueous solution. The use of fused salts as an electrolyte and solvent for lanthanum salts is being considered as a possible method of plating metallic lanthanum. Trombe,¹ Shumacher,² Mazza,³ Wiebke,⁴ and Kremers,⁵ have prepared metallic lanthanum by electrolytic reduction from fused salt baths of lanthanum chloride or of a mixture of alkali metal salts containing lanthanum chloride as a major constituent. Since only microquantities of actinium (represented here by lanthanum) salt will be available for reduction to the metal, an electrolysis method is desired which is applicable to trace quantities of lanthanum salts dissolved in a fused salt electrolyte. The polarographic technique is particularly applicable for studying electroreduction of materials present as minor constituents. Steinberg and Nachtrieb⁶ have adapted the polarographic method for studying the reduction of weakly basic elements as lead or cadmium from eutectic mixtures of sodium, potassium, and lithium nitrates at 160°.

DETAILED REPORT

The apparatus described by Steinberg and Nachtrieb⁶ was assembled. All cells were swept with nitrogen dried by passage through a sodium sulfate tube, and freed from oxygen by passing over hot copper turnings for a half hour prior to electrolysis to remove oxygen from the cell. During the electrolysis the nitrogen inlet tube was raised to a position just above the melt and the gas flow continued. When the dropping mercury cathode was used, the decomposition potential of the sodium, potassium, and lithium nitrate solution was 0.9 volts more negative than the calomel electrode. A satisfactory polarogram was obtained for the reduction of 10 millimolar lead nitrate by a dropping mercury cathode in the fused nitrate electrolyte at 160°.

The reduction of an element as basic as lanthanum would probably require potentials more negative than the nitrate decomposition potential, so fused chlorides were considered as solvents. Since the vapor pressure of mercury becomes too great for use at the temperatures of molten chlorides, solid metal electrodes were substituted for mercury cathodes. Satisfactory polarograms for lead reduction could not be produced in the nitrate fused salt mix when a platinum cathode was used because of solvent decomposition at potentials of the same value as those required for lead reduction (-0.45 volt). Solvent decomposition also occurred at low applied voltages when the fused nitrate mixture was electrolyzed with tantalum, gold, or tungsten cathodes.

Fused Chlorides

A eutectic mixture of 59.5 per cent potassium chloride and 40.5 per cent lithium chloride with a melting point of 352° was electrolyzed with platinum electrodes (5-millimeter length by 0.5-millimeter diameter) at 425° . Current was found to be proportional to applied cell voltage (Figure 1-A). Similar results were obtained when the platinum electrodes were replaced by graphite electrodes. This result was surprising, since the usual flat current-voltage curve up to the decomposition potential was not produced. Steinberg and Nachtrieb⁶ found similar results when electrolyzing fused chlorides at 1000° with a dropping silver cathode and suggested that metallic sodium was produced at the cathode, even at very low applied voltages. In any case, the high background current makes polarography difficult or impossible. If sodium is reduced at low applied potentials, any reduced lanthanum would be contaminated with alkali metals.

Fused Potassium Acetate

Some indication was found that fused potassium acetate (melting point 292°) could be used for electrolysis. The salt shows the expected flat decomposition curve when electrolyzed between platinum electrodes (5-millimeter length by 0.5-millimeter diameter) at 330° (Figure 2-A). Lead chloride solutions in fused potassium acetate showed immediate reduction and plateaus qualitatively proportional to their concentrations (Figures 2-B and 2-C.)

Lanthanum chloride (prepared by dissolving the oxide in concentrated hydrochloric acid and evaporating) was added to the potassium acetate solvent in concentrations of 0.07 and 0.18 per cent. Definite polarograms were not obtained, but some evidence of reduction was indicated by larger currents than background at all applied voltages (Figures 2-D and 2-E.) At a cell voltage of 1.4 volts, a slight leveling of the current-voltage relation suggested the presence of a diffusion current.

To determine if the cell currents, noticed when electrolyzing lanthanum solutions in molten potassium acetate, were caused by lanthanum reduction, the following experiment was performed. A mixture of 0.5 gram of lanthanum acetate (prepared by dissolving the oxide in glacial acetic acid and evaporating) and 10 grams of potassium acetate was prepared. The solubility of the lanthanum salt was exceeded, so most of it existed as a suspended solid. The mixture was electrolyzed between platinum electrodes with an applied cell voltage of 0.75 volt for 5 hours at 315° . Nitrogen was continually passed through the melt to exclude oxygen and to remove any gaseous anode products. There was little change of appearance of the platinum cathode after electrolysis. When the cathode was immersed in dilute hydrochloric acid, a brief but vigorous gassing was noticed. This gassing might have been either metallic potassium or lanthanum being attacked by the acid. When portions of the solidified melt were

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added to dilute hydrochloric acid, similar gassing was noticed. A small piece of the melt was added to liquid ammonia to test for the presence of metallic sodium by the characteristic blue color. The absence of the blue color with liquid ammonia indicated that minute quantities of metallic lanthanum rather than sodium had been produced by the electrolysis and were responsible for reduction of hydrogen gas from hydrochloric acid. The metallic lanthanum, if present, must have been disseminated in the melt as well as being present on the cathode.

