To the Graduate Council.

I am submitting herewith a thesis written by Rebecca Joan Mack entitled "Reduction of Yb(III) to Yb(II) to Separate Yb from other Lanthanides." I have examined the final copy of this thesis for form and content and recommend that it be accepted in partial fulfillment of the requirements for the degree of Master of Science, with a major in Chemistry

Geo. K. Schweitzer

George K Schweitzer, Major Professor

We have read this thesis
and recommend its acceptance

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Interim Vice Provost
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# REDUCTION OF Yb(III) TO Yb(II) TO SEPARATE Yb FROM OTHER LANTHANIDES

A Thesis

Presented for the

Master of Science

Degree

The University of Tennessee, Knoxville

Rebecca Joan Mack

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## DEDICATION

The author wishes to dedicate this thesis to her mother, Carmella Toombs, for her love, guidance and endless supply of support throughout the years

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## ABSTRACT

The electrolytic reduction of Yb(III) to Yb(II) using a Pb cathode was performed in various media The effects of the medium, current and pH on the formation of Yb(II) were studied The best experimental conditions for the reduction of Yb(III) to Yb(II) and the subsequent precipitation of $YbSO_4$ were found to be ~0 11M $YbCl_3 \cdot 6H_2O$ in 1 1 ethanol dioxane, direct current of ~20 mA and a pH of approximately 2 0, followed by precipitation with 3 0M $(NH_4)_2SO_4$ Under these conditions, a maximum of 30% of the Yb(II) could be removed from the system

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# Chapter 1

## INTRODUCTION

### A History

The rare earth element Lu, in high purity, is the major constituent in the best solid-state gamma scintillation detectors known [1] The production of high purity Lu is a very difficult process because it is a member of the rare earth (lanthanide) family The lanthanide elements, Ln, are very similar in their chemical properties and the chemistry is dominated by a highly stable Ln(III) ion They resemble each other so closely that multi-staged operations are needed for effective separations The higher the purity required, the more stages that are called for

Classical methods for rare earth separations included fractional crystallization and fractional precipitation [2] However, these techniques are so inefficient and time consuming that high purity rare earths are not obtained

Early on, two of the rare earths were found to be susceptible to oxidation state change in aqueous solution, one to oxidation, (Ce(III) to Ce(IV)), one to reduction, (Eu(III) to Eu(II)) The properties of the Ce(IV) and Eu(II) differed considerably from those of the other rare earths in their Ln(III) forms, thus permitting more effective separations and higher purity products [2]

The introduction of the processes of ion-exchange and counter-current solvent extraction represented a marked improvement upon the classical techniques These methods

permitted much greater efficiencies and much easier handling of multi-staged operations They are, at present, the most widely employed means for the production of high purity rare earths other than Ce and Eu [2]

Lu is the second rarest of the lanthanides, its terrestrial abundance being 0 8 ppm [3] Fortunately, it occurs at the high end of the lanthanide series, and therefore, its separation from the next highest element, Hf, is quite simple because of sharp chemical differences However, its separation from the other 13 lanthanides is difficult The most difficult separation is that from Yb, the adjacent rare earth The ease of separation of Lu from the other rare earths increases as the distance from Lu increases If Yb could be removed from a Lu-containing rare earth mixture, the separation of Lu would be enhanced measurably and many fewer stages would be needed.

If Yb(III) could be reduced to Yb(II), the possibility of separating Yb from the other rare earths chemically is introduced because Yb(II) would have different chemical properties in comparison to the other rare earths in their (III) oxidation states For example, the Yb(II) could be separated by using $SO_4^{2-}$ since $YbSO_4$ is insoluble whereas Ln(III) sulfates are soluble [4,5] Once Yb(III) is reduced to Yb(II), the rest of the rare earths could be separated more easily from Lu using counter-current solvent extraction or ion exchange since the separation coefficient between Lu and Tm is much larger than that between Lu and Yb

W Klemm and W Schuth first prepared Yb(II) in the form of $YbCl_2$ in 1929 This was accomplished by treating $Yb_2O_3$ with a stream of $Cl_2$ - $S_2Cl_2$ The conversion was done at a temperature between 600 - 620 °C , and thus, was not a solution technique.[6]

In 1930, L F Yntema electrolyzed Eu(III) to produce $EuSO_4$ A solution of Eu(III)

and Sm(III) was made by dissolving the oxides in hydrochloric acid to form the chlorides The excess HCl was evaporated off and sulfuric acid was added to produce the trivalent sulfates These sulfates were electrolyzed in an acidic solution using a Hg pool cathode and Pt anode The anode and cathode were contained in separate compartments The anode compartment contained dilute $H_2SO_4$ The cathode compartment contained 125 mL of a solution consisting of Eu(III) sulfate, Sm(III) sulfate and 2 0 ml of $H_2SO_4$ The current was 0 18 A, the current density was 0 010 $A/cm^2$ and the voltage drop between electrodes was 65 V [7]

Later that year, L F Yntema along with R W Ball reduced Yb(III) to Yb(II) and produced $YbSO_4$ The cathode compartment in the electrolytic cell contained a Hg cathode and an yttrium group chloride solution The anode compartment was filled with 0 05N HCl solution and contained a Pt anode A current of 0.10 A, a current density at the cathode of 0 025 $A/cm^2$ and a voltage between electrodes of 110 V was used It was reported that the sulfate was stable in acid solution as long as the current was still applied It was also reported that it was necessary for the cathode to have a high overvoltage The high overvoltage suppresses the formation of hydrogen, as addressed in the following section It was also reported that the purity of the Yb(II) separated from a mixed yttrium group material was 98% although the original percent of Yb(III) in the yttrium group material was only 2% [8]

The next attempt to produce Yb(II) was performed by W Prandtl in 1932 A reduction/oxidation preparation of $YbSO_4$ was attempted This attempt was based on previous work done by L F. Yntema and R W. Ball The electrolytic reduction was carried out in an aqueous solution of the sulfate of the yttrium group using a Hg cathode and a Pt

anode The current was between 0 20 and 0 40 A and the voltage drop was 110 V The temperature range selected for electrolysis was between 40 and 60°C The precipitated $YbSO_4$ reacted with acid, liberating hydrogen gas The purity of the material that was recovered from the reduction was not reported [9]

D W Pearce, C R Naesar and B S Hopkins performed a reduction of Yb(III) using a Hg cathode and a Pt anode The anode consisted of a piece of Pt foil that was enclosed in a glass tube The glass tube was not sealed but rather turned upward to form a hook The Hg cathode was enclosed in a cone-shaped tube The anode compartment resided in the cathode compartment, which was surrounded by a water jacket to control temperature The Yb(III) was in the form of the chloride, 0 40N, and was dissolved in dilute sulfuric acid, 1 2N The reduction was carried out using a voltage of 110 V and a current density of 0 16 $A/cm^2$ The sulfate was produced but a complete reduction was not obtained The authors speculated that a complete reduction was not obtained due to an incomplete reduction of Yb(III) to Yb(II) and a partial decomposition of $YbSO_4$ that occurred when the current was discontinued When no current was present, the following reaction occurred

$$2\ YbSO_{4\,(s)} + 2H^+_{(aq)} \rightarrow 2\ Yb^{3+}_{(aq)} + 2SO_4^{2-}{}_{(aq)} + H_{2\,(g)}$$

They reported that a low temperature aided in removing small amounts of Yb from large amounts of Lu or Tm They also reported that $Yb^{2+}$ resembles $Ba^{2+}$ in that they have similar sized radii [10]

J K Marsh produced $YbSO_4$ in 1937 using an amalgamated Pb cathode and an anode consisting of lead pipe The cell consisted of a 400 mL beaker and a porous pot set in the beaker The anode and a solution of dilute sulfuric acid resided in the porous pot The

cathode and the Yb(III) sulfate solution was in the beaker A voltage of 100 V was applied to the system and the cathode current density was 0 30 A/cm$^2$ The entire system consisted of six of the previously mentioned cells in a series. March reported that a 95% reduction of Yb (III) to Yb (II) was obtained He also reported that Yb (II) was more stable if no heavy metals were present in the starting solution Marsh observed that in order to obtain a 95% reduction, the Pb used in the cathode needed to be pure [11]

The first value of the Yb(III) / Yb(II) electrode potential was reported in 1940 by G C Walters and D W Pearce as -0 578 V using a Pt indicator electrode.[12] H A Laitinen disagreed with this value and performed a study in 1942 with a dropping mercury electrode A potential between -1 05 and -1 17 V with a half wave potential of -1 15 V was reported Laitinen believed this to be the most probable potential for the Yb(III) / Yb(II) couple Laitinen disagreed with the value that Walters and Pearce reported based on the fact that erroneous results will generally be obtained with a Pt indicator electrode due to mixed potential behavior in the solutions of Yb(III) and Yb(II) salts [12]

The preparation of Yb(II) chloride using magnesium was described in 1972 by N B Mikheev, *et. al.* A mixture of Sm(III) chloride, Eu(III) chloride and Yb(III) chloride in an acid aqueous ethanolic solution was reduced using Mg An isomorphous cocrystallization of $EuCl_2$ and $YbCl_2$ occurred on the surface of the Mg [13]

The reduction of Eu(III), Sm(III), Tm(III), Er(III) and Am(III)to the divalent state in acetonitrile was reported in 1975 by B F Myasoedov, *et. al.*, using potential-controlled electrolysis and polarography The authors reported that the divalent ions were attacked by water that was present in the acetonitrile and oxidized to the hydrolyzed trivalent cation

during the electrolysis The stability of the divalent cations was dependent on the cation, Eu(II), Sm(II), Tm(II), Er(II), and Am(II) The rate of oxidation of the divalent cation to the trivalent cation was also dependent upon the cation.[14]

In 1994, T Hanamoto, *et. al.* reported that treating a solution of Sm(III) triflate and Yb(III) triflate in tetrahydrofuran with ethylmagnesium bromide at room temperature formed Sm(II) triflate and Yb(II) triflate The interest here lay in using the Ln(II) complexes as catalyst in organic reactions [15]

Recently, 1998, J D Siler reduced Yb(III) to Yb(II) in the form of $YbCl_3 \cdot 6H_2O$ in 1 1 ethanol dioxane The reduction was accomplished through the addition of Mg powder to a Yb(III) chloride solution forming a precipitate of Yb(II) chloride [16] The idea of reducing Yb(III) to Yb(II) in a system consisting of 1 1 ethanol dioxane came from previous work performed by A F Clifford and H C Beachell in 1948. Clifford and Beachell successfully reduced Sm(III) to Sm(II) in the form of $SmCl_3 \cdot 6H_2O$ This was accomplished by dissolving the $SmCl_3 \cdot 6H_2O$ in 1 1 ethanol dioxane saturated with $BaCl_2$ and $SrCl_2$ The reducing agent used was Mg metal [17] Siler used this information to help establish his best system for the reduction of Yb(III) to Yb(II) using Mg in 1·1 ethanol.dioxane [16]

## B Proposed Problem

Mercury is often used in aqueous reductions as a cathode due to its large overvoltage Overvoltage is the difference between the actual potential at which $H_{2\,(g)}$ evolution begins and the reversible value in the same solution In other words, it is the excess potential, over the

reversible value, at the cathode at which the evolution of $H_{2\,(g)}$ occurs [18] This property is important in that the net effect is that the $H^{+}_{(aq)}$ acts as a less powerful oxidizing agent and the $H_{2\,(g)}$ as a less powerful reducing agent than the E° value would indicate [19] Although this characteristic of Hg makes it a very useful cathode, the toxicity of Hg in the human body dissuades the use of Hg in an industrial setting [20]

Due to this severe toxicity of Hg, an alternate cathode was selected for study [19] The selection was made by consulting a table of overvoltages, Table 1, and Pourbaix diagrams, see Appendix Lead was selected as the cathode since Pb has an overvoltage somewhat comparable to that of Hg

**Table 1 - Cathodic Overvoltages in Dilute Sulfuric Acid.** [19]

| Element | Overvoltage | Element | Overvoltage |
|---|---|---|---|
| | | | |
| Platinized Platinum | 0 005 V | Copper | 0 23 V |
| Gold | 0 02 V | Cadmium | 0 48 V |
| Iron (in NaOH) | 0 08 V | Tin | 0.53 V |
| Smooth Platinum | 0 09 V | Lead | 0 64 V |
| Silver | 0 15 V | Zinc | 0 70 V |
| Nickel | 0 21 V | Mercury | 0 78 V |

## Chapter 2

## EXPERIMENTAL

### A Materials and Apparatus

The solvents used in the experiments were reagent grade All water used was deionized The $YbCl_3 \cdot 6H_2O$ was obtained from Aldrich and was 99 9% pure

The Pb electrode was constructed from a piece of 99 999% pure Pb obtained from Sigma-Aldrich Chemical Co The electrode measured 0 20 cm x 1 0 cm x 2.5 cm The Pb was abraded using silicon carbide abrasive paper, CC 400 A, obtained from Sun Abrasives Co., Ltd

The Pt electrode was constructed from a piece of 99 9% pure Pt obtained from Fisher Scientific Co The electrode measured 0 010 cm x 0.20 cm x 0.20 cm The piece of Pt foil was rolled The electrode was lengthened by attaching a piece of Pt wire to the foil and enclosing the wire in glass

The DC power supply used contained a dual output labeled either 1 or 3 Amps The variable voltmeter was manufactured by Triplett and enabled variance of the voltage between 0 and 60 V The ammeter used was manufactured by Simpson and measured between 0 and 300 mAmps

The cell was constructed from a piece of fritted straight tubing from the Ace Glass Corporation with porosity E, 4-6 μ The tube was bent into a "U" shape to give separate compartments for the anode and the cathode The tube was 19.6 cm long and the frit was

centrally located

The atomic emission spectrometer used was a Perkin Elmer AAnalyst 100 The wavelength used for Yb analysis was 398 nm

## B General Procedure

The experiments performed during this project were conducted in six basic steps (1) selection of the solvent, (2) measurement of the solubility of $YbCl_3 \cdot 6H_2O$ in the solvent, (3) preparation of the sample and system, (4) observations of reaction times and characteristics, (5) separation of precipitates and (6) analysis of precipitates These basic steps will be discussed in detail in the following section

## C Detailed Procedures

### 1 Selection of Solvents

The solvent to be used in the experiment was the first consideration Suitable solvents were obtained by searching the literature for applicable possibilities based on previous studies The following solvents were used water, ethanol, 1 1 ethanol dioxane, 1 1 ethanol nitromethane, 1 1 ethanol diethylcarbonate, 1 1 ethanol dimethyl sulfoxide, 1 1 ethanol toluene and 1 1 ethanol acetone

### 2 Measurement of the Solubility of $YbCl_3 \cdot 6H_2O$ in Solvents

Determining the solubility of $YbCl_3 \cdot 6H_2O$ in each solvent was the next step The

solubility was first tried in the specific solvent If the $YbCl_3 \cdot 6H_2O$ was insoluble, the mixture was then heated in an attempt to increase solubility If the $YbCl_3 \cdot 6H_2O$ was still insoluble, a 1·1 mixture of the solvent and ethanol was made in order to dissolve $YbCl_3 \cdot 6H_2O$, if the solvent was not water or ethanol

3 Preparation of the Sample and the System

The Yb(III) solution needed to be acidified with 3M HCl until a pH of approximately 2 0-3 0 was obtained In most experiments, ~3 5 mL of water was added to 8 0 mL of the Yb(III) solution in order to increase the conductivity

The cell was cleaned by soaking it for approximately 30 minutes in a dilute solution of $NH_4OH$ and then soaking it briefly in a 2M $HNO_3$ bath The cell was then removed, rinsed with water, 3M HCl was forced through the frit and then it was rinsed with water again.

The Pb electrode was cleaned by abrading with silicon carbide abrasive paper to give a new surface and to remove any residue on the Pb. The Pt electrode was cleaned by dipping it in dilute HCl and then rinsing with water

4 Observation of Reaction Times and Characteristics

The reaction time was the amount of time that occurred from the time the voltage was applied until the time that no further observations were made on the system The reaction time was recorded in hours and minutes

The following characteristics were observed during the reaction change in color of the solution, evolution of gas, the pH of the $YbCl_3 \cdot 6H_2O$, current output, and formation of a precipitate. The times that the characteristics were observed during the reactions were also recorded

5 Separation of Precipitates

There were two different precipitates that formed in some of these experiments The first precipitate would form in the bottom of the cell during the reaction The precipitate was separated from the solution by removing the solution with a pipette

The second precipitate formed when a sufficient amount of Yb(II) was present during the reaction and a fraction of the solution was removed and injected into a solution of 3M $(NH_4)_2SO_4$ A precipitate would form at the interface of the aqueous and non-aqueous media The solution and precipitate was centrifuged The supernatant was separated from the precipitate and both were saved for further analysis

6 Analysis of Precipitates

The first precipitate, probably $YbCl_2$, was tested through the addition of dilute HCl to the precipitate to test for the presence of Yb(II) Upon the addition of HCl, an oxidation of Yb(II) to Yb(III) would cause the formation of $H_2$ gas, which would indicate the presence of Yb(II) The precipitate would then change from green Yb(II) to colorless Yb(III) The precipitate was also tested through the addition of $H_2O$ which would yield the same results as the addition of HCl

The second precipitate, $YbSO_4$, was tested for Yb(II) by the addition of a dilute solution of $KMnO_4$ The presence of Yb(II) would be indicated through the precipitate dissolving and changing from green to colorless since it would be oxidized from Yb(II) to Yb(III) The $KMnO_4$ would be reduced and would change from purple to colorless The precipitate was also tested by adding dilute HCl and $H_2O$, the same as the first precipitate was treated

The supernatant, which was separated from the second precipitate, was analyzed to obtain the amount of Yb(III) not reduced to Yb(II) This was done by diluting the supernatant and then preparing an appropriate solution to be analyzed by atomic emission spectroscopy The data obtained from the atomic emission would indicate the amount of Yb(III) present The percentage of Yb(III) that was reduced to Yb(II) could be calculated by difference from a standard consisting of the same amount of Yb(III) as the supernatant

## D Experiments

### 1 Explanation of Tables

The tables contain the following information system, voltage, current, $T_{green}$, $T_{max\ green}$, $T_{fading/duration}$ and acid added The column labeled System lists what solution is contained in the cathode compartment and what solution is contained in the anode compartment The columns labeled Voltage and Current list what the voltage and the current were at the beginning of the experiment $T_{green}$ stands for the time it took for the first appearance of green to occur during the experiment $T_{max\ green}$ is used for the amount of time that was required to obtain the maximum color $T_{fading/duration}$ is the amount of time into the experiment when the color of the solution went from green to colorless or the amount of time the experiment was conducted if no green color was obtained The acid used to acidify the Yb(III) solution is listed in the column labeled Acid Added

### 2 The Tables

The tables are located on the following pages.

**Table 2 Electrolysis Results: Data for $5.1x10^{-3}$M $YbCl_3 \cdot 6H_2O$ and $1.2x10^{-1}$ M $K_3Cit$ in $H_2O$.**

| System | Voltage /Volts | Current /mA | $T_{green}$ /min | $T_{max\ green}$ /hrs,min | $T_{fading}$ /hrs,min | Acid Added |
|---|---|---|---|---|---|---|
| Pb Cathode<br>5 1 $x10^{-3}$M<br>$YbCl_3 \cdot 6H_2O$ | 38 | 100 | 7 min | 7 min | 27 min | 3d 3M HCl |
| in $H_2O$<br>1 2 $x10^{-1}$ M<br>$K_3Cit$ | 28 | 100 | 12 min | 15 mın | 30 min | 3d 3M HCl |
| Pt Anode<br>1M $H_2SO_4$ | 30 | 100 | 5 min | 5 min | 1 hour 2 min | 3d 3M HCl |

$K_3Cit$ = potassium citrate  3d = three drops

**Table 3 Electrolysis Results: Data for 0.35M $YbCl_3 \cdot 6H_2O$ and 0.70M $K_3Cit$ in $H_2O$.**

| System | Voltage /Volts | Current /mA | $T_{green}$ /min | $T_{max\ green}$ /hrs,min | $T_{duration}$ /hrs,min | Acid Added |
|---|---|---|---|---|---|---|
| Pb Cathode: 0 35M $YbCl_3 \cdot 6H_2O$ in $H_2O$ | 16 | 100 | - | - | 2 hrs 50 min | 3d 3M HCl |
| 0 70 M $K_3Cit$ Pt Anode 1M $H_2SO_4$ | 18 | 100 | - | - | 1 hr 45 min | 3d 3M HCl |

$K_3Cit$ = potassium citrate  3d = three drops

**Table 4 Electrolysis Results: Data for 0.14M $YbCl_3 \cdot 6H_2O$ and 0.28M $K_3Cit$ in $H_2O$.**

| System | Voltage /Volts | Current /mA | $T_{green}$ /min | $T_{max\ green}$ /hrs,min | $T_{fading}/_{duration}$ /hrs,min | Acid Added |
|---|---|---|---|---|---|---|
| Pb Cathode 0 14M | 25 | 100 | 3 min | 1 hr 13 min | 2 hrs 3 min | 3d 3M HCl |
| $YbCl_3 \cdot 6H_2O$ in $H_2O$ | 21 | 100 | 2 min | 29 min | 2 hrs 14 min | 3d 3M HCl |
| 0 28M $K_3Cit$ | 21 | 100 | - | - | 2 hrs 4 min | 3d 3M HCl |
| | 21 | 100 | - | - | 2 hrs 37 min | 3d 3M HCl |
| Pt Anode | 28 | 100 | - | - | 2 hrs 5 min | 3d 6M HCl |
| 1M $H_2SO_4$ | 21 | 100 | 1 min | 7 min | 25 min | 3d 3M HCl |
| | 19 | 100 | 1 min | 16 min | 1 hr 50 min | 3d 3M HCl |
| | 24 | 100 | 1 min | 11 min | 1 hr 30 min | 3d 3M HCl |
| | 29 | 100 | - | - | 2 hrs | 3d conc HOAc |
| | 30 | 100 | - | - | 1 hr 45 min | 3d conc HOAc |
| Pb switched during exp | 25 | 100 | 2 min 1 min | 7 min 1 min | 9 min 3 min | 3d 3M HCl |
| Pb switched during exp | 28 | 100 | 11 min 2 min | 147 min 35 min | 2 hr 34 min 55 min | 3d 3M HCl |

$K_3Cit$ = potassium citrate  3d = three drops

**Table 5 Electrolysis Results: Data for 0.14M $YbCl_3 \cdot 6H_2O$, 0.28M $K_3Cit$ and 0.14M $(NH_4)_2SO_4$ in $H_2O$.**

| System | Voltage /Volts | Current /mA | $T_{green}$ /min | $T_{max\ green}$ /hrs,min) | $T_{fading}$ /hrs,min) | Acid Added |
|---|---|---|---|---|---|---|
| Pb Cathode· 0.14M $YbCl_3 \cdot 6H_2O$ in $H_2O$ 0 28M $K_3Cit$ 0 14M $(NH_4)_2SO_4$ | 19 | 120 | 1 min | 1 min | 50 min | 3d 3M $H_2SO_4$ |
| | 22 | 110 | 32 min | 32 min | 45 min | 3d 3M $H_2SO_4$ |
| | 28 | 100 | 2 min | 2 min | 11 min | 3d 3M $H_2SO_4$ |
| Pt Anode 1M $H_2SO_4$ | 22 | 100 | 2 min | 2 min | 9 min | 3d 3M $H_2SO_4$ |
| Pb switched during exp | 25<br>25 | 100<br>100 | 9 min<br>- | 22 min<br>- | 30 min<br>- | 3d 3M $H_2SO_4$ |

$K_3Cit$ = potassium citrate  3d = three drops

**Table 6 Electrolysis Results: Data for 0.10M $YbCl_3 \cdot 6H_2O$ in 1:1 EtOH:Dioxane.**

| System | Voltage /Volts | Current /mA | $T_{green}$ /min | $T_{max\ green}$ /hrs,min | $T_{fading}$ /hrs,min | Acid Added |
|---|---|---|---|---|---|---|
| Pb Cathode 0 10M $YbCl_3 \cdot 6H_2O$ in 1 1 EtOH·dioxane | 58 | 40 | 20 min | 30 min | 36 min | 3d 3M HCl |
| | 60 | 50 | 30 min | 2 hr 38 min | 3 hrs 41 min | 3d 3M HCl |
| Pt Anode 0 400mL conc $H_2SO_4$ | 58 | 50 | 16 min | 36 min | 1 hr 27 mın | 3d 3M HCl |
| 7 60mL of 1 1 EtOH dioxane | 58 | 45 | 2 mın | 10 min | 40 mın | 3d 3M HCl |
| | 55 | 50 | 10 min | 1 hr 3 min | 2 hrs 30 min | 3d 3M HCl |
| | 60 | 50 | 17 min | 1 hr 33 min | 5 hrs | 3d 3M HCl |
| | 55 | 40 | 9 min | 43 min | 4 hrs 54 mın | 3d 3M HCl |

EtOH = ethanol conc = concentrated 3d = three drops

**Table 7 Electrolysis Results: Data for 0.12M $YbCl_3 \cdot 6H_2O$ in 1:1 EtOH:Nitromethane.**

| System | Voltage /Volts | Current /mA | Color Observed | Time of first appearance | Acid Added |
|---|---|---|---|---|---|
| Pb Cathode 0 12M | 60 | <10 | orange | 9 min | 3d 3M HCl |
| $YbCl_3 \cdot 6H_2O$ in 1 1 EtOH nitro | 60 | <10 | orange | 5 min | 3d 3M HCl |
| Pt Anode 0 400mL conc HCl | 60 | <10 | orange | 20 min | 3d 3M HCl |
| 7 60mL of 1 1 EtOH nitro | 60 | <10 | colorless - no Yb(III) present | - | 3d 3M HCl |

EtOH = ethanol nitro = nitromethane conc = concentrated 3d = three drops

**Table 8 Electrolysis Results: Data for 0.11M $YbCl_3 \cdot 6H_2O$ in 1:1 EtOH:Diethyl Carbonate.**

| System | Voltage /Volts | Current /mA | $T_{green}$ /min | $T_{max\ green}$ /hrs,min | $T_{duration}$ /hrs,min | Acid Added |
|---|---|---|---|---|---|---|
| Pb Cathode 0 11M $YbCl_3 \cdot 6H_2O$ in 1 1 EtOH diEtCar | 60 | 5 | - | - | 2 hrs 28 min | 3d 3M HCl |
| Pt Anode 0 400mL conc HCl 7 60mL of 1 1 EtOH diEtCar | 60 | 10 | - | - | 2 hrs 17 mın | 3d 3M HCl |

EtOH = ethanol diEtCar = diethyl carbonate conc = concentrated 3d = three drops

**Table 9 Electrolysis Results: Data for 0.11M - 0.12M $YbCl_3 \cdot 6H_2O$ in 1:1 EtOH:DMSO.**

| System | Voltage /Volts | Current /mA | $T_{green}$ /min | $T_{max\ green}$ /hrs,min | $T_{fading}/_{duration}$ /hrs,min | Acid Added |
|---|---|---|---|---|---|---|
| Pb Cathode 0 11M - 0 12M | 60 | <10 | - | - | 5 hrs 29 min | 3d 3M HCl |
| $YbCl_3 \cdot 6H_2O$ in 1 1 EtOH DMSO | 55 | <10 | - | - | 5 hrs 15 mın | 3d 3M HCl |
| Pt Anode 0 400mL conc HCl | 60 | <10 | 195 min | 3 hrs 15 min | 3 hrs 30 min | 3d 3M HCl |
| 7 60mL of 1 1 EtOH DMSO | 60 | <10 | - | - | 4 hrs 56 min | 3d 3M HCl |
| | 55 | <10 | - | - | 7 hrs 36 min | 3d 3M HCl |

EtOH = ethanol DMSO = dımethyl sulfoxide conc = concentrated 3d = three drops

**Table 10 Electrolysis Results: Data for 0.16M $YbCl_3 \cdot 6H_2O$ in 1:1 EtOH:Toluene.**

| System | Voltage /Volts | Current /mA | $T_{green}$ /min | $T_{max\ green}$ /hrs,min | $T_{duration}$ /hrs,min | Acid Added |
|---|---|---|---|---|---|---|
| Pb Cathode· 0 16M | 60 | < 10 | - | - | 1 hr 20 min | 6d 3M HCl |
| $YbCl_3 \cdot 6H_2O$ in 1 1 EtOH toluene | 58 | < 10 | - | - | 5 hrs | 6d 3M HCl |
| Pt Anode 0 400mL conc HCl | 55 | < 10 | - | - | 5 hrs | 6d 3M HCl |
| 7 60mL of 1 1 EtOH·toluene | 60 | < 10 | - | - | 5 hrs 55 min | 6d 3M HCl |

EtOH = ethanol conc = concentrated 6d = six drops

**Table 11 Electrolysis Results: Data for 0.16M $YbCl_3 \cdot 6H_2O$ in 1:1 EtOH:Acetone.**

| System | Voltage /Volts | Current /mA | $T_{brown}$ /min | $T_{max\ brown}$ /hrs,min | $T_{fading/duration}$ /hrs,min | Acid Added |
|---|---|---|---|---|---|---|
| Pb Cathode 0 16M | 55 | 30 | 10 min | 25 min | 3 hrs 50 min | 3d 3M HCl |
| $YbCl_3 \cdot 6H_2O$ in 1·1 EtOH acetone | 55 | 30 | 2 min | 3 hrs 10 min | 5 hrs 13 min | 3d 3M HCl |
| Pt Anode 0 400mL conc HCl | 55 | 30 | 3 min | 3hrs 30 min | 2 hrs 7 min | 3d 3M HCl |
| 7 60mL of 1 1 EtOH acetone | 52 | 20 | 85 min | 87 min | 4 hrs 40 min | 3d 3M HCl |
| | 55 | 15 | 110 min | 4 hrs 45 min | 4 hrs 45 min | 3d 3M HCl |
| | 50 | 20 | 5 min | 4 hrs 5 min | 6 hrs 20 min | 3d 3M HCl |
| 0 079M $EuCl_3 \cdot 6H_2O$ | 50 | 20 | - | - | 3 hrs 47 min | 3d 3M HCl |
| | 50 | 20 | - | - | 5 hrs 57 min | 3d 3M HCl |
| 0 17M $SmCl_3 \cdot 6H_2O$ | 50 | 10 | - | - | 3 hrs | 3d 3M HCl |

EtOH = ethanol conc = concentrated 3d = three drops

**Table 12 Electrolysis Results: Data for ~0.11M $YbCl_3 \cdot 6H_2O$ in 1:1EtOH:Dioxane.**

| System | Voltage /Volts | Current /mA | $T_{green}$ /min | $T_{max\ green}$ /hrs,min | $T_{fading}$ /hr,min | Acid Added |
|---|---|---|---|---|---|---|
| Pb Cathode ~0.11M $YbCl_3 \cdot 6H_2O$ in 1 1EtOH dioxane Pt Anode 0 500mL conc HCl 7 50mL of 1 1 EtOH dioxane | 60 | 25 | 5 min | 1 hr 10 min | 5 hrs 3 min | 3d 3M HCl |
| | 55 | 20 | 40 min | 1 hr 11 min | 2 hrs 56 min | 3d 3M HCl |
| | 50 | 20 | 13 min | 1 hr 15 min | 6 hrs 10 min | 3d 3M HCl |
| | 55 | 28 | 12 min | 2 hrs 38 min | 6 hrs 1 min | 3d 3M HCl |
| | 60 | 28 | 16 min | 1 hr 48 min | 4 hrs 48 min | 3d 3M HCl |
| | 60 | 30 | 20 min | 30 min | 4 hrs 52 min | 3d 3M HCl |
| | 55 | 25 | 7 min | 34 min | 5 hrs | 3d 3M HCl |
| | 50 | 30 | 25 min | 1 hr | 5 hrs 45 min | 3d 3M HCl |
| | 55 | 28 | 13 min | 13 min | 4 hrs 10 min | 3d 3M HCl |
| | 60 | 30 | 10 min | 1 hr 35 min | 4 hrs 28 min | 3d 3M HCl |
| | 65 | 40 | 5 min | 1 hr 15 min | 3 hrs 35 min | 3d 3M HCl |
| | 60 | 25 | 5 min | 1 hr | 10 hrs 10 min | 3d 3M HCl |
| | 58 | 25 | 4 min | 40 min | 6 hrs 40 min | 3d 3M HCl |
| | 65 | 45 | 20 min | 30 min | 3 hrs 30 min | 3d 3M HCl |
| | 55 | 10 | 20 min | 20 min | 1 hr 30 min | 3d 3M HCl |

EtOH = ethanol conc = concentrated 3d = three drops

**Table 12 (Continued) Electrolysis Results: Data for ~0.11M $YbCl_3 \cdot 6H_2O$ in 1:1EtOH:Dioxane.**

| System | Voltage /Volts | Current /mA | $T_{green}$ /min | $T_{max\ green}$ /hrs,min | $T_{fading}$ /hrs,min | Acid Added |
|---|---|---|---|---|---|---|
| Pb Cathode ~0 11M | 55 | 20 | 137 min | 2 hrs 17 min | 5 hrs | 3d 3M HCl |
| $YbCl_3 \cdot 6H_2O$ in 1 1 EtOH.dioxane | 45 | 10 | 330 min | 5 hrs 30 min | 6 hrs 35 min | 3d 3M HCl |
| | 50 | 20 | 15 min | 2 hrs 15 min | 4 hrs 30 min | 3d 3M HCl |
| Pt Anode 0 500mL conc HCl | 45 | 10 | 140 min | 2 hrs 20 min | 3 hrs 55 min | 3d 3M HCl |
| 7 50mL of 1 1 EtOH dioxane | 55 | 20 | 10 min | 30 min | 4 hrs 10 min | 3d 3M HCl |
| | 50 | 20 | 35 min | 2 hrs 20 min | 5 hrs 30 min | 3d 3M HCl |
| | 45 | 15 | 8 min | 55 min | 3 hrs | 3d 3M HCl |
| piece of impure Pb used | 50 | 25 | 120 min | 2 hrs | 6 hrs 10 min | 3d 3M HCl |
| saturated solution used | 60 | 20 | 15 min | 40 min | 1 hr | 3d 3M HCl |
| | 60 | 20 | 30 min | 1 hr 10 min | 2 hrs | 3d 3M HCl |
| impure Pb used | 60 | 25 | 253 min | 4hrs 13 min | 4 hrs 53 min | 3d 3M HCl |
| Pb switched during experiment | 60 | 20 | 25 min | 1 hr 20 min | 2 hrs 55 min | 3d 3M HCl |
| 0 089M $YbCl_3 \cdot 6H_2O$ used | 60 | 10 | 63 min | 1 hr 3 min | 2 hrs 2 min | 3d 3M HCl |

EtOH = ethanol conc = concentrated 3d = three drops

**Table 12 (Continued) Electrolysis Results: Data for Saturated $YbCl_3 \cdot 6H_2O$ in 1:1EtOH:Dioxane.**

| System | Voltage /Volts | Current /mA | $T_{green}$ /min | $T_{max\ green}$ /hrs,min | $T_{fading/duration}$ /hrs,min | Acid Added |
|---|---|---|---|---|---|---|
| Pb Cathode sat'd $YbCl_3 \cdot 6H_2O$ | 60 | 25 | 8 min | 8 min | 3 hrs | 3d 3M HCl |
| in 1·1 EtOH dioxane solid present | 60 | 25 | 13 min | 13 min | 3 hrs 8 min | 3d 3M HCl |
| majority of Pb cathode in glass | 60 | 15 | - | - | 2 hrs 23 min | 3d 3M HCl |

EtOH = ethanol sat'd = saturated 3d = three drops

3 The Best System

The solvent system that gave maximum reduction of Yb(III) to Yb(II) was one that contained ~0 11M $YbCl_3 \cdot 6H_2O$ in 1:1 ethanol:dioxane. An ~0 17M $YbCl_3 \cdot 6H_2O$ solution was made by weighing out the appropriate amount of solid $YbCl_3 \cdot 6H_2O$ and putting it into solution using a 1.1 ethanol:dioxane solution Eight milliliters of the ~0 17M $YbCl_3 \cdot 6H_2O$ was placed in a beaker and 4 00 mL of $H_2O$ was added The solution was made acidic with 3M HCl until a pH around 2 0-3 0 was obtained, this requiring approximately 3 drops of acid The cathode compartment contained 8 00 mL of this solution The anode compartment contained 0 500 mL of concentrated HCl diluted with 7 50 mL of 1 1 ethanol dioxane to obtain 8 00 mL of solution A voltage between 55-60 V was applied to the system The experiment was continued until the solution went from the green color that is characteristic of a Yb(III) to Yb(II) reduction to a colorless solution, which is characteristic of the oxidation of Yb(II) to Yb(III) A variation of the experiment was done by changing the amount of $H_2O$ from 4 0 mL to 3 5 mL

This particular type of experiment was performed twenty times In 5 of these experiments, three 1 00 mL aliquots of the solution from the cathode were removed and injected into three 1 00 mL aliquots of a 3 0M $(NH_4)_2SO_4$ solution. A green precipitate formed at the interface between the 3 0M $(NH_4)_2SO_4$ solution and the cathode solution In each of these 5 experiments, the precipitate, as well as the supernatant, was tested

The precipitate was tested by adding $H_2O$ to a small amount There was an evolution of gas and the precipitate changed from green to colorless Another small portion of the precipitate was tested by adding to it some dilute HCl This too gave an evolution of gas and

the precipitate changed from green to colorless A third test was performed on the remaining fraction of the precipitate A very dilute solution of $KMnO_4$ was added The precipitate went from green to colorless The solution of $KMnO_4$ changed from purple to colorless These three tests indicate that the precipitate was $YbSO_4$

The supernatant from the precipitates were also tested This was done by diluting the supernatant with $H_2O$ and then preparing an appropriate solution to be analyzed by atomic emission spectroscopy Standard solutions were also prepared The data obtained from the atomic emission would indicate the amount of Yb(III) present The percentage of Yb(III) that was reduced to Yb(II) could be calculated by difference It was concluded that a maximum of approximately 30% Yb(II) yield could be obtained, see Table 13 on page 28 for data

A precipitate formed in the bottom of the cell in all 20 experiments during the reductions The precipitate was separated by removing the solution by pipette The precipitate was tested by adding dilute HCl and by adding $H_2O$ In both cases, the precipitate dissolved and there was an evolution of gas This indicated that the precipitate was most likely $YbCl_2$.

4 The Second Best System

The solvent system that gave the next best reduction of Yb(III) to Yb(II) was one that contained 0.14M $YbCl_3 \cdot 6H_2O$ and 0 28M potassium citrate in deionized $H_2O$

This solution was made by weighing out the appropriate amount of solid $YbCl_3 \cdot 6H_2O$ to obtain a 0.14M solution and adding to it twice the molar amount of solid potassium citrate These compounds were put into solution using $H_2O$ Eight milliliters of the 0 14M $YbCl_3 \cdot 6H_2O$ and 0 28M potassium citrate solution was placed in a beaker and made acidic

**Table 13 Analysis Results: Data from Atomic Emission Spectroscopy.**

| Supernatant Sample | Starting Material | Percent Yb as Yb(III) | Percent Yb as Yb(II) |
|---|---|---|---|
| 50.8 ppm | 60 0 ppm | 85% | 15% |
| 49 4 ppm | 59 0 ppm | 84% | 16% |
| 48 8 ppm | 58 0 ppm | 84% | 16% |
| 44 5 ppm | 61 0 ppm | 73% | 27% |
| 44.2 ppm | 61 3 ppm | 72% | 28% |
| 43 6 ppm | 61.0 ppm | 72% | 28% |
| | | | Average 22% |

ppm = parts per million

with 3M HCl until a pH around 2 0-3 0 was obtained, this requiring approximately 3 drops of acid The cathode compartment contained 8 00 mL of this solution The anode compartment contained 8.00 mL of 1M $H_2SO_4$. A voltage between 55-60 V was applied to the system The experiment was continued until the solution went from the green color that is characteristic of a Yb(III) to Yb(II) reduction to a colorless solution, which is characteristic of the oxidation of Yb(II) to Yb(III) A variation of the experiment was done by changing the acid added to make the solution acidic from 3M HCl to concentrated acetic acid This experiment, variations included, was performed 12 times In the cases in which 3M HCl was used, a precipitate formed in the bottom of the cell during the reduction The precipitate was separated by removing the solution by pipette The precipitate was tested by adding dilute HCl and by adding $H_2O$ In both cases, the precipitate dissolved and there was an evolution of gas This indicated that the precipitate was most likely $YbCl_2$

5 Additional Systems

There were several other solvent systems tried to obtain a maximum reduction of Yb(III) to Yb(II)

Type 1 The first type was one that contained a 0 12M $YbCl_3 \cdot 6H_2O$ in 1 1 ethanol nitromethane A 0 17M $YbCl_3 \cdot 6H_2O$ solution was made by weighing out the appropriate amount of solid $YbCl_3 \cdot 6H_2O$ and putting into solution using a 1 1 ethanol nitromethane solution Eight milliliters of the 0 17M $YbCl_3 \cdot 6H_2O$ was placed in a beaker and 3 50 mL of $H_2O$ was added The solution was made acidic with 3M HCl until a pH around 2 0-3 0 was obtained, this requiring approximately 3 drops of acid The cathode compartment contained 8 00 mL of this solution The anode compartment contained

0 400 mL of concentrated HCl diluted with 7.60 mL of 1 1 ethanol nitromethane to obtain 8 00 mL of solution A voltage of 60 V was applied to the system The system exhibited an orange color The system also exhibited an orange color when the $YbCl_3 \cdot 6H_2O$ was replaced with $LaCl_3 \cdot 6H_2O$ but remained colorless when no rare earth was present The cause for the orange color was not determined

Type 2 The second type was one that contained a 0 11M $YbCl_3 \cdot 6H_2O$ in 1 1 ethanol diethyl carbonate A 0 16M $YbCl_3 \cdot 6H_2O$ solution was made by weighing out the appropriate amount of solid $YbCl_3 \cdot 6H_2O$ and putting into solution using a 1 1 ethanol diethyl carbonate solution Eight milliliters of the 0 16M $YbCl_3 \cdot 6H_2O$ was placed in a beaker and 3 50 mL of $H_2O$ was added The solution was made acidic with 3M HCl until a pH around 2 0-3 0 was obtained, this requiring approximately 3 drops of acid The cathode compartment contained 8 00 mL of this solution The anode compartment contained 0 400 mL of concentrated HCl diluted with 7 60 mL of 1.1 ethanol diethyl carbonate to obtain 8 00 mL of solution A voltage of 60 V was applied to the system There was no detectable reduction of Yb(III) to Yb(II)

Type 3 The third type was one that contained a 0 11M - 0 12M $YbCl_3 \cdot 6H_2O$ in 1 1 ethanol DMSO A 0 16M $YbCl_3 \cdot 6H_2O$ solution was made by weighing out the appropriate amount of solid $YbCl_3 \cdot 6H_2O$ and putting into solution using a 1 1 ethanol DMSO solution Eight milliliters of the 0 16M $YbCl_3 \cdot 6H_2O$ was placed in a beaker and $H_2O$ was added The amount of $H_2O$ added varied between 2 50 mL to 3 50 mL The solution was made acidic with 3M HCl until a pH around 2 0-3.0 was obtained, this requiring approximately 3 drops of acid The cathode compartment contained 8 00 mL of this solution The anode

compartment contained 0.400 mL of concentrated HCl diluted with 7.60 mL of 1·1 ethanol:DMSO to obtain 8 00 mL of solution. A voltage between 55- 60 V was applied to the system. This experiment was performed 5 times and a reduction of Yb(III) to Yb(II) was only obtained once

Type 4 The fourth type was one that contained a 0 16M $YbCl_3 \cdot 6H_2O$ in 1 1 ethanol·toluene This solution was made by weighing out the appropriate amount of solid $YbCl_3 \cdot 6H_2O$ and putting into solution using a 1:1 ethanol.toluene solution Eight milliliters of the 0 16M $YbCl_3 \cdot 6H_2O$ was placed in a beaker. The solution was made acidic with 3M HCl until a pH around 2 0-3 0 was obtained, this requiring approximately 6 drops of acid The cathode compartment contained 8 00 mL of this solution The anode compartment contained 0 400 mL of concentrated HCl diluted with 7.60 mL of 1·1 ethanol toluene to obtain 8.00 mL of solution A voltage between 55- 60 V was applied to the system. This experiment was performed 5 times and no reduction of Yb(III) to Yb(II) was obtained

Type 5 The fifth type was one that contained a 0 16M $YbCl_3 \cdot 6H_2O$ in 1:1 ethanol.acetone This solution was made by weighing out the appropriate amount of solid $YbCl_3 \cdot 6H_2O$ and putting into solution using a 1 1 ethanol.acetone solution Eight milliliters of the 0 16M $YbCl_3 \cdot 6H_2O$ was placed in a beaker and was made acidic with 3M HCl until a pH around 2 0-3 0 was obtained, this requiring approximately 3 drops of acid The cathode compartment contained 8 00 mL of this solution The anode compartment contained 0 400 mL of concentrated HCl diluted with 7 60 mL of 1 1 ethanol acetone to obtain 8 00 mL of solution. The anode and cathode compartments were parafilmed to keep the solvent from evaporating A voltage between 50-55 V was applied to the system A brown

color formed in all six experiments No brown color was obtained when the $YbCl_3 \cdot 6H_2O$ was replaced with $EuCl_3 \cdot 6H_2O$ or $SmCl_3 \cdot 6H_2O$ The source of the brown color was not determined.

Type 6. The sixth type was one that contained a 5 $1x10^{-3}$M $YbCl_3 \cdot 6H_2O$ in and $1.2x10^{-1}$M potassium citrate in $H_2O$ This solution was made by weighing out the appropriate amount of solid $YbCl_3 \cdot 6H_2O$ to obtain a 5 $1x10^{-3}$M solution and adding to it twice the molar amount of solid potassium citrate These compounds were put into solution using $H_2O$ Eight milliliters of the 5 $1x10^{-3}$M $YbCl_3 \cdot 6H_2O$ and 1 $2x10^{-1}$M potassium citrate solution was placed in a beaker and made acidic with 3M HCl until a pH around 2 0-3 0 was obtained, this requiring approximately 3 drops of acid The cathode compartment contained 8 00 mL of this solution The anode compartment contained 8 00 mL of 1M $H_2SO_4$ A voltage between 28-38 V was applied to the system A minimal reduction of Yb(III) to Yb(II) was obtained

Type 7 The seventh type was one that contained 0 35M $YbCl_3 \cdot 6H_2O$ and 0 70M potassium citrate This solution was made by weighing out the appropriate amount of solid $YbCl_3 \cdot 6H_2O$ to obtain a 0 35M solution and adding to it twice the molar amount of solid potassium citrate These compounds were put into solution using $H_2O$ Eight milliliters of the 0 35M $YbCl_3 \cdot 6H_2O$ and 0 70M potassium citrate solution was placed in a beaker and made acidic with 3M HCl until a pH around 2.0-3 0 was obtained, this requiring approximately 3 drops of acid The cathode compartment contained 8 00 mL of this solution The anode compartment contained 8 00 mL of 1M $H_2SO_4$. A voltage between 16-18 V was applied to the system There was no reduction of Yb(III) to Yb(II) but there was a formation of a white precipitate, probably $Yb(OH)_3$

Type 8 The eighth type was one that contained 0 14M $YbCl_3 \cdot 6H_2O$, 0 28M potassium citrate and 0 14M $(NH_4)_2SO_4$ This solution was made by weighing out the appropriate amount of solid $YbCl_3 \cdot 6H_2O$ and solid $(NH_4)_2SO_4$ to obtain a 0 14M solution of each and adding to it twice the molar amount of solid potassium citrate These compounds were put into solution using $H_2O$ Eight milliliters of the 0 140 $YbCl_3 \cdot 6H_2O$, 0 14M $(NH_4)_2SO_4$ and 0 28M potassium citrate solution was placed in a beaker and made acidic with 3M $H_2SO_4$ until a pH around 2.0-3 0 was obtained, this requiring approximately 3 drops of acid The cathode compartment contained 8 00 mL of this solution The anode compartment contained 8 00 mL of 1M $H_2SO_4$ A voltage between 19-28 V was applied to the system There was no precipitate that formed in the cell during the reduction A minimal reduction of Yb(III) to Yb(II) was obtained in this system long with a white precipitate, probably $Yb(OH)_3$.

## Chapter 3

## INTERPRETATIONS AND CONCLUSIONS

A good separation technique is needed for the production of high purity Lu since it is the major constituent in the best solid-state gamma scintillation detectors The production of high purity Lu is difficult due to Lu being a member of the rare earth family The production of high purity Lu can be make easier if Lu can be separated from the adjacent rare earth Yb If Yb could be removed from a Lu-containing rare earth mixture, the separation of Lu would be enhanced measurably

To obtain this separation, a reduction of Yb(III) to Yb(II) was attempted Yb(II) could be removed from the mixture since it would have different chemical properties than most of the other rare earths due to the (II) oxidation state Once Yb is removed from the rare earth mixture, the "gap" between Lu and the remaining rare earths would be greater and separation of Lu would be made easier The reduction of Yb(III) to Yb(II) can be obtained electrolytically.

Previous electrolytic reductions of Yb(III) to Yb(II) were obtained through the use of a Hg cathode Hg is most often used as a cathode in aqueous reductions of Yb(III) to Yb(II) due to its large overvoltage. However, due to the severe toxicity of Hg in the human body, its use in an industrial setting is prohibited This, and the fact that Pb has a comparable overvoltage, are the primary reasons Pb was selected for the study

There were numerous solvent systems tried using Pb as the cathode and Pt as the anode The first system was one in which contained $YbCl_3 \cdot 6H_2O$ and potassium citrate in

water This system gave a minimal reduction of Yb(III) to Yb(II), if any The reduction of Yb(III) to Yb(II) was very sensitive due to the instability of Yb(II) in water The optimum pH for the reduction of Yb(III) to Yb(II) is approximately 2.0 No reduction was obtained in any system if the pH was greater than 3 0 If the pH approached or became greater than 4 0, $Yb(OH)_3$ formed at the electrode/solution interface The pH was difficult to control during the reduction and the formation of $Yb(OH)_3$ at the interface of the electrode and the solution was almost inevitable It has been concluded that the system is highly pH dependent

A second system contained 0.12M $YbCl_3 \cdot 6H_2O$ in 1 1 ethanol nitromethane In this system, an orange color formed during the experiment The orange color was present when $YbCl_3 \cdot 6H_2O$ and $LaCl_3 \cdot 6H_2O$ were electrolyzed However, when no rare earth was present, the solution remained colorless when electrolyzed This would indicate that the orange color could possibly be from the nitromethane decomposing and complexing with the lanthanide ion or perhaps the lanthanide ion is acting as a catalyst and causing the reduction of the nitromethane to a product with a nitrogen to nitrogen double bond, which could possibly be colored However, these possible interpretations have not been analyzed to give a conclusive result

A third system contained 0 11M $YbCl_3 \cdot 6H_2O$ in 1 1 ethanol diethyl carbonate In this system, no reduction of Yb(III) to Yb(II) was obtained The pH could not be regulated to keep the pH at a low value The system was abandoned due to the belief that since acid was present in the solution that the diethyl carbonate was decomposing to carbonic acid and perhaps forming a buffer There was an evolution of gas when acid was added and this would indicate that the carbonic acid was forming carbon dioxide and water

A fourth system contained 0 16M $YbCl_3 \cdot 6H_2O$ in 1:1 ethanol·acetone In this system, a brown color was obtained during electrolysis This color was only obtained when $YbCl_3 \cdot 6H_2O$ was present and not when $LaCl_3 \cdot 6H_2O$ or $EuCl_3 \cdot 6H_2O$ was electrolyzed. The system remained colorless when the electrolysis was performed and no rare earth was present Since no brown color was observed during the electrolysis of $LaCl_3 \cdot 6H_2O$ or $EuCl_3 \cdot 6H_2O$, it was concluded that perhaps the color was not due to the degradation of the solvent and was more likely specific to a Yb(II) complex. No further studies were performed to support this conclusion

The next two systems consisted of 0 11M - 0 12M $YbCl_3 \cdot 6H_2O$ in 1.1 ethanol DMSO and 0 16M $YbCl_3 \cdot 6H_2O$ 1.1 ethanol toluene These systems were abandoned due to no reduction of Yb(III) to Yb(II) being obtained

The system that contained ~0 11M $YbCl_3 \cdot 6H_2O$ in 1.1 ethanol dioxane gave the maximum amount of Yb(III) reduction During the reduction, a precipitate formed at the bottom of the cell The precipitate was crystalline and pale green The precipitate was tested by adding water and dilute acid to it In both cases, the precipitate went colorless and a gas was evolved It was concluded that the precipitate was $YbCl_2$ due to the color change when acid and water was added and also due to the evolution of gas This conclusion was made based on fact that the Yb(II) would be oxidized to Yb(III) which is colorless and during this process, $H_2$ gas is evolved

When the Yb(II) solution was taken from the system and injected into a solution of 3 0M $(NH_4)_2SO_4$, a green precipitate formed The precipitate, as well as the supernatant, was tested The precipitate was tested in several ways First, water was added to the precipitate

The precipitate changed from green to colorless and a gas was evolved Secondly, dilute acid was added to the precipitate. Again, the precipitate changed from green to colorless and a gas was evolved Thirdly, a very dilute solution of $KMnO_4$ was added to the precipitate The precipitate changed from green to colorless and the $KMnO_4$ changed from purple to colorless From these results, it was concluded that the precipitate formed upon injecting the Yb(II) solution into the $(NH_4)_2SO_4$ was $YbSO_4$

The supernatant was tested using atomic emission to obtain the amount of Yb(III) that was not reduced during the experiment From these data, the percent of Yb(II) reduced could be calculated by difference It was concluded that a yield of approximately 30% Yb(II) was the maximum obtained

An introduction of air to the system from a stream blowing over the cell when the cell was situated in the hood was not conducive to reduction However, if the cell was removed from the hood and set on the bench top to reduce the introduction of air to the system, the reduction occurred There seems to be an apparent air effect on the reduction No further studies were performed to support this conclusion

Although the literature reports that the reduction of Yb(III) to Yb(II) is hampered by the presence of heavy metal ions, it has been concluded that the reduction of Yb(III) to Yb(II) can be obtained in the presence of heavy metal ions since the reduction was obtained using a Pb cathode It has also been concluded that approximately 30% is the maximum reduction of Yb(III) that may be obtained using a Pb cathode in the tested system The literature reports that a 95% Yb(III) reduction may be obtained by using a Hg cathode under similar conditions

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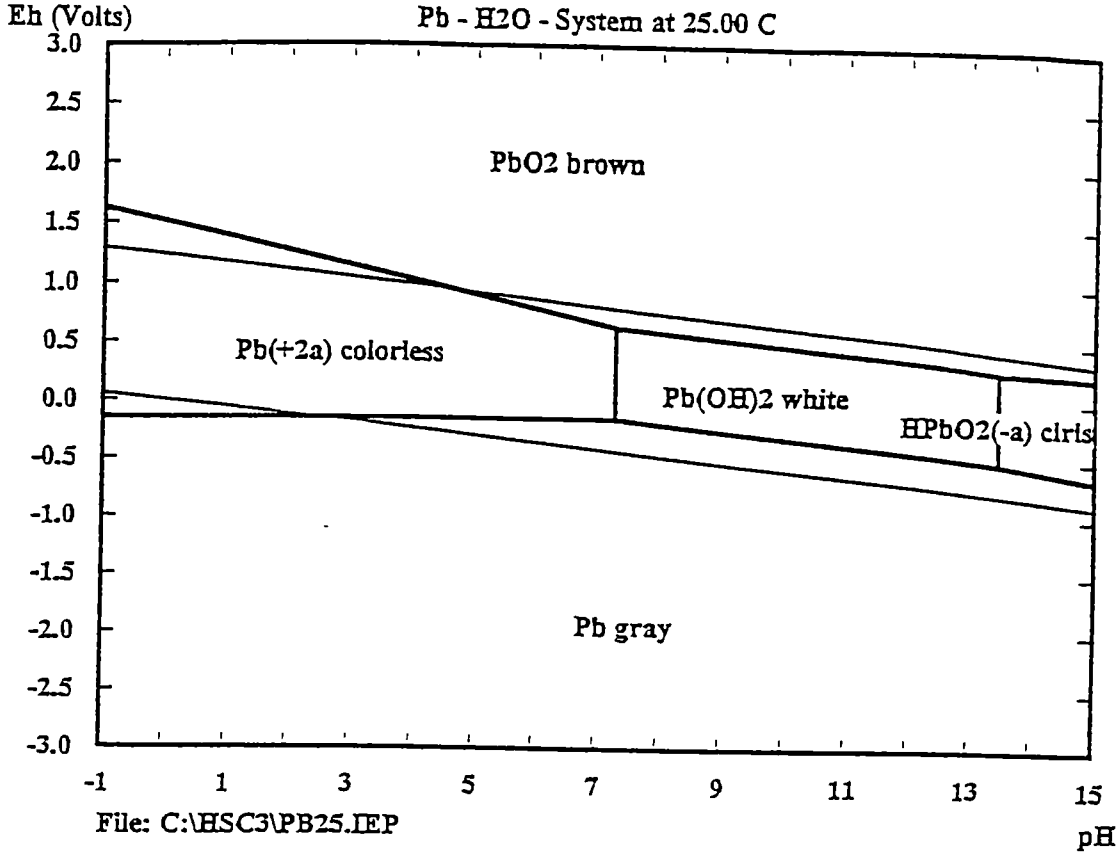
# APPENDIX



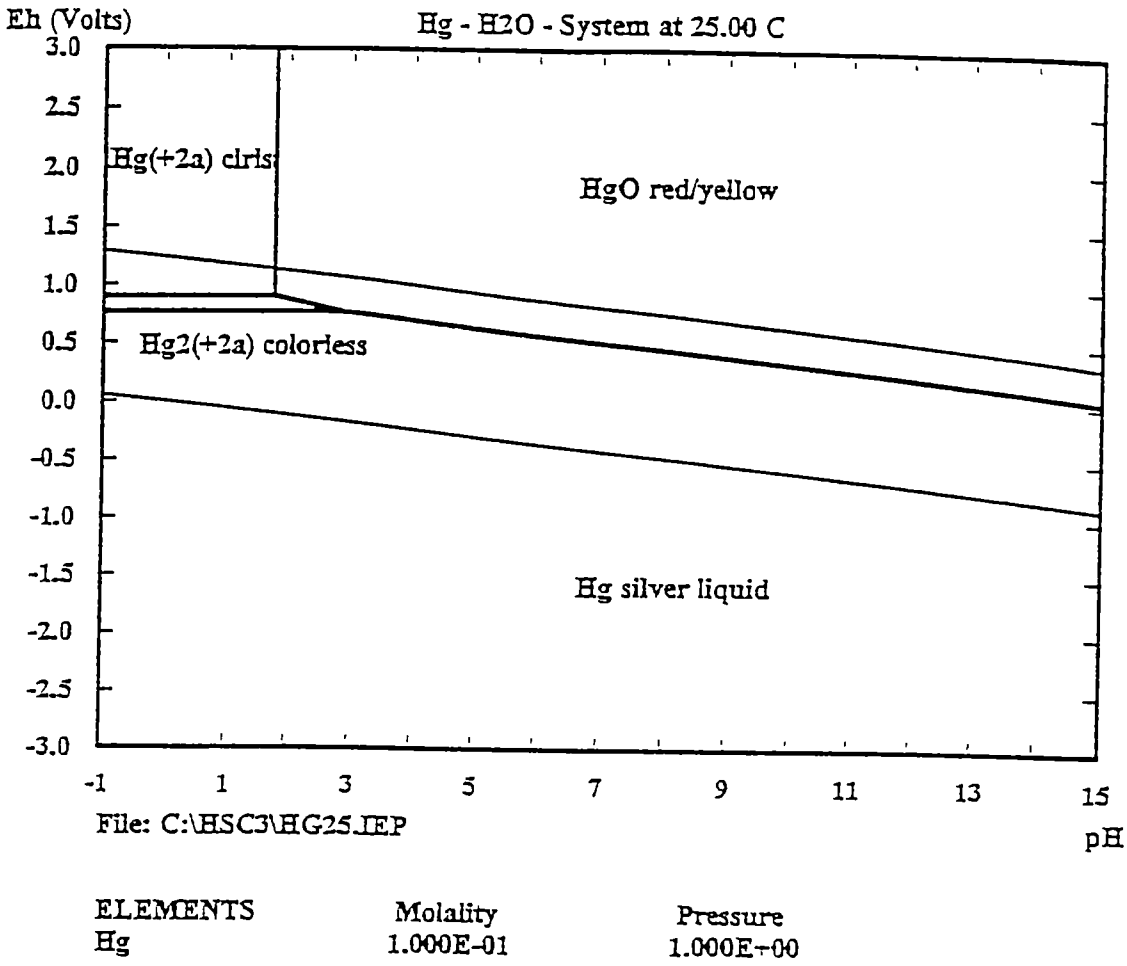

| ELEMENTS | Molality | Pressure |
|---|---|---|
| Pb | 1.000E-01 | 1.000E+00 |

E-pH Diagram for $10^{-1}$ M Pb using the species ($\Delta G^{\circ}$ in kJ/mole) Pb (0 0) $Pb^{+2}$ (-24 7) $Pb(OH)_2$ (-421 3) $PbO_2$ (-215 5) $HPbO_2^-$ (-338.9) HOH (-237 2) $OH^-$ (-157.3)

Equations for the lines

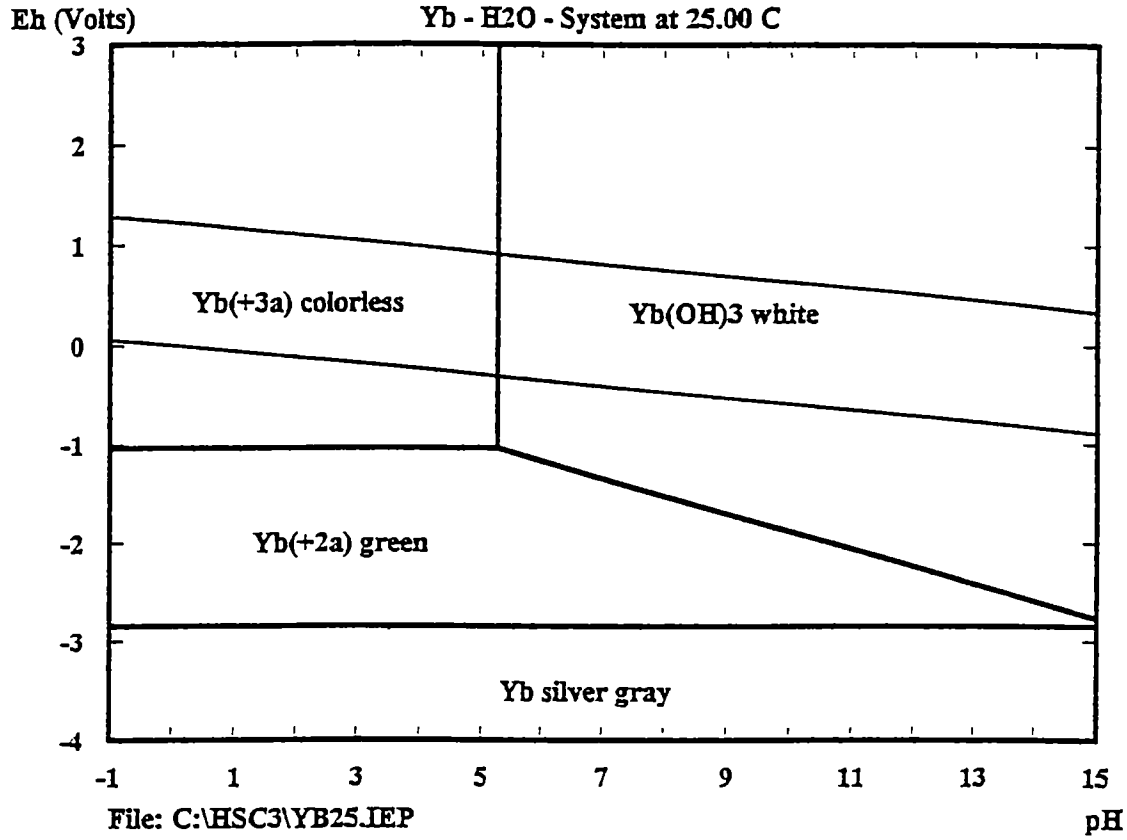
| | |
|---|---|
| $Pb^{+2}/Pb$ | $E = -0\ 13 + 0\ 030 \log [Pb^{+2}]$ |
| $Pb(OH)_2/Pb$ | $E = 0\ 28 - 0\ 059pH$ |
| $HPbO_2^-/Pb$ | $E = 0\ 70 - 0\ 089pH + 0\ 030 \log [HPbO_2^-]$ |
| $PbO_2/Pb^{+2}$ | $E = 1\ 46 - 0\ 118pH - 0\ 030 \log [Pb^{+2}]$ |
| $PbO_2/Pb(OH)_2$ | $E = 1\ 07 - 0\ 059pH$ |
| $PbO_2/HPbO_2^-$ | $E = 0\ 64 - 0\ 030pH - 0\ 030 \log [HPbO_2^-]$ |
| $Pb^{+2}/Pb(OH)_2$ | $2pH = 13.7 - \log [Pb^{+2}]$ |
| $Pb(OH)_2/HPbO_2^-$ | $pH = 14\ 5 + \log [HPbO_2^-]$ |

**Figure 1 : Pourbaix Diagram for Pb in an Aqueous Medium.**[21]




E-pH Diagram for $10^{-1}$ M Hg using the species ($\Delta G^{o}$ in kcal/mole) Hg(0.0) $Hg_2^{+2}$(36.7) $Hg^{+2}$(39.3) $Hg_2O$(-13.0) HgO(-14.0)

**Figure 2: Pourbaix Diagram for Hg in an Aqueous Medium.**[21]



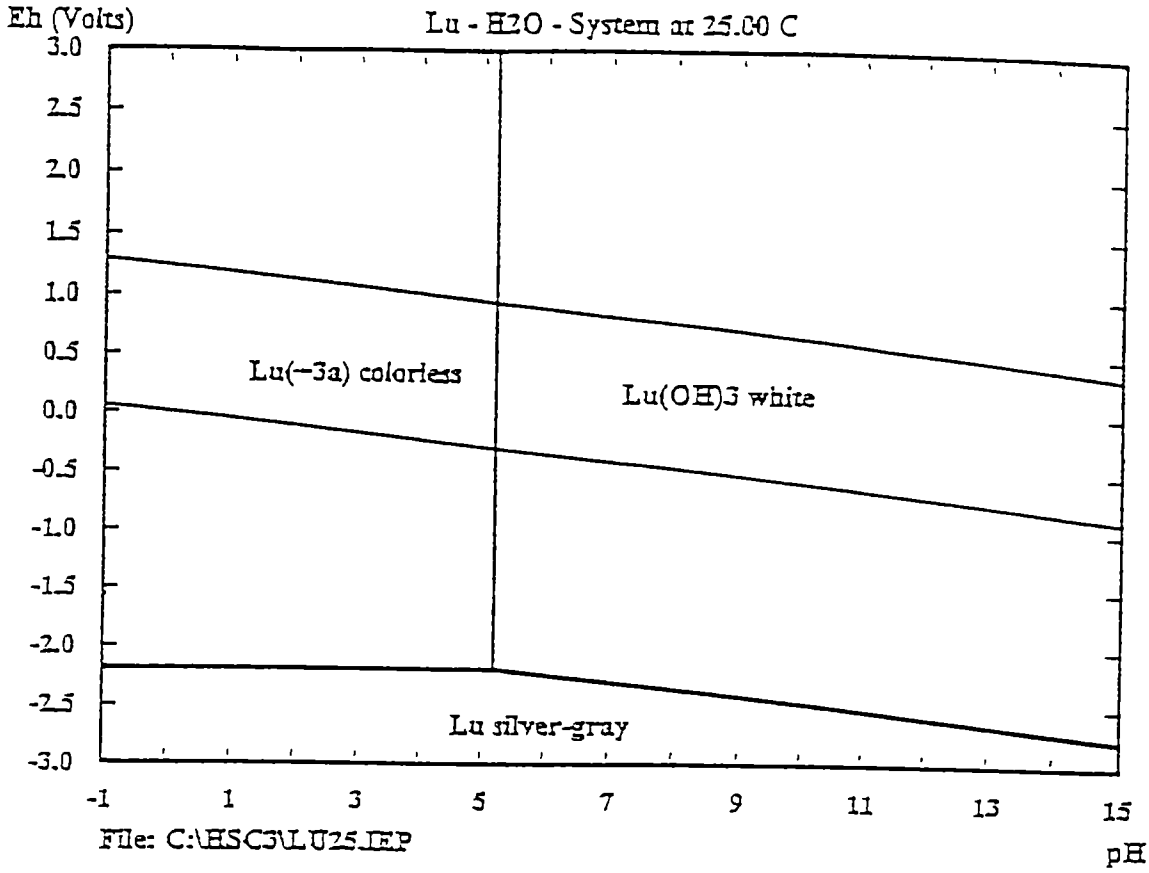

| ELEMENTS | Molality | Pressure |
|---|---|---|
| Yb | 1.000E-01 | 0.000E+00 |

E-pH Diagram for $10^{-1}$ M Yb using the species ($\Delta G^o$ in kJ/mole) Yb(0.0), $Yb^{+2}$(-543.9) $Yb^{+3}$(-644.3), $Yb(OH)_3$(-1271.5), HOH(-237.2), $H^+$(0.0), $OH^-$(-157.3).

Equations for the lines

| | |
|---|---|
| $Yb^{+3}/Yb^{+2}$ | $E = -1.04$ |
| $Yb(OH)_3/Yb^{+2}$ | $E = -0.56 - 0.177\ pH - 0.059 \log [Yb^{+2}]$ |
| $Yb^{+2}/Yb$ | $E = -2.82 + 0.030 \log [Yb^{+2}]$ |
| $Yb(OH)_3/Yb^{+3}$ | $3\ pH = 14.8 - \log [Yb^{+3}]$ |

Figure 3 : Pourbaix Diagram for Yb in an Aqueous Medium.[21]




| ELEMENTS | Molality | Pressure |
|---|---|---|
| Lu | 1.000E-01 | 1.000E+00 |

E-pH Diagram for $10^{-1}$ M Lu using the species ($\Delta G^{o}$ in kJ/mole) Lu(0.0), $Lu^{+3}$(-629.7), $Lu(OH)_3$(-1258.1), HOH(-237.2), $H^{-}$(0.0), $OH^{-}$(-157.3).

Equations for the lines

| | |
|---|---|
| $Lu^{+3}/Lu$ | $E = -2.18 + 0.020 \log [Lu^{+3}]$ |
| $Lu(OH)_3/Lu$ | $E = -1.89 - 0.059\ pH$ |
| $Lu(OH)_3/Lu^{+3}$ | $3\ pH = 14.6 - \log [Lu^{+3}]$ |

Figure 4 : Pourbaix Diagram for Lu in an Aqueous Medium.[21]

# VITA

Rebecca Joan Mack was born in Olean, New York, on February 18, 1976 She graduated from Port Allegany High School of Port Allegany, Pennsylvania in June 1994 She attended the Pennsylvania State University where she was awarded a Bachelor of Science Degree in Chemistry in May 1998 In the fall of 1998, she entered the Graduate School of the University of Tennessee, Knoxville where she held a Teaching Assistantship