NEUTRON CAPTURE EXPERIMENTS ON UNSTABLE NUCLEI

Annual Technical Report for Period November 2002 –November 2003
Issued: December 2003

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1.0. EXECUTIVE SUMMARY

A primary objective of this project is to study neutron capture cross sections for various stable and unstable isotopes that will contribute to the Science Based Stockpile Stewardship (SBSS) program by providing improved data for modeling and interpretation of nuclear device performance. The information obtained will also be important in astrophysical modeling of nucleosynthesis. During this reporting period, the emphasis has been on preparing a radioactive target of ^{155}Eu (half-life= 4.7 years), and several stable targets, including isotopically separated ^{154}Sm, ^{151}Eu, and ^{153}Eu. Measurements of their neutron capture cross sections will be conducted in collaboration with researchers at the Los Alamos Neutron Science Center (LANSCE) facility using the Detector for Advanced Neutron Capture Experiments (DANCE).

A suitable backing material (beryllium) for the targets has been selected after careful calculations of its contribution to the background of the measurements. In addition, a high voltage plating procedure has been developed and optimized. Stable targets of ^{151}Eu and ^{153}Eu and a target of natural Eu (~50% ^{151}Eu and ~50% ^{153}Eu) have each been plated to a mass thickness of >1 mg/cm^2 and delivered to the DANCE collaboration at Los Alamos National Laboratory (LANL). Natural Eu targets will be tested first to confirm that the target dimensions and backing are appropriate prior to performing measurements on the extremely valuable targets of separated isotopes.

In order to prepare a target of the radioactive ^{155}Eu, it must first be separated from the ^{154}Sm target material that was irradiated in a very high neutron flux of 1.5x10^{15} neutrons/cm^2/s for 50 days. The reaction is ^{154}Sm (n,γ)^{155}Sm (half-life = 22 minutes) $\rightarrow$ ^{155}Eu. Considerable progress has been made in developing a suitable high-yield and high-purity separation method for separating Eu from targets containing about twenty times as much Sm. An exhaustive review of the literature indicated that a multiprocess approach in which Eu(III) is reduced to Eu(II) prior to separation should provide an effective and efficient means of separation from the Sm(III). To date, three multiprocess methods have been developed and tested for their ability to meet the design requirements set forth by this project. These methods combine an initial reduction step using Zn(Hg) with either cation exchange resin in (1) column form or in (2) a batch reactor and

hydroxyisobutyrate (α-HIB) as the eluant for trivalent lanthanides. Another multiprocess method uses solvent extraction with 0.1 M thenoyl trifluoroacetone (TTA) in benzene. Preliminary experiments indicate that: (a) A multiprocess approach using α-HIB as a complexing agent for trivalent lanthanides is ineffective for separating Eu from Sm because α-HIB stabilizes Eu(III) even in the presence of excess amounts of the reductant; (b) A multiprocess approach using solvent extraction shows promise, indicating that 0.1 M TTA in benzene favors extraction of trivalent over divalent metal ions by a factor of greater than 750. However, the reduction step using Zn(Hg), when combined with the TTA extraction, becomes less effective at reducing Eu during subsequent extractions and may also affect the stability of the TTA. Use of the amalgam also introduces Zn(II) contamination that must be separated from the Eu with additional solvent extraction steps.

A PhD student from the group has visited the LANSCE facility, participated in several parameter checks of the DANCE, and acquainted himself with the data acquisition system. During these initial experiments, data were collected and brought back to UC Berkeley for analysis.

A high purity P-type germanium detector was purchased, set up, and calibrated to assist with the determination of separation yields and efficiencies using ?-ray spectroscopy measurements of suitable radioactive tracers.

2.0. INTRODUCTION AND BACKGROUND

New initiatives in the national security arena have called for the systematic review and reinterpretation of 50 years of archived data from the nuclear testing program. As a result, the Science Based Stockpile Stewardship (SBSS) program was established as one of the primary missions of the National Nuclear Security Administration[1]. As part of this program, vast computational resources specifically directed towards understanding nuclear weapons physics are being developed. However, these efforts will only be successful if commensurate efforts are made to provide better experimental data for utilization in the computer models and codes. Evaluations of detonation performance rely on various radiochemical tracers strategically placed within the device. Under the high neutron fluences existing in a typical nuclear test, multiple nuclear reactions on a single atom are possible. Knowledge of the probability of occurrence (cross section) of the various possible reactions is required in order to decipher this complex of possible reactions, but few actual measurements of cross sections are available. As a result, predictions of device performance have been based mostly upon theoretical estimates rather than experimentally determined values of nuclear cross sections. Unfortunately, large errors are associated with the theoretical estimates of cross sections for low energy neutron capture reactions. Although these low energy reactions may not greatly affect the overall nuclear yields, they may significantly alter the isotopic inventory of radiochemical detectors observed after detonation of a device, thus leading to inaccurate interpretations of device performance. The ability to fulfill this mission while maintaining compliance with the Comprehensive Test Ban

Treaty is directly related to the ability to obtain accurate experimental data on neutron capture cross sections for various isotopes.