Potassium Formate

Potassium formate is being investigated as a possible solvent for the reduction of lanthanum. The low melting point of potassium formate (168°) allows the use of the dropping mercury electrode and the mercury anode for polarographic cells.

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-24-

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FIGURE 2

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Problem Title - Preparation of Lanthanum Metal by the DeBoer Process

Report by G. Pish

Work done By - G. Pish and J. M. Goode

INTRODUCTION

The preparation of lanthanum from its iodide by the DeBoer process was under investigation to determine whether the method worked and could be applied to the preparation of actinium. The method required the preparation of anhydrous LaI₃ which was then heated *in vacuo* and vaporized. These vapors were thermally reduced by a heated wire depositing the lanthanum on the wire while the free iodine vapors evolved were removed. This coated wire could possibly be used as a filament in a vacuum metallizer and the film redeposited upon any suitable surface.

Historical Note

During 1930 DeBoer and Fast¹ reported a method for purifying hafnium, zirconium, and other metals by a process in which impurities were avoided and even ductile single crystals prepared. A cylindrical bulb was made containing a small side arm, a vacuum connection, and a Vee tungsten filament. The impure metal was placed in the bottom of the bulb, and a small amount of iodine was placed in the small side arm. During the evacuation of the bulb, the metal was heated to 550° to remove most of the absorbed gases. Then the apparatus was sealed and placed in an electric furnace where the iodine vapor attacked the metal, i.e. hafnium. The readily volatilized hafnium tetraiodide was formed and soon reduced on the glowing tungsten wire (heated to 1200-1400°) leaving a deposit of pure hafnium.

Subsequent workers modified the DeBoer process and extended its use to other types of reactions. Campbell² and his co-workers presented an excellent review of the vapor-phase deposition of refractory materials. "Two general plating methods are used. (1) Chemical reduction or reaction at the surface. In this class are (a) hydrogen reduction of halides, (b) reaction of halides with a gas containing C, N, B, Si, or O, (c) displacement or reaction of the base material with one of the constituents of the gas phase. (2) Thermal decomposition at the surface. (a) at high temperatures - halides and oxygen-containing compounds, and (b) at low temperatures - carbonyls and hydrides." The following metals were prepared by the DeBoer process by one or more of the above generalized reactions: Ti, Zr, Hf, Th, V, Co, Ta, Cr, Mo, W, U, Re, Ru, Rh, Os, Ir, Pt. Similarly the process can be adapted to prepare carbides, nitrides, borides, silicides, and oxides² of a large number of metals or their compounds.

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SUMMARY

Several experiments to prepare lanthanum by the DeBoer process were without success, since a suitable, small-volume DeBoer apparatus which could withstand temperatures above 700° presented practical problems. The conventional Pyrex apparatus began to soften just above 532° at 10^{-4} millimeter pressure. A similar apparatus of Pyrex and Vycor (components joined by tapered joints) was made. The Vycor portion was heated while the Pyrex portion remained comparatively cool. Upon heating the LaI_3 in the Vycor portion it vaporized, redeposited on the cooler walls of the Pyrex and was not available for decomposition by the heated wire.

To heat the entire DeBoer tube successfully it is desirable to have an all quartz apparatus of small volume. However, vacuum-tight quartz-metal seals are extremely difficult to prepare and no one at Mound Laboratory was able to prepare suitable seals of this type. Therefore a number of quartz-metal seals were prepared by different methods and tested. The most recently designed quartz-molybdenum seals easily pumped down to 5×10^{-5} millimeter pressure but still were not completely vacuum tight. It is believed further experimentation will produce successful quartz molybdenum seals which can be incorporated in a small-volume, quartz DeBoer reaction tube.

DETAILED REPORT

Experiment 1 A DeBoer reaction bulb of Pyrex was constructed as shown in Figure 1. In all experiments the temperature of the hot wire was determined with an optical pyrometer, and the furnace temperature was controlled with a Leeds and Northrup control unit. The LaI_3 used was supplied by J. B. Otto of the Chemistry Section.

