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Yb Separation Through Tetrphenylborate Complexation

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**Appendix E - UNIVERSITY HONORS PROGRAM
SENIOR PROJECT - APPROVAL**

Name: Michael Darekas

College: Arts & Sciences Department: Chemistry

Faculty Mentor: Dr. George K. Schweitzer

PROJECT TITLE: Yb Separation Through Tetraphenylborate
Complexation

I have reviewed this completed senior honors thesis with this student and certify that it is a project commensurate with honors level undergraduate research in this field.

Signed: Geo. K. Schweitzer, Faculty Mentor

Date: 5/8/01

General Assessment - please provide a short paragraph that highlights the most significant features of the project.

Comments (Optional):

A notable attempt to stabilize Yb(II) and thus to enhance the separation from its neighbors Tm and Lu. The work has important implications for detectors in body-scan instruments since they use extremely pure Lu. He has done a very good piece of work.

GKS

**Yb SEPARATION
THROUGH TETRAPHENYLBORATE COMPLEXATION**

**Senior Research Project
For the Honors Department
The University of Tennessee, Knoxville**

Michael Gene Danekas

May 2001



Acknowledgements

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Thanks is also given to CTI for their financial support of this research.

Abstract

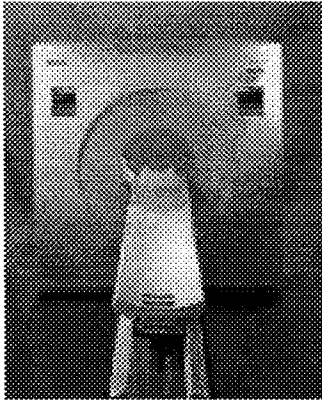
By removing Yb from a mixture of rare earths, the ability to separate and purify Lu is greatly enhanced. With the high commercial value of Lu, namely in positron emission tomography scanners, the need to reduce the production costs of Lu is very great. The unique properties of the (II) oxidation state of Yb allows it the ability to form a highly stable complex with tetraphenylborate ions. The feasibility of using this complex after electrolytically producing Yb(II) was studied based on its application to industrial processes. The difficulties that were encountered when dealing with this system -- insolubility of Yb(III)/TPB and various solvent effects -- were very difficult to overcome and led to the failure of current attempts at isolating Yb from other rare earths using the tetraphenylborate ion as a complexing agent.

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Introduction/History

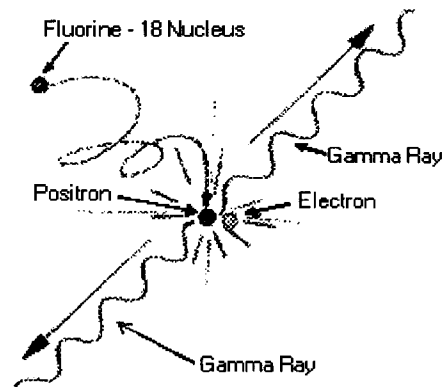
Positron Emission Tomography (PET) is a relatively new scanning technique that is being used in medical research. By being able to study the metabolic or chemical activity of the body rather than simply the body's form, physicians are able to sooner and better detect the



presence of cancerous growths that CT scans and MRIs may have missed. Using PET, researchers can now measure the chemical processes involved in the working of healthy or diseased human brains in a way previously impossible, all while keeping the patient comfortable, conscious, and alert. PET scanners also present the research community with a better platform to study how the body

operates on a metabolic level.

Unlike an x-ray machine that sends x-rays through the body in order to view structures such as cartilage and bone, the PET scanners are a passive scanner that detects the emission of gamma rays from the body after the collision of a positron and an electron in the body. Positrons are the products of radioactive decay of a chemical that must be introduced into the body. Oxygen gas labeled with oxygen-15 can be used to study oxygen metabolism in the body. Similarly, glucose can be labeled with fluorine-18 in order to find



areas of the body where glucose uptake is very high – such as in a growing tumor. In order to detect the gamma rays that are emitted from the body, solid-state gamma scintillation detectors are needed.