The neutron capture process is also of interest in astrophysics for understanding the creation of the elements in stars and in waste management for controlling the burn-up of nuclear waste. A rather lengthy list of radioactive and rare isotopes for which neutron capture cross sections are needed has been compiled [2,3]. To provide sufficient quantities of three of the radioactive isotopes from that list for studies of their neutron capture cross sections, our Los Alamos collaborators had already arranged for irradiations of isotopically pure samples of stable ^{146}Nd, ^{154}Sm and ^{170}Er in a high flux (2 x 10^{15} n $cm^{-2}s^{-1}$) reactor for about 50 days. The radioactive products ^{147}Pm (β^-, 2.6 y), ^{155}Eu(β^-, 4.7 y), and ^{171}Tm(β^-, 1.9 y) were produced in the following reactions: ^{146}Nd (n,γ)^{147}Nd(β^-, 11 d,)^{147}Pm; ^{154}Sm(n,γ)^{155}Sm(β^-, 22 min)^{155}Eu; ^{170}Er(n,γ)^{171}Er(β^-, 7.5 hr)^{171}Tm. Details about the samples, irradiations, and products are shown in Table 1. These products are "branching point" nuclei where there is competition between β-decay to a heavier element and neutron capture to a next heavier isotope and determination of their capture cross sections in the astrophysically critical keV neutron energy region will provide seminal information in the quest to understand element production in stars. Although these isotopes are of interest to both the SBSS program and astrophysics, no accurate measurements of their neutron capture cross sections have yet been made.

Table 1. Neutron irradiations of ^{146}Nd, ^{154}Sm and ^{170}Er to produce ^{147}Pm, ^{155}Eu and ^{171}Tm

Sample	Mass (mg)	Est. σ (Barns)	$t_{1/2}$ (years)	Product	Activity (Ci)	Atoms (10^{19})	Mass (mg)	Sample/Product Mass Ratio
Nd-146	430	1.4	2.62	Pm-147	3.53	1.56	3.79	113.5
Sm-154	200	7	4.75	Eu-155	4.34	3.48	8.89	22.5
Er-170	250	6	1.92	Tm-171	10.28	3.33	9.39	26.7

A primary goal of our project is to study neutron capture reactions on both stable and unstable nuclei. The research necessary for this project can be divided into two equally important parts: (1) Cross section measurements, which include neutron bombardment of the target, data collection and analysis; (2) Target preparation, which includes development and application of suitable purification procedures and methods for depositing the purified isotopes of interest on suitable backing materials. To carry out this research, close collaboration among personnel from LANL, LBNL, and UC Berkeley will be required. Measurements will be made using the Detector for Advanced Neutron Capture Experiments (DANCE) located at the Los Alamos Neutron Science Center (LANSCE). Stable targets of interest will be prepared at LBNL, while radioactive targets will be prepared at special facilities located at LANL. Personnel from UC Berkeley and LBNL will develop the required separation and plating procedures. These personnel will also assist in preparing radioactive targets and measuring radioactive and stable targets at LANL.

We have chosen the Sm-Eu system for our initial chemical separation studies because separation procedures based on reduction of Eu to the divalent (II) state while leaving Sm in the trivalent (III) state appeared especially attractive. The other systems will require separation of trivalent species from one another, which requires a much more difficult chemical separation procedure.

3.0. EXPERIMENTAL FACILITIES

Neutron-induced reactions may include the ejection of a proton (n, p), gamma ray (n, γ), or one or a number (x) of neutrons (n, xn') or may cause the nucleus to fission (n, f). The type of reaction that occurs is partially determined by the energy of the incident neutron. As such, four designations have been developed for neutrons of different energy regions: Thermal (~0.025 eV), Epithermal (~1 eV), Slow (~1 keV), and Fast (100 keV – 10 MeV) neutrons. A number of nuclear reactions is possible with fast neutrons including (n, p), (n, γ), or (n, xn'), while reactions involving thermal neutrons typically result in neutron capture (n, γ). The cross section of neutron capture increases as the neutron energy decreases. Therefore, the capture of thermal neutrons is much more likely than that of fast neutrons[4].

Figure 1 illustrates typical processes that occur during capture of thermal neutrons. Here neutron capture by I leads to an excited state I', which then emits primary and secondary γ rays in order to reach a more stable state. The sum of the neutron separation energy (S_n) and the energy of the incident neutron (E_n) is equal to the energy of the excited state, I'. The S_n may be related back to the neutron capture cross section and can be measured if all γ rays emitted from the excited state can be accounted for and if E_n is known. For pulsed neutron sources that produce a range of incident energies, careful time of flight measurements provide enough information to calculate E_n. A high intensity source of neutrons with energies in the keV region such as that provided at the LANSCE is needed to perform the required measurements of neutron capture cross sections as a function of neutron energy. In addition, in order to account for nearly all γ rays emitted as a result of the neutron capture requires a highly efficient array of detectors in 4π geometry around a target[3] such as DANCE.