About 2 grams of LaI_3 were transferred into the DeBoer bulb and outgassed for two hours at 200° and 10^{-4} millimeter pressure. The temperature and pressure were changed to 532° and 10^{-5} millimeter pressure and at the same time the filament temperature was approximately 1100° . At the beginning of the run, copious volumes of iodine vapors were evolved, and the pressure dropped to 10^{-2} to 10^{-3} millimeter. Some uncombined iodine was presumably present in the starting salt. During the remainder of the run (6 hours), no vapor was observed and no change in pressure was noted. However, some vacuum grease did seep through from the system to the hot wire. The temperature of the reaction bulb could not be increased as the Pyrex showed visible signs of softening.

Since the temperature was not high enough to vaporize LaI_3 , the salt remained at the bottom of the bulb. X-ray diffraction analysis of the filament from the bulb showed the presence of tungsten carbide which was attributed to decomposition of the vacuum grease.

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Experiment 2. The DeBoer apparatus was redesigned (Figure 2) for operation at higher temperatures. Three grams of LaI_3 were transferred to the DeBoer bulb under a dried helium atmosphere. Both sections of the bulb were sealed with silicone grease on the taper joints and evacuated first without heating. At this point considerable free iodine vapor was drawn off. During the outgassing period at 2 to 3 microns pressure and 220° , iodine vapor continued to be evolved.

After raising the temperature of the furnace gradually to 890° (hot wire temperature about 1100°), the pressure dropped to 10^{-4} to 10^{-5} millimeter the heating process was continued for four hours.

The apparatus was then cooled to room temperature. Examination of the contents in the bulb showed that all the LaI_3 vaporized and again redeposited in the upper, cooler portion of the unheated Pyrex section.

X-ray diffraction examination of the wire filament showed the presence of tungsten carbide and some unknown compounds. The diffraction lines for the unknown compounds were too faint to be classified.

Further examination of the coated DeBoer bulb showed a minute crack in the base of the Vycor tube (perhaps responsible for the impurities detected on the wire). X-ray diffraction analysis of a control sample of tungsten wire showed no impurities present.

In order to avoid future problems of moisture air contamination etc LaI_3 will be made directly in the vacuum system. To heat the entire DeBoer bulb successfully, a small-volume all-quartz apparatus is considered. However metal quartz electrode seals were considered extremely difficult to prepare and unavailable commercially.

Experiment 3. All attempts to seal quartz directly to tungsten resulted in cracked seals and very brittle tungsten electrodes. These seals were as follows:

- 1 Quartz capillaries collapsed onto 040-inch tungsten wire.
2. Very thin quartz tubing collapsed onto 040 inch tungsten wire
- 3 Very thin quartz tubing collapsed onto 005-inch tungsten wire

Similarly several indirect schemes failed and are illustrated in Figure 3

Experiment 4. Dry helium gas was passed through and around a quartz tube (2-millimeter bore and 1-millimeter wall thickness) containing strips of molybdenum foil .010 by 1/16-inch in cross-section. After heating the assembly to outgas the components, the tube was collapsed onto the foil and further heated to flow the quartz and provide a glass-metal bond. Examination of this seal showed that the sealed portions leaked and that the electrode became very brittle. A number of repeated efforts with .006 to .015-inch foils and wire of both molybdenum and tungsten gave the same results

A number of molybdenum foil strips from 1/32 to 1/16-inch wide and .002 to .010-inch thick were sheared from a sheet and used in experiments without further treatment. With 4-millimeter outside diameter (2-millimeter inside diameter) quartz capillary, a strip of molybdenum foil was placed into a sealed-off end (Illustration 1, Figure 4). The open end was attached to a high-vacuum system. First the tube and foil were evacuated to 10^{-4} to 10^{-5} millimeter without heating and then flamed to degas the parts. The tube was carefully collapsed onto the foil and then it was heated strongly to flow the quartz and provide a vacuum-tight seal (Illustration 2, Figure 4). Upon cooling and reheating no fractures or cracks appeared in the quartz. The sealed end of the quartz was cut open (Illustration 3, Figure 4) and tested on the same vacuum system for vacuum tightness. The electrodes did not show any signs of embrittlement. Results of the tests are given in Table I.

TABLE I

VACUUM TEST OF MOLYBDENUM-QUARTZ SEALS

SIZE OF ELECTRODE (INCHES)	VACUUM MAINTAINED (CONT'D PUMPING) (MILLIMETERS)	REMARKS (SYSTEM CLOSED OFF)
1/16 BY 0.010	4 BY 10^{-4}	SEAL LEAKED RATHER RAPIDLY.
1/32 BY 0.010	4 BY 10^{-4}	
1/16 BY 0.002	5 BY 10^{-5}	VERY SLOW LEAK.
1/32 BY 0.002	5 BY 10^{-5}	

Since the results with 0.002-inch molybdenum foil look promising, further modifications may result in satisfactory metal-quartz seals.

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FIGURE 1

MLM-519

TOTAL LENGTH 7"
REACTION PORTION 4" X 1 1/4" DIA.

- ① TUNGSTEN ELECTRODE 0.50" DIA.
- ② TUNGSTEN WIRE 0.015" DIA.
- ③ CORE TYPE FURNACE
- ④ ASBESTOS PLUG
- ⑤ ANHYDROUS LaI_3

PYREX DE BOER BULB

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TOTAL LENGTH 7"

- ① PYREX TAPER JOINT ASSEMBLY
- ② VYCOR TAPER JOINT ASSEMBLY 6" X 1" DIA.
- ③ TUNGSTEN ELECTRODE 1/16" DIA.
- ④ TUNGSTEN WIRE 0.015" DIA.
- ⑤ CORE TYPE FURNACE
- ⑥ ASBESTOS PLUG
- ⑦ ANHYDROUS LiI_3

PYREX-VYCOR DE BOER BULB.

UNCLASSIFIED
-31-

0.015" TUNGSTEN SEALED IN PYREX THEN SEALED TO TIP OF QUARTZ TUBE. PYREX CRACKED UPON COOLING.

0.015" TUNGSTEN FIRST SEALED IN PYREX. PL FILM FORMED ON QUARTZ END. THEN PYREX SEALED TO PL OF QUARTZ AFTER COOLING PYREX CRACKED.

SAME AS (2) EXCEPT URANIUM GLASS SUBSTITUTED FOR PYREX. URANIUM GLASS CRACKED AFTER COOLING.

SIMILAR TO (2). PYREX GLASS SWEATED ONTO PLATINUM COATED QUARTZ END. THEN PYREX, WITH ELECTRODE, SEALED TO THE FILM. PYREX FILM CRACKED AFTER COOLING.

ATTEMPTED QUARTZ TO METAL SEALS.

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FIGURE 3

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QUARTZ-METAL SEALS PREPARED BY VACUUM METHOD.

Problem Title - The Separation of Lanthanum from Lanthanum Chloride with an Ion Gun with Variable Geometry.

Report By - D. L. Haas, D. B. Wehmeyer

Work Done by - D. L. Haas, C. L. Leshner, C. H. Mellor, D. B. Wehmeyer

INTRODUCTION

In preparation for work with actinium and its compounds, an attempt is being made to perform operations with lanthanum as a substitute for actinium. In this connection, the problem of the preparation of metallic lanthanum from the compound LaCl_3 was approached from a physical standpoint. If anhydrous LaCl_3 is bombarded with an intense electron beam in high vacuum, it will volatilize and dissociate, forming lanthanum ions. If then a difference of potential exists between the unvolatilized LaCl_3 and a plate, lanthanum ions will be deposited on this plate.

DETAILED REPORT

Two heavy tungsten filaments were placed on opposite sides of a large glass bulb (9-inch diameter) and two copper plates were mounted, one at the top and one at the bottom of the bulb, with a spacing of about three inches between them. The bottom copper plate was water cooled and was covered with a thin sheet of stainless steel on which was placed a charge of anhydrous LaCl_3 . The bottom plate was grounded, and the filaments were run at a potential of -300 to -500 volts. With filament temperatures of 1700° to 1900° , emission current of 10 to 20 milliamperes was obtained. The collector plate on the top was at a potential of 500 to 1,000 volts negative with respect to the charge plate on the bottom. No ion currents greater than one milliampere were observed. Operating pressure was of the order of 10^{-4} millimeter of mercury.

Two runs were made with negative results. The first run terminated when a soft-solder seal broke and the vacuum was lost. The second run was maintained for a week, after which no apparent plating had occurred on the top plate. The experiment was discontinued in favor of an improved design and other methods of obtaining larger ion currents.

Problem Title - **The Separation of Lanthanum from Lanthanum Chloride with an Ion Gun with Fixed Geometry**

Report By - L G Fauble

Work Done By - L G Fauble

INTRODUCTION

The production of pure actinium and its deposition on complex metal forms is complicated by the present lack of actinium compounds with which to work. Lanthanum compounds should have closely similar chemical and physical properties and therefore are being used as "standins" until actinium becomes available.

The high melting point and high reactivity of the metal make it difficult to use standard methods of preparation and deposition such as electrolysis or volatilization. For this reason it would be advantageous if preparation and deposition of the pure metal could be accomplished in a single step. Ionic beam techniques should be a viable solution of both problems if an intense beam of the metal ions can be separated from the other ions formed.

Smith and Scott¹ have set forth the condition required for producing intense ion beams. Their work was largely concerned with protons, deuterons, and alpha particles. Production of ions occurred by bombardment of the molecules with electrons of suitable energies.

Intense ion beams have been used in the calutron-type mass spectrograph in the separation of isotopes at Oak Ridge, but with the consumption of large quantities of power and with rather low yields.²

To test the feasibility of electron bombardment on solid materials to produce ions, a simple apparatus has been designed and built. It will be flexible so that a large number of conditions can be varied to select the best method for use in this problem.

DETAILED REPORT

The apparatus shown in Figures 1 and 2 has been constructed. The base plate is made of a six-inch-square brass plate one-fourth inch thick. Six electrical leads, made of Stupakoff seals, have been provided. Supports for the ionization plate, the filament ring, and the collection plate are made of aluminum and are screwed to the baseplate. A belljar, made of a section of four-inch Pyrex pipe, is lowered over the assembly and held in place by four quarter-inch bolts through the flange and the baseplate so that the unit may be operated in a vacuum. A well-greased rubber gasket makes the joint vacuum tight.

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Electrical leads, shown in the photographs as solid wires, have been replaced by flexible copper wires with porcelain-bead insulation.

The ionization plate as well as the collector plate are made of gold-plated brass. The filament support and reflector is made of a brass ring with a circular groove cut in the lower inside portions into which the filament is recessed. The groove acts as the reflector. A single No. 26 tungsten wire was originally installed, but subsequent experimentation has shown that a filament made of tantalum produces a higher electron current and will be used in all future experiments.

In operation, the filament is heated to incandescence with a low-voltage high-amperage alternating-current transformer controlled by a Variac. An arbitrary potential is applied between the filament and the ionization plate to attract the electrons from the filament to the plate. Samples of lanthanum halides will be placed on the surface of this plate so that the bombarding electrons will strike them, thereby ionizing the salt to lanthanum ions and halide ions as well as other mixed ions. By varying the accelerating voltage it is hoped to produce mainly lanthanum ions with only small amounts of mixed lanthanum halide ions.

To remove the ions as rapidly as they are formed, a high potential (up to 5000 volts) is applied between the ionization plate and the collection plate. Ions accelerated to the collection plate are neutralized and deposited on this plate.

To date, an electron current of eight milliamperes has been achieved with an electron accelerating potential of 300 volts. The apparatus was not operated for a sufficient length of time to show any deposit on the collector plate because the requisite low pressure required for efficient operation has not been reached. Experimentation will be continued.

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ION SOURCE
(ASSEMBLED)

ION SOURCE

Project Title **The Separation of Lanthanum Chloride with Modified Calutron**
Report By D B Wehmeyer
Work Done By D B Wehmeyer

INTRODUCTION

A small calutron-type mass spectrometer has been constructed as a possible physical means of preparing lanthanum metal from anhydrous LaCl_3 . If the method works well in this case, it may be applicable to the preparation of pure actinium under similar circumstances. Construction and testing of the equipment has been completed and a first trial run is ready to proceed.

DETAILED REPORT

Ion sources are generally fairly inefficient, but high ionization efficiency (of the order of 100 per cent) has been obtained by the use of oscillating electrons.² The present source, (shown in Figure 1) is of this type. A stream of oscillating electrons is maintained in a hole in a carbon block. The hole is aligned with a magnetic field so that the electrons are free to move only along the length of the hole. Two filaments are mounted, one on each side of the carbon block at the ends of the hole. An electron emitted by one of these filaments is accelerated by a potential of about 100 volts, travels through the hole, and is decelerated on the other side by an opposing potential as it approaches the other filament. If the electron has lost a small amount of energy in an ionizing collision, it will be turned back by the potential before it hits the second filament. It then passes through the hole again and is reflected again on the first side, thus oscillating until its energy is gone, and permitting a large number of ionizing collisions per electron.

A sample of LaCl_3 is placed on a third filament, inside and near the bottom of the carbon block. Heating this filament will volatilize the LaCl_3 , which then passes through the stream of oscillating electrons where ions of lanthanum and chlorine are formed. The positive ions formed are pulled out through a slit in the top of the carbon block by a high potential into a copper cage. The positive-ion beam should consist of La^+ and Cl^+ ions in the greatest concentration, though other ions may be present in large numbers. The magnetic field will separate these ions by mass and charge so that a collector plate placed a distance along the La^+ path should receive almost only La^+ . This may be a means of plating lanthanum metal directly, or it may be that a further process will have to be used for plating.

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Construction of the spectrometer was kept as simple as possible. The carbon block was machined with a file and a small hand drill. The high-voltage cage was made of bare copper wire and silver solder. The tungsten filaments were spiral wound and originally designed for an X-ray source. The source itself was mounted on the base of an ion-gauge tube which had four metal-to-glass lead-ins for electrical connections.

The spectrometer has an overall length of six inches and a width of about one and one-half inches.

The high voltage is planned to be of the order of 1,000 volts, and the magnetic field about 1,000 gauss. A one-half inch separation of La^+ and Cl^+ ions should be achieved after about four inches of ion path length in the field. The four-inch magnet, used in the Hall effect measurements,² will be used to supply the magnetic field.

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Problem Title **Actinium Counting**
Report By **R. W. Moshier**
Work Done By **N. E. Rogers**

INTRODUCTION

In order to assay actinium-227 and to follow the progress of an actinium purification process, a rapid method is needed for obtaining the amount of actinium present. There are several possibilities for making such an assay. These depend upon the counting of the actinium or any of its daughters which have a sufficiently long half-life to permit a chemical or physical separation. In all counting the value obtained will need to be corrected for growth and decay during the time elapsed between separation and counting.

Since the age of an actinium sample will be uncertain, it would be necessary to repurify it by making a chemical separation from its daughters before assaying. An alpha count on the purified sample can then be made. The energy of the actinium beta emission is too low for efficient counting.

A method for the isolation of the francium-223, daughter of actinium-227, has been described for the accurate assay of actinium.¹ Francium is an alkali metal and remains in solution after chemical removal of all other radioactive elements except thallium. It is a beta emitter of 21 minute half-life and the claim is that an assay can be made in a few hours by this method. It must be borne in mind that accurate timing would be necessary. Since francium-223 is the product of the 1.2 per cent alpha decay of actinium, the activity could be no greater than direct alpha counting of freshly purified actinium. However, the amount of beta activity present from the decay products would be less for the francium than for the actinium from which it was separated.

Baranov² has developed an absolute quantitative determination of actinium by the emanation method. By this method it is obvious that the actinium would need to be aged to be in equilibrium with its daughters to obtain equilibrium actinon, unless its age was accurately known. From the experience of our laboratory the emanation method is difficult to operate.

As observed at the Argonne National Laboratory, the thorium and radium daughters of actinium may readily be separated from the actinium by chemical means. These daughters have desirably long half-lives: thorium-227, 18.9, radium-223, 11.2 days. Here it would be necessary to repurify the actinium, allow the daughters to grow for a definite interval, make the separation, and then count.

From the point of rapidity the francium method would be best, since the growth to equilibrium would be very rapid in comparison to that of other daughters. This is off-set by the fact that only 1.2 per cent of the actinium decays to francium which puts the actual number of disintegrations per unit time on about a par with thorium counting.

Thorium can be isolated from a 0.1 normal hydrochloric acid solution by extraction with 0.25 molar thenoyltrifluoroacetate in benzene,⁹ and counted. As an alternate method, all of the radioactive daughters except radium and francium may be removed by a similar extraction at pH 6. The radium thus left in the aqueous solution can be used for the assay after the francium has decayed.

Since the thorium extraction is the simplest for isolation of only one daughter element, a method is being developed for actinium assay by extraction and counting of thorium.

DETAILED REPORT

The actinium stock solution is a portion of actinium-227 prepared at the Argonne National Laboratory. This solution contains 0.01 microcurie per milliliter, and a 1-milliliter sample mounted on a 2-inch disk gave 47,662 alpha and 55,357 beta counts per minute per milliliter. Its age is sufficient to be in equilibrium with its daughters.

The thorium extract from one milliliter of this stock solution gave 5013 alpha and 4192 beta counts per minute per milliliter. Its growth is being observed.

At definite time intervals this one milliliter of actinium solution will be re-extracted and the growth will be followed. One such re-extraction was made 24 hours after the removal of the above equilibrium thorium. This extract produced 919 alpha and 1339 beta counts per minute per milliliter. The beta activity found present is an abnormal behavior. Its source is at present unknown and may be caused by an unexpected chemical behavior of one of the components of the solution.

From early results it is expected that actinium may be assayed from measurement of its thorium daughter

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Problem Title **Preparation of Actinium 228 (Quantitative Data)**

Report By **J. B. Otto**

Work Done By **J. B. Otto**

INTRODUCTION

The isolation of actinium 228 from thorium-232 has been described in a previous report.¹ This separation involves two steps (1) the isolation of radium-228 from its parent, thorium-232, and (2) the separation of actinium-228 from the isolated radium 228 by the Haissinsky McLane and Peterson method. The second step may be repeated on the same sample every two days indefinitely since radium-228 and actinium 228 attain equilibrium in this length of time. The relationship between thorium 232, radium-228, and actinium-228 can best be seen by reference to the decay scheme of thorium-232.¹

The present report deals with some of the quantitative relationships involved in these separations.

DETAILED REPORT

One-gram samples of the same thorium nitrate were used as the starting material in these and all previous experiments with actinium-228. Analysis of this thorium nitrate as it was used in experiments (without drying) showed it to contain 41.38 per cent thorium. This result indicates that the thorium nitrate used has a formula corresponding fairly well with $\text{Th}(\text{NO}_3)_4 \cdot 4\text{H}_2\text{O}$ in which the per cent thorium is 42.03.

The radium-224 and 228 isotopes (see decay scheme of thorium-232) were coprecipitated with ten milligrams of barium from one-gram samples of the thorium nitrate by both the chloride and nitrate procedures. The resulting barium radium 224 and 228 sulfate produced a deposit about one centimeter in diameter on a Bradley slide and represented only an estimated 80 to 90 per cent of the total precipitate. These samples were counted on a Bradley counter for alpha and beta activity as soon after separation as possible and once a day thereafter for 23 days. The results of these counts are shown in Table I. Only the results from the chloride procedure are given since those from the nitrate procedure were nearly identical. The growth and decay of the total beta activity is shown graphically in Figure 1. The sharp rise at the start is caused by a combination of the rapid growth of actinium-228 into equilibrium with its parent, radium-228, and the activity of the beta emitting decay products of radium-224. The beta activity due to the decay products of actinium-228 does not

build up to significant levels during the course of this decay study since the half life of the daughter of actinium-228, thorium-228 is relatively long. The maximum in the curve occurs in the neighborhood of two days at which point radium 228 and actinium-228 as well as radium-224 and its decay products have had time to reach equilibrium. The activity due to actinium-228 remains essentially constant for the rest of the time since its parent, radium-228, has a relatively long half-life. The weak beta activity due to radium-228 seems to be totally absorbed by the precipitate and therefore does not count. All the decay products of radium 224 have a shorter half life than the latter. Therefore the rest of the curve represents a combination of the constant activity due to the actinium-228 and the decay of radium-224. The flat portion of the curve is due to the actinium-228 alone, the radium-224 activity having completely died out. The actual beta counts in the flat portion are due only to actinium-228 since radium-228 has too weak a beta to count. When the essentially constant (after one day) 20,000 beta counts due to actinium-228 are subtracted from the total beta activity the beta activity due to the decay of radium 224 is obtained. Values for this decay are found in the last column in Table I and are shown graphically in Figure 2. The half-life of the beta decay found, 3.55 days corresponds quite well with that given in the literature for radium-224, 3.64 days. The decay of alpha activity is also shown graphically in Figure 2. The half life of the alpha decay 3.65 days found also corresponds very well with the half-life of radium 224. The alpha decay curve does not remain a straight line after about 12 days however because the alpha activity due to thorium-228 the long-lived daughter of actinium 228 starts to become significant at this point.

As previously indicated the nearly constant value of approximately 20,000 beta counts per minute (50 per cent geometry) obtained in the flat portion of the curve Figure 1, is due to actinium-228 alone. Assuming 90 per cent of the precipitate was transferred to the slide this figure becomes 22,200 actinium-228 beta counts per minute per gram of thorium nitrate (41.38 per cent thorium) 53,700 counts per minute per gram of thorium or approximately 107,400 disintegrations per minute per gram of thorium. This result serves as a basis for an estimation of the yield of actinium 228 obtained in the Blaisinsky-McLane and Peterson method. Rough calculations show that radium 228 (and hence actinium-228) is 45 per cent in equilibrium with thorium 232 in six years and produces 111,000 beta disintegrations per minute per gram of thorium. The experimental value of 107,400 actinium-228 beta disintegrations per minute per gram of thorium confirms the assumption that the thorium nitrate used was about six years old.

Radium-228 was separated from one gram samples of the thorium nitrate by both the chloride and nitrate procedures. After equilibrium between radium 228 and actinium 228 had been attained (two days) in the resulting barium radium 228 actinium 228 nitrate

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mixture, the actinium-228 was separated from the mixture by the Haissinsky McLane and Peterson method. One milligram of lanthanum was used as a carrier and the final lanthanum - actinium-228 oxalate precipitate produced a deposit about two centimeters in diameter on a one-inch watch glass. The results obtained for both the samples separated by the chloride procedure (Sample Numbers 1 and 2) and the nitrate procedure (Sample Numbers 3 and 4) are given in Table II. When the actinium-228 beta counts per minute corrected for decay are compared to the corresponding value 22 200 obtained in the decay study described previously, it will be seen that the method gives high yields of actinium-228. The apparently extremely high yield in the case of the chloride procedure sample may be caused by the much lower weight and wider spread of precipitate used in the Haissinsky-McLane and Peterson method compared to that used in the decay study. This should make the self absorption of the precipitate much less in the case of the Haissinsky-McLane and Peterson method.

Radium-228 was separated from thorium-232 by the chloride method and this was repeated twice with the same carrier. Actinium-228 was then isolated from the sample by the Haissinsky-McLane and Peterson method. The results of this experiment is shown in Table II (Sample Number 5) The results are as should be expected - the amount of actinium-228 associated with the fixed weight of carrier is about three times that present after one coprecipitation.

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TABLE I

GROWTH AND DECAY OF ACTIVITY FROM RADIUM 224 AND 228 ISOTOPES SEPARATED
FROM THORIUM 232 AND ITS DECAY PRODUCTS

LAST BARIUM RADIUM CHLORIDE PRECIPITATION. 0 DAYS 9 HRS. 10 MINS

TIME COUNTED			COUNTS PER MINUTE AT		50 PER CENT GEOMETRY	
DAYS	HRS.	MINS.	ALPHA AND BETA	ALPHA	BETA	BETA - 20,000
0	11	45	26 969	12,863	14 106	
1	14	18	50,684	13,856	36,828	16 828
2	13	20	47,853	12,026	35,827	15,827
5	11	45	36 547	6 938	29 609	9 609
6	13	10	33 422	5 686	27 736	7 736
7	14	37	30 839	4 705	26 134	6 134
8	12	37	29 235	3,997	25 238	5 238
9	13	50	29 075	3 268	25 807	5 807
12	9	51	24 750	2 188	22 562	2 562
13	9	18	23 575	1,872	21 703	1 703
14	9	35	23 095	1 564	21 532	1 532
15	10	49	22 613	1 467	21 146	1 146
16	10	08	22 345	1 211	21 134	1 134
19	13	40	21,373	922	20 451	451
21	9	45	21 195	834	20 361	361
23	13	38	21 077	785	20 292	292

TABLE II

THE SEPARATION OF ACTINIUM 228 FROM RADIUM 228
BY THE HAISSINSKY MCLANE AND PETERSON METHOD

RADIUM-228 SEPARATED FROM THORIUM-232 BY THE CHLORIDE PROCEDURE

STEP 1 FINISHED 9 15 A M 9 20 50
SEPARATION TIME 10 30 A M 9 20 50

SAMPLE NUMBER	TIME COUNTED	COUNTS PER MINUTE AT		50 PER CENT GEOMETRY BETA
		ALPHA AND BETA	ALPHA	
1	3 48 P M 9 20 50	12 469	9	12 460 (23 200)*
2	4 00 P M. 9 20 50	12 273	3	12 270 (22 800)
1	9 37 A M 9 22 50	155	14	141
2	9 50 A M 9 22 50	139	12	127

RADIUM 228 SEPARATED FROM THORIUM-232 BY THE NITRATE PROCEDURE

STEP 1 FINISHED 11 00 A M 9 19 50
SEPARATION TIME 11 30 A M 9 19 50

3	3 08 P M 9 19 50	11 037	9	11 028 (16 850)
4	3 18 P M 9 19 50	11 168	1	11 67 (17 050)
3	3 05 P M 9 20 50	874	15	859
4	3 20 P M 9 20 50	902	15	887

RADIUM 228 SEPARATED FROM THREE PORTIONS OF THORIUM 232 BY THE CHLORIDE PROCEDURE
USING THE SAME RADIUM CARRIER EACH TIME

STEP 1 FINISHED A M 10 11 50
SEPARATION TIME A M 10 11 50

5	P M 10 11 50	42 045	66	41 919
5	P M 10 12 50	3 951	79	3 872

* CORRECTED FOR DECAY TO SEPARATION TIME

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FIGURE 1

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FIGURE 2

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