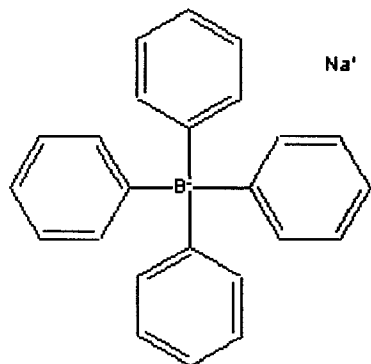
The best of these scintillation detectors contains the rare earth element Lu in the form of lutetium orthosilicate crystals that have an extremely high purity. The production of high purity Lu is a very difficult process due to great chemical similarities of the rare earth (lanthanide) family. The lanthanide elements have very similar chemical properties and their chemistry is dominated by a highly stable ion with a positive three charge. Lu is the second rarest of the lanthanides with a terrestrial abundance of 0.8 ppm. Its difficulty in separation stems from the similarities of all the rare earths. Lying at the high end of the lanthanide series, Lu is therefore easy to separate from Hf, the next highest element. However, the most difficult separation with Lu is from its lanthanide neighbor on the periodic table, Yb. The ease of separation of Lu from the other rare earths is proportional to the distance from Lu on the periodic table. Classical methods of separation often involved fractional crystallization and fractional precipitation. However, these inefficient and time-consuming techniques have been replaced recently by the introduction of ion-exchange and counter-current solvent extractions. These new methods are currently the most widely used means for producing high-purity rare earths other than Ce and Eu. If Yb could be removed from a Lu-containing rare earth mixture, then the separation of Lu would be enhanced greatly so that the number of solvent extraction steps could be reduced. Previous methods of removing Yb, though, also centered around solvent extraction, so no real gain in separation efficiency could be made.

The separation of Yb can be discussed, however, because of the interesting chemistry of Yb. Unlike most other rare earths (Eu and Sm excluded), Yb can form a (II) oxidation state. This second oxidation state gives Yb chemical properties that are much different from those of other rare earths in (III) oxidation states. For example, Yb(II) could be separated by precipitating it with SO_4^{2-} since the Ln(III) sulfates are soluble. Once Yb(III) is reduced to

Yb(II), the separation of Lu could be carried out more easily using a method such as counter-current solvent extraction since the separation coefficient between Lu and Tm is much greater than that between Lu and Yb.

The first preparation of Yb(II) was in 1929 when Yb_2O_3 was treated with a stream of Cl_2 - S_2Cl_2 . W. Klemm and W. Schüth performed this reduction at 600-620°C. Later solution reduction techniques were performed using electrolysis under various solvent conditions. A third reported reduction technique has been to use Mg powder to reduce Yb(III) to Yb(II).

The biggest problem with the reduction of Yb to its (II) oxidation state is the short life of the Yb(II) ion in aqueous solution. In solution, any free Yb(II) will quickly oxidize back to Yb(III) if there is any H^+ present. The two most obvious solutions to this problem would be to either run the electrolysis in basic solution or in an aprotic solvent. Running the electrolysis in a basic solution would form the $\text{Yb}(\text{OH})_3$ precipitate and therefore prevent successful electrolysis. Since the ultimate goal of this research is in the commercial production of PET scanners, the use of aprotic solvents would increase the health and environmental concerns of the Lu production. With neither of these two obvious solutions to spontaneous reoxidation being viable, another solution had to be found.



In 1983, A.N. Kamenskaya and N.B. Mikheev found that Yb(II) was made approximately 50 times more stable when the tetraphenylborate (TPB) ion was present in solution in a ratio of $[\text{Yb}^{2+}]:[\text{TPB}] = 1:4$. They found that the oxidation rate constant was $\sim 1 \times 10^{-6} \text{ s}^{-1}$ making the half-oxidation time more than 200 hours. They theorized that the TPB ion apparently enters the inner coordination sphere of the Ln(II) ion, forming the complex $[\text{Ln}(\text{TPB})_4]^-$. The large size of

the TPB complexing agent then provides an effective barrier between the Ln(II) ion and the water molecules of the solution, the principal oxidizing agent in the solution. Although other people have theorized different complexation mechanisms such as some charge-transfer scenarios, the fact remains that tetraphenylborate ions are able to stabilize Yb(II) ions in aqueous solution.

Statement of Problem

In order to achieve the end goal of lowering PET scanner production costs, Lu must be produced much cheaper. Removal of Yb from a Lu-containing solution would greatly enhance the ease of Lu separation. Using the electrolysis of Yb to its (II) oxidation state, the process of isolating the Yb using TPB ions as a complexing agent was studied. While many different approaches were used, the main consideration was in the final application to industrial processes. Therefore, lead was selected for the cathode instead of mercury (which has a larger overvoltage) due to the health ramifications of industrial mercury usage. Also, organic solvents were largely ignored due to the higher costs of waste disposal.

Materials/Apparatus

The solvents used in the experiments were reagent grade. All water used was deionized. The $\text{YbCl}_3 \cdot 6\text{H}_2\text{O}$ 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 400A, 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 was a Protek 3006B (60V/1.5A single output) Regulated Digital DC Power Supply operating at a constant current of 100 mA with a variable voltage somewhere between 17V and 14V.

The electrolytic 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.

Procedure

Preparation of the Sample and the System

Since the most industrially-sensitive solution was aqueous, the ideal solution characteristics for this study were 0.14M $\text{YbCl}_3 \cdot 6\text{H}_2\text{O}$, 0.28M K_3Cit . This solution was acidified with 2M HCl to a pH of approximately 2-3. The anode compartment required an acid solution of approximately 1M H_2SO_4 .

The cell was cleaned between each use 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 again.

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

Detailed Procedure

Initially, the first step to be completed was the reproduction of past work by other researchers. Since Rebecca Mack's work was to be the procedural basis to this research, the electrolytic setup was duplicated along with some of her basic steps. In her research, tests were conducted in order to determine the best solution characteristics in order to reduce Yb to its (II) oxidation state. She determined that the best solutions to reduce Yb were in nonaqueous solutions. Therefore, the exact details of maximizing Yb(II) production in aqueous solutions is not fully described. However, due to the nature of this work, organic solutions are not preferred and the reduction must occur in an aqueous solution.

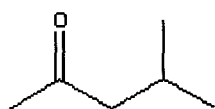
The aqueous solutions were very sensitive to acidity when undergoing electrolysis. If the acidity is too high, the $\text{Yb}(\text{OH})_3$ is quickly produced and the reduction is blocked by the Yb all

being in a precipitate. If the acidity is too low, the H^+ is the recipient of the reduction and hydrogen gas is emitted from the cathode solution. After much trial and error, the ideal pH for reduction in the aqueous solutions is around 1. It was determined that about 6 mL of the Yb(III) solution should be added to the cathode compartment and then 2M HCl was added until the pH was around 1 as measured by pH paper. During the course of the electrolytic reduction, acid was added intermittently in order to keep the pH in the proper range to ensure Yb reduction. With the pH in the proper range, the yellow cloud of Yb(II) ions surrounding the cathode would develop and remain there for about an hour as long as current was applied to the system.

Based on the information that was received from journals, the tetraphenylborate ion has the ability to complex the Yb(II) ion and increase its stability in aqueous solution. It was assumed that this TPB ion, when added to the cathode solution would complex the Yb(II) ions and simply increase their life in solution. However, when the TPB was added to the cathode solution, the solution filled with a white precipitate. Under initial assumption that this may have been an accident or error, the process was repeated with the same results. After conducting other tests, it was determined that the precipitate was created because the Yb(III) ions were insoluble with TPB. This problem that arose was a very significant complication to the industrial usage of TPB to remove Yb from a rare earth solution. Because the TPB could not just be added to an aqueous solution of lanthanides to stabilize only the (II) ions, the entire conceived process had to be revised.

To attempt to overcome this new difficulty, new solvent configurations were attempted to solubilize the Yb(III)/TPB precipitate. About 1 mL of pure ethanol was added to three different test tubes. Into those test tubes individually was added Yb(III) solution prepared for the electrolysis, TPB solution, and then both. The first two test tubes remained clear, but the third

test tube with the Yb(III) and the TPB in it formed a precipitate. This precipitate was produced in ethanol, 50:50 ethanol:water, acetone, and toluene. The solvent that was best able to solubilize the Yb(III)/TPB precipitate was methyl isobutyl ketone. This solvent has enough



organic character to make the large phenyl groups on the precipitate go into solution as well as the ketone group which helps put the precipitate into

solution through charge transfer.

With methyl isobutyl ketone being a solvent in which the Yb(III)/TPB precipitate is soluble, it was necessary to determine if the organic solvent could support any water before the precipitate fell out of solution. To test this, another solvent had to be added to the methyl isobutyl ketone so that the organic and aqueous phases would be at least slightly miscible. Using one milliliter of methyl isobutyl ketone with Yb(III)/TPB dissolved in it, approximately 8 drops of water could be added to the solvent along with 13 drops of acetone and the Yb(III)/TPB remained in solution in the organic phase. This was also done using ethanol and propanol instead of acetone, but these solvents produced precipitate in the aqueous phase of the mixture.

The aqueous capacity of the organic solution of methyl isobutyl ketone and acetone was then tested. In 10 test tubes, one milliliter of methyl isobutyl ketone and one milliliter of acetone were added. A small amount of sodium tetraphenylborate was then added to each test tube. Various amounts of green aqueous Yb(II) solution from the electrolytic reduction were then added to each test tube. The results for this test were seen in following table. It was determined that the 2 mL organic solution of 1:1 acetone:methyl isobutyl ketone could support about 0.5 mL of aqueous Yb(II)/Yb(III) solution.

Aqueous solution (μL)	250	500	550	600	625	650	700	750	850	1000
Appearance	Clear	Clear	Clear	Faintly cloudy	Slightly cloudy	Slightly cloudy	Slightly cloudy	Slightly cloudy	Slightly cloudy	cloudy

During the testing for solubility, it was noticed that the Yb(III)/TPB precipitate did not remain in solution but fell out of the organic phase and precipitated in the aqueous phase after about one hour of standing. It was also noticed that the characteristic yellow-green color of the Yb(II) solution was once again not evident in this solution even though the masking effect of the Yb(III)/TPB precipitate was taken out of the system. It was theorized that adding some acidified Na_2SO_3 would help solve that problem by keeping the Yb(II) from being oxidized. However, when the solutions from the solubility tests were observed later, the organic phases in all of the test tubes was a golden yellow. This color was possibly the indication of the presence of Yb(II) in the organic phase, most likely being complexed by the tetraphenylborate ion.

With this first observation of the TPB complexation, duplicate tests were conducted to verify that this was not just a product of some contamination. With successful duplication, the presence of Yb(II) was tested by adding a compound that would be easily reduced. A dilute solution of potassium permanganate was added to the samples of the organic phases supposedly containing Yb(II). With every test, the permanganate was quickly reduced to brown manganese dioxide. To verify that the reduction was being caused solely by the Yb(II) in solution, each of the solution components was tested for its ability to reduce permanganate. It was then discovered that methyl isobutyl ketone has the ability to reduce permanganate. Since the solvent for the Yb(II) can reduce the permanganate as well, the same test was done after evaporating away the solvent. The samples that were theorized to contain the Yb(II) still reduced the permanganate to the same extent as when the solvent was present. The blanks of just solvent also reduced the permanganate but to a much lesser extent than before. While this provides some proof that the Yb(II) is in the organic phase and is stabilized by the TPB, conclusive evidence has not been produced.

Because of the lack of success using the original theory of tetraphenylborate complexation and using that to remove Yb from solution, a new approach was attempted. This new approach comes from combining previous knowledge about the ability of magnesium powder to reduce a solution of Yb(III) to Yb(II) with the new discovery that tetraphenylborate will precipitate Yb(III) and likely the rest of the lanthanides in the (III) oxidation state. The new approach is to precipitate all of the Yb(III) in the solution using TPB and then reduce that Yb in a solid state using magnesium powder. It is thought that the Yb(II) that is generated from the reduction would then stay in solution stabilized by TPB.

This theory was tested several times by using the Yb(III) solution made for the electrolysis and adding NaTPB to the solution in a test tube. After precipitation, the test tube was centrifuged, and Mg powder and acid were added. Using this process, there seemed to always be a slight yellow tint around the Mg where the reduction of Yb(III) should be taking place. However, the production of the Yb(II) was never significant enough to warrant any more investigation into this approach.

Conclusions

After spending much time attempting to reproduce the electrolytic production of Yb(II) from a Yb(III) solution, the real work at hand was finally able to commence. However, with each step that was taken toward the goal, new complications would arise. Seeking to use TPB to enhance the stabilization of Yb(II) in aqueous solution, the TPB was initially thrown into a solution containing Yb(II) but also Yb(III). Unfortunately the presence of a precipitate from Yb(III) required the search for different solvents. Having to resort to using methyl isobutyl ketone, the reality of using the tetraphenylborate as a complexing agent in our system was fading. Without clear evidence as to its solubility and the difficulty of isolation of the Yb(II), the original approach was abandoned. The second approach of reducing the Yb(III) in the TPB precipitate using Mg powder was attempted but then also abandoned due to inefficiency and lack of Yb(II) production.

The novel approach of ytterbium complexation using tetraphenylborate to separate Yb from Lu based on oxidation state characteristics seemed too good to be true. Based on the literature sources on using TPB to complex Yb(II), it seemed as if it were a magic substance that would isolate Yb(II) and only Yb(II). However, on initial testing, the TPB was found to complex just about everything in solution. While it may have lengthened the stability and life of Yb(II) in aqueous solution, it was not the compound that was the answer to the PET production problems that were in consideration. With a need to stabilize Yb(II) in a safe, inexpensive, environmentally-friendly way, TPB was not the solution. The necessity of using large quantities of organic solvents or magnesium creates a setup that is not as favorable in an industrial setting and may not be worth the costs of implementing a new procedure.

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