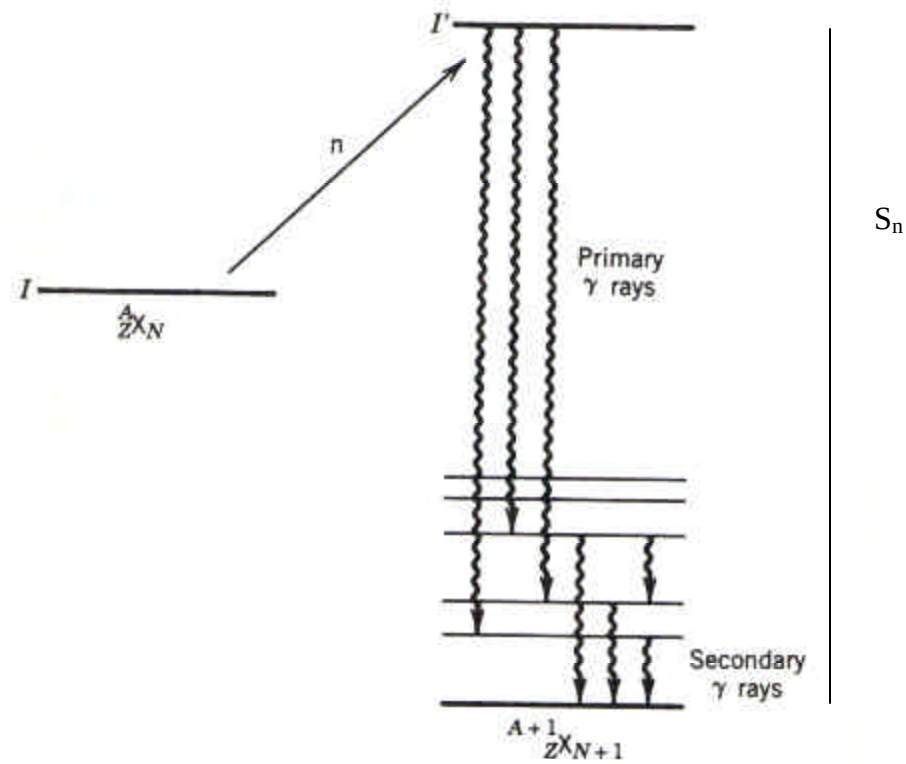

Figure 1. Low energy neutron capture resulting in the emission of primary and secondary gamma rays (adapted from Crane [4]).

The LANSCE is an accelerator-based facility capable of producing high fluence beams of neutrons in the low keV region and is uniquely suited for measuring neutron capture cross sections of interest to SSBS. At the facility, H^- and H^+ particles are produced within two separate high-voltage domes, mixed, and accelerated initially by a drift-tube linear accelerator (linac) to 100 MeV and then further accelerated to 800 MeV using side-coupled cavity linac. The H^- are separated from H^+ and sent to the Proton Storage Ring, where macropulses (750 ms) of these particles are converted to micropulse (0.13 μs) bursts of intense H^+. These protons are subsequently sent to the Lujan center for producing neutrons suitable for a variety of precise time of flight (TOF) experiments. At an incident energy of 800 MeV, approximately 20 neutrons are produced via spallation for every proton that hits the Lujan tungsten metal production target. This produces neutrons too high in energy for most applications, so prior to delivering beam to one of the 16 flight paths (FPs) at the Lujan Center, the energies of the neutrons are decreased by interaction with water, a light, neutron-scattering material[5].

The DANCE is located at flight path 14 in the Lujan Center at the LANSCE facility. A schematic of DANCE is shown in Figure 2. It consists of a shell of 160 BaF_2 detectors in nearly 4π geometry around the beam line and was designed to have high efficiency for γ-ray detection, good neutron-energy resolution, and low background with respect to neutrons. The BaF_2 crystal detector material was chosen for its high efficiency, energy resolution, and the relatively fast recovery that is needed to prevent pileup of decay events between the rapid beam pulses to the

target. In addition, DANCE is capable of a timing resolution of 135 ns (FWHM), which allows for accurate time of flight estimates of incident neutron energies[5].

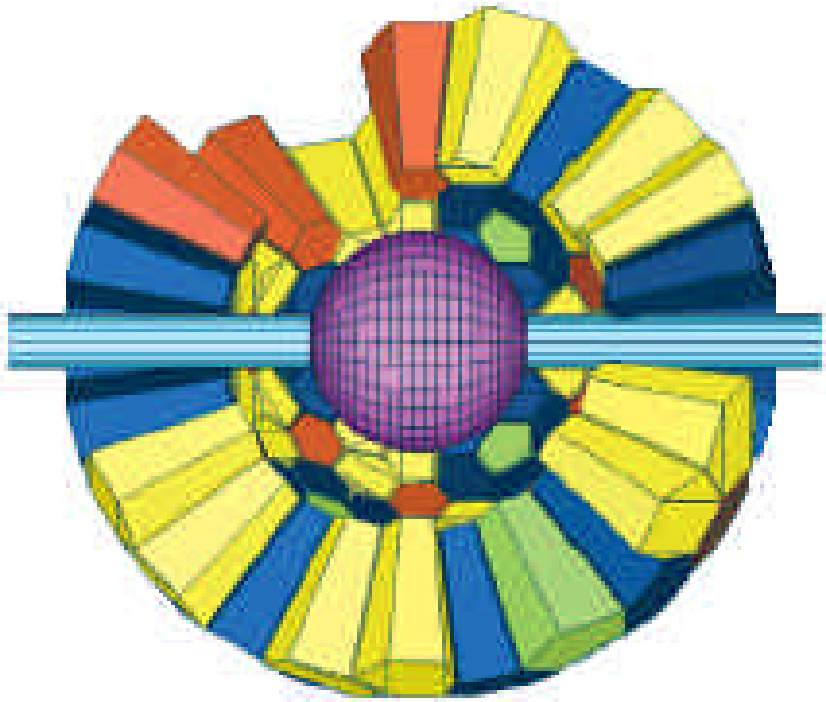

Figure 2. Schematic of DANCE. Each color represents a different shape of the crystal array required for 4π geometry around the target[5].

4.0. TARGET PREPARATION

After choosing the Sm-Eu system for our initial studies, the first priority was to prepare several targets of isotopes of Eu, including stable Eu-151 and Eu-153, and radioactive Eu-155. It was also decided that a target of "normal" Eu (approximately 1:1 ratio of Eu-151 and Eu-153) would be of interest for comparison with the isotopically pure targets. Purified, stable isotopes were available at LANL. However, the radioactive ^{155}Eu produced by neutron bombardment of stable Sm-154 must be separated from the Sm prior to preparation.

Some of the most frequent target preparation techniques include evaporation or condensation, electrospraying, precipitation, and electrodeposition[6]. The method of electrodeposition, which is the process of depositing one metal upon another using electrolysis[7], was chosen for this work as it provides for relatively high yields, simple handling, easy recovery of the target material, and the ability to deposit homogeneously over a range of mass thicknesses[6].

The selection of a suitable backing material for targets was based upon several factors including: (1) nuclear cross-section characteristics; (2) ease of handling and durability; (3) cost of the material. Backing material with the lowest overall total cross section, s(n, tot.), is

preferred. The total cross section is the sum of both neutron capture s(n, ?) and neutron scattering s(n, n') cross sections; both are a function of the energy range of the beam. Figures 3a and 3b show the integral total (Σs(n, tot.)) cross section as a function of backing thickness and energy for both Be and Ti. Figure 3c presents the ratios of the Be/Ti total cross section as a function of energy. From these figures it is evident that within the energy range of interest for the DANCE (i.e., 1 keV – 30 keV), Be has a lower s(n, tot.) than that of equal thickness Ti. Also, at the resonance peak of Ti within the 1 - 30 keV energy range, 0.5-mil Be has a lower total cross section than that of 0.1 mil Ti. Typically Ti is cheaper than Be; however, cost is increased for producing extremely thin backings so that there is no cost benefit in using 0.1-mil Ti over 0.5-mil Be. Therefore, ***0.5-mil Be was selected over 0.1-mil Ti*** because of its better handling and durability, and the presence of a neutron scattering resonance peak for Ti within the energy range of interest that would interfere with the cross section measurements.

The design of the high voltage plating cell was based upon several criteria: (1) design requirements for the targets, which specified a 1 cm diameter deposit and a 2.57 cm diameter foil backing based upon the DANCE beam spot size and the target holder; (2) safety, to include fully enclosed electrodes; and (3) ease of use, to allow for operation within a glove box environment. Figure 4 presents pictures of the HV cell. Future upgrades include a keyless cell design, a new base that handles multiple foil sizes, corrosion resistant base inserts for protection from strong acids during cleaning, an integrated spout and cover.

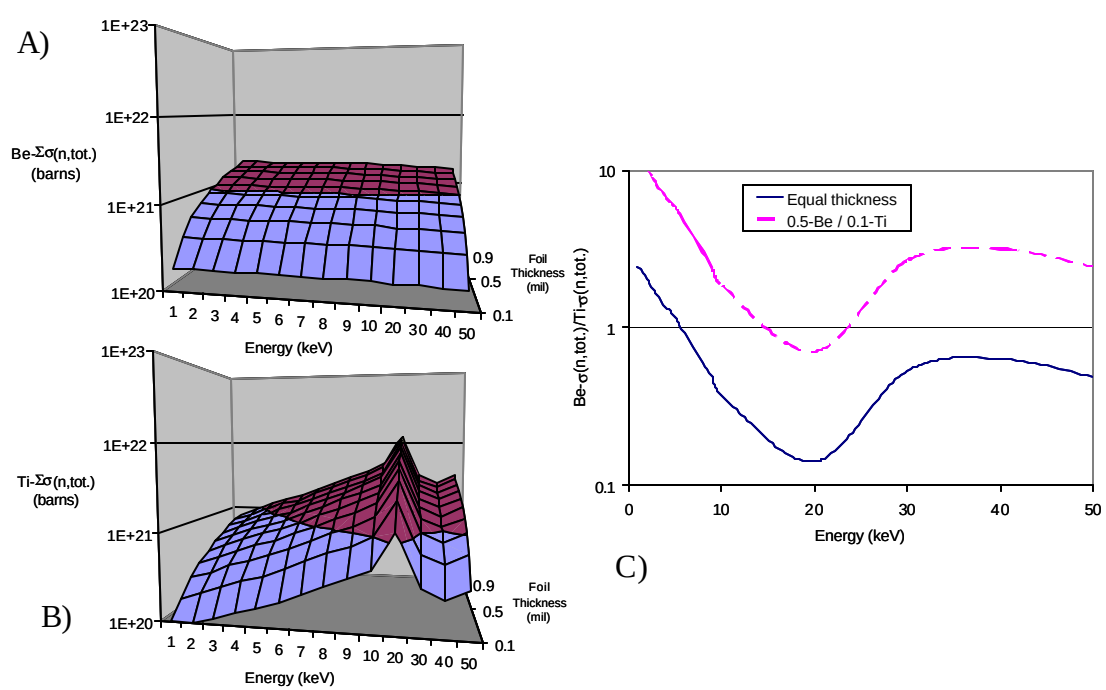

Figure 3. Integral total neutron cross sections (Σ σ(n, tot.)) for Be (A) and Ti (B) backing materials as a function of energy and foil thickness and (C) the ratio of these values for specific foil thicknesses as a function of energy.

A) B)

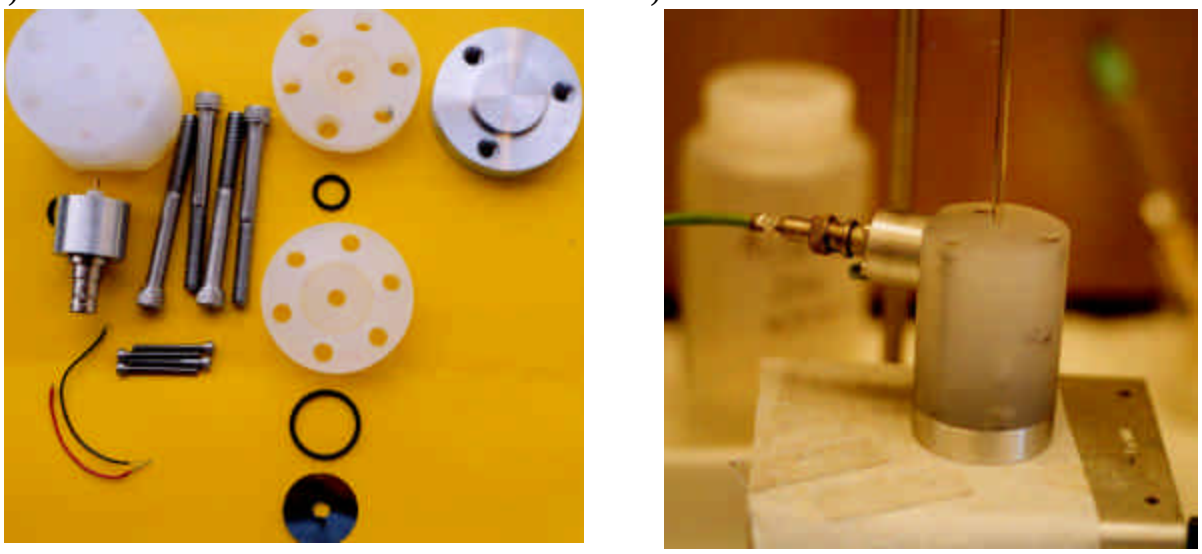

Figure 4. Diagrams and pictures of electroplating cell: A) Diagram of base; B) Diagram of base and mid sections.

A high voltage plating procedure from isopropanol solution was adapted from a LBNL heavy element group procedure (Internal procedure - Gregorich, 1999). Briefly, a lanthanide (Ln) stock solution in isopropanol was prepared by first converting the Ln to a nitrate form by dissolution in concentrated nitric acid followed by evaporation to dryness. Following several dissolution-evaporation cycles to ensure complete conversion, the dried nitrate salt was dissolved in isopropanol. Target backing foil was placed on the O-ring between the bottom of the cell and the Al base. Approximately 4 ml of isopropanol was added to the plating cell, followed by the addition of the Ln stock of volume (~200 µl) required to reach the desired initial Ln concentration. The high voltage cable was connected to the plating cell and the glass stir rod was lowered into the solution and rotated at 10 – 60 Hz. A voltage of ~+100 V to +300 V sufficient to keep a current density around 0.8 mA cm^{-2} was applied to the cell for 30 minutes. Samples for analyses were taken from the cell before and after plating. Targets were deposited in cycles, after gently drying them under a heating lamp for 10 minutes and baking them for 20 minutes at 550^0C. Optimization of the method was carried out over a range of starting Eu concentrations from 10 µg ml^{-1} to 265 µg ml^{-1}. The optimal initial Eu concentration that minimized the plating cycles needed to reach the design criteria mass thickness of 1 mg cm^{-2} and maximized the yield or percent of the total Eu deposited per plating cycle was found to be ~100 µg/ml (Figure 5).

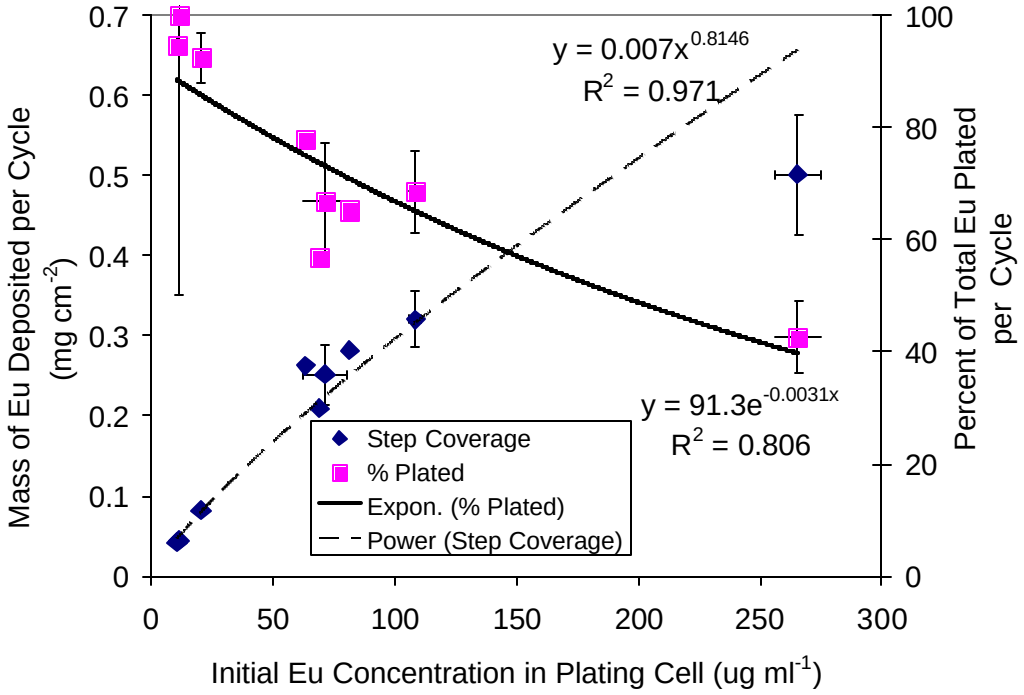

Figure 5. Comparison of the mass and the percent of the total Eu deposited per plating cycle as a function of initial Eu concentration.

Microscopic photographs were taken of Eu targets 0520 and 0522 to investigate the relative homogeneity of the material across the foil surface. Little difference in appearances of the photos of 0520 and 0522 was observed. A series of photographs transecting the center of target 0522 are shown in Figure 6 and depict a relatively homogeneous deposit.

Assays of two targets, 0520 and 0522, were conducted in order to investigate the homogeneity of the deposition radially across the foil. Results from these assays were compared to analyses of the cell solution before and after plating to ensure Eu was being quantitatively transferred to the foil and not being lost to the walls of the plating apparatus. The method used to electrodeposit Eu onto 0520 and 0522 were identical to that described previously, with the exception that the initial Eu concentration in the cell for 0520 and 0522 was 111 $\mu g\ ml^{-1}$ and 265 $\mu g\ ml^{-1}$, respectively. Targets 0520 and 0522 were sectioned radially into 0.32-cm, 0.55-cm, and 1-cm diameters (Figure 7), and the deposit was extracted in 1 M HNO_3 for 6 hours followed by total dissolution of the foil and remaining deposit in 8 M HNO_3 for > 24 hours. Extractant was analyzed by two independent methods using fluorometry and inductively coupled plasma atomic emission spectroscopy (ICP-AES). Less than 5% of the total extractable Eu remained on the foil following the extraction with 1 M HNO_3. Acid extracted Eu material balances by fluorometry and ICP-AES were comparable and not significantly different from estimates derived from Eu

solution concentrations and foil masses measured before and after electroplating. Fluorometry of the assay indicated 90% ± 23% and 100% ± 30% of Eu targets 0520 and 0522, respectively, was recovered based upon solution concentration differences before and after plating. Analyses by ICP-AES indicated the similar but more accurate result that 91% ± 3% and 92.7% ± 2.6% of the plated Eu had been recovered from targets 0520 and 0522, respectively. Figure 7 illustrates that while there was no significant difference in mass thickness of Eu detected radially for target 0520, mass thickness of Eu on target 0522 drops off by 66% in section "C" towards the edge of the foil. The heterogeneity of the mass thickness of Eu on target 0522 relative to that observed for 0520 was attributed to differences in the initial concentration of Eu used within the cell and illustrates the negative effect of higher initial Eu concentrations on the quality of the deposit. Using an initial Eu concentration of ~100 μg/ml in the plating cell, as was used for target 0520, should result in a relatively homogeneous deposit of Eu.

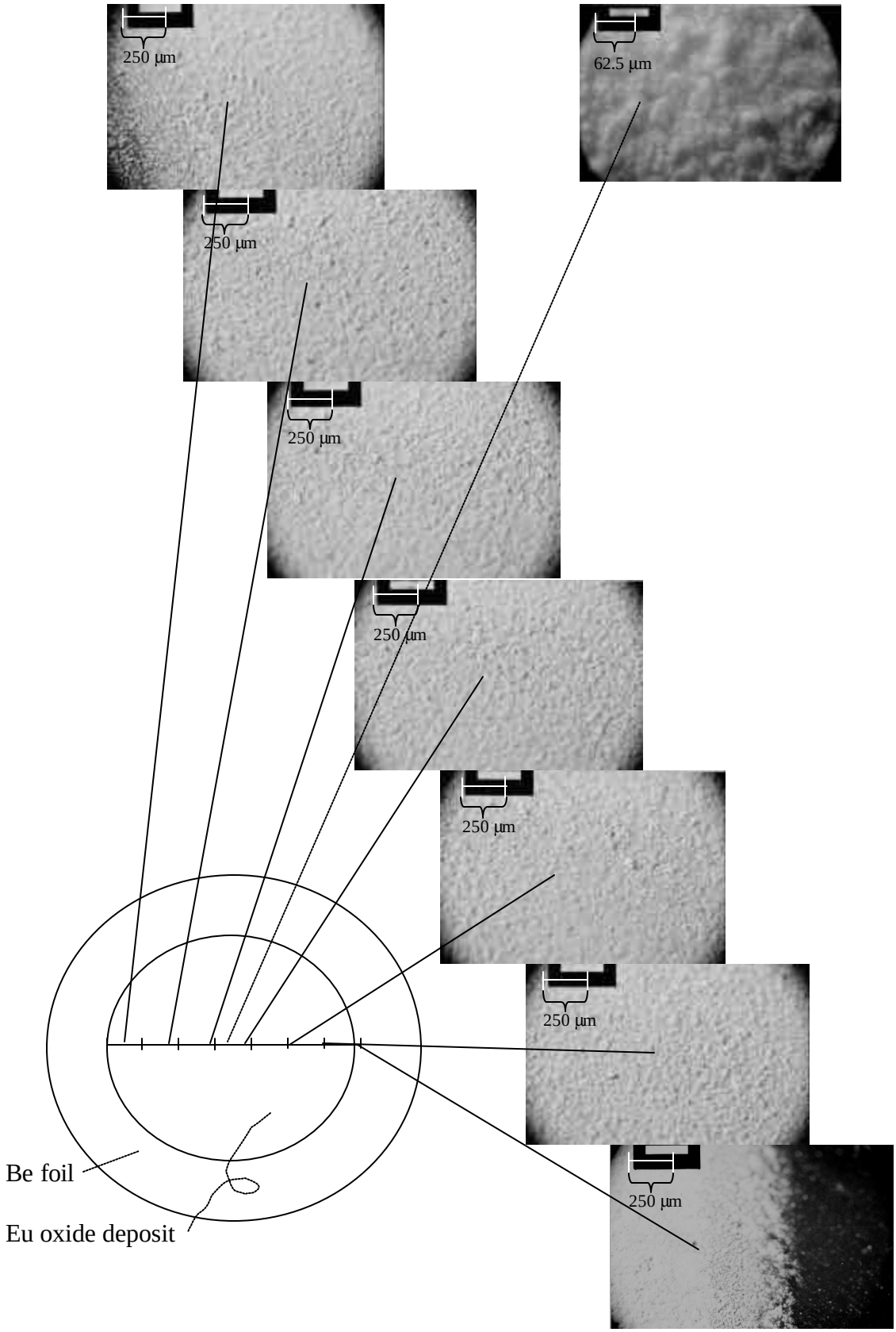

Figure 6. Photographs of electrodeposited Eu on Be. Photographs taken by a MC 100 spot camera coupled to a Zeiss, Axioskop, 10x objective with 10x (and 40x) lens with a Zeiss Reflective KL 1500 light source using Kodak Gold 200 ASA.

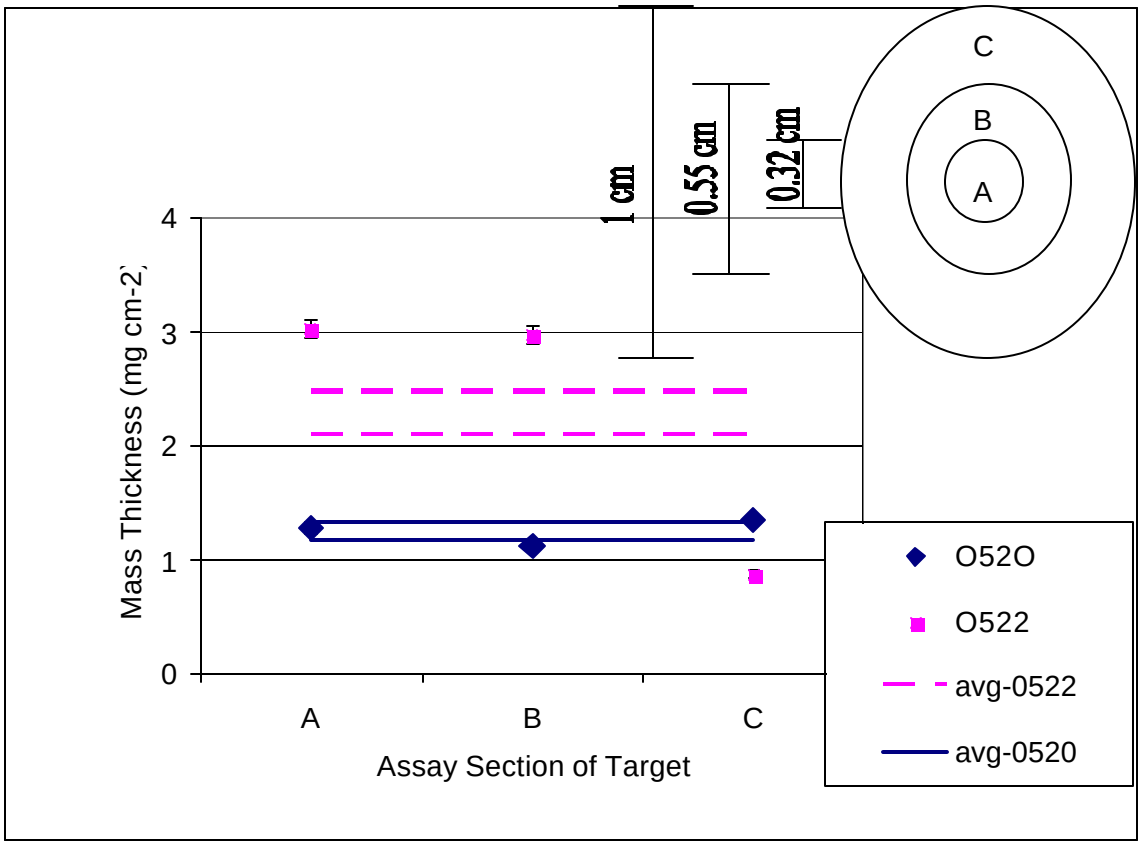

Figure 7. Radial symmetry of Eu mass thickness on targets 0520 and 0522. Solid lines represent the bounds of the 95% confidence limits of the average mass thickness on target 0520. Dashed lines represent the bounds of the 95% confidence limits of the average mass thickness on target 0522.

The most likely two solids deposited during electroplating are $Eu_2O_{3(c)}$ and $Eu(OH)_{3(a)}$. The amorphous solid would be expected to deposit initially and form the crystal solid following baking. However, a mixture of the two solids might persist if the crystallization step were incomplete. Figure 8 compares the amount of Eu deposited calculated from concentration differences within the cell with the total mass differences of the foil measured before and after electroplating. Assuming only hydroxide or oxide Eu solids are allowed to deposit, the slope of the curve in Figure 8 is the ratio of mass of Eu to that of the total solid and may be related back to a hypothetical stoichiometry of a oxy-hydroxide solid, $EuO_y(OH)_z$ by the following equation.

$$\frac{M_{Eu}}{M_T} = \frac{151}{151 + 16y + 17z} \tag{1}$$

If only Eu(III) is present within the solid and its charge is balanced to zero,

$$y = \frac{3 - z}{2} \tag{2}$$

Which may be substituted into equation 1 in order to solve for z. For reference, a solid with a stoichiometry of Eu_2O_3 would have a M_{Eu}/M_T ratio of 0.864, while that of $Eu(OH)_3$ would have a ratio of 0.749. From the figure, the best fit slope of the line is equal to 0.864, which seems to qualitatively indicate an oxide solid has formed as expected. However, the 95% confidence interval bounding the slope ($\pm$0.14) is not statistically different than the expected slopes for either an oxide or hydroxide solid. A comprehensive report on the electroplating cell design, methodology, and performance is in preparation[6].

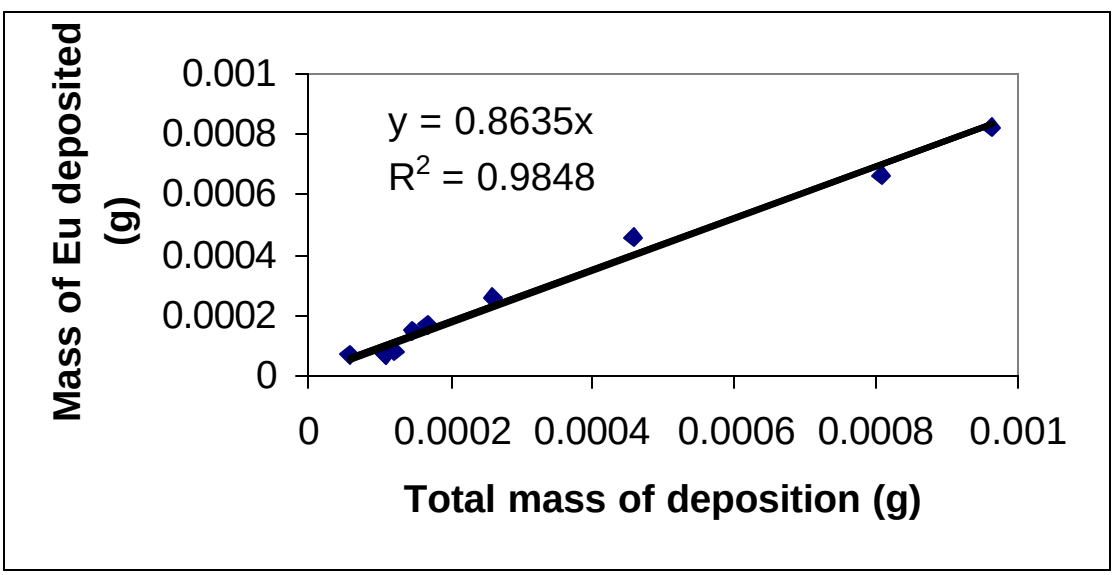

Figure 8. Ratio of Eu to total mass of the deposit.

5.0. CHEMICAL SEPARATION AND PURIFICATION PROCEDURES

An efficient and effective separation procedure is required to maximize the amount and purity of the radioactive Eu-155 on the target. The design criteria for the target in question is that it be >99% pure and plated on backing material at a diameter of 1 cm and a thickness of > 1 mg cm^{-2}. Optimally, two foils each with Eu deposited to a thickness of 1 mg cm^{-2} will be sandwiched together to make one target. This means the minimum amount of Eu required for one target is roughly 1.6 mg and represents a significant fraction of the total un-separated Eu-155 (~ 5 mg) that is expected to be available from LANL. If just one target is to be made, the minimum overall yield of the target preparation (yield of separation times yield of plating) must be at least 32%. If two targets are to be made, the overall yield would need to be twice that or 64%. Assuming a plating yield of 70% (see Figure 5), the minimum required separation yield for creating one target is 46% or 91% for two targets. Currently, the most capable separation procedures reported in the literature are about 60% efficient when purities greater than 99% are required. Therefore, a more efficient separation process must be developed if more than one target of ^{155}Eu is to be produced.

Rare earth elements (REEs) typically exist in solution as plus three cations. Their like charge and similar ionic radii account for their similar chemical behavior This presents a challenge in developing procedures capable of separating a particular REE from its closest neighbors within the group. However, several REEs can exist in other than the 3+ oxidation state and this fact has been proven in the past to be useful in separating them from other members of the REEs[7]. These include: Ce (III, IV), Pr (III, IV), Tb (III, IV), Eu (II, III), Yb (II, III), and Sm (II, III).

Eu and Sm (along with Yb) can be reduced to 2+ in solution. Eu is the easiest of these elements to reduce[8]; E^0 = -0.43 V, -0.578 V, and >-0.9 V for Eu, Yb, and Sm, respectively. This means by careful selection of a reductant, the redox characteristics of Eu may be exploited to enhance its separation from other lanthanides.

Historical approaches to separating Eu from neighboring REE-Sm may be grouped into one of two categories: single and multiprocess methods. A single process methods use a single technique to separate the mixture, while multiprocess methods first reduce Eu(III) to Eu(II) prior to separation. An exhaustive review of the literature concerning single and multiprocess separation methods used for separating mixtures of Eu and Sm has been conducted and is presented in the Appendix of this report (Section 8.0). A brief summary of this review is presented below.

5.1. Summary of Single Process Separation Methods

Figure 9 presents a flow chart of the various single process separation methods. Problems were associated with each of these methods. For instance, relatively low separation factors (SF<2) were associated with solvent extraction (SE). While, electrochemical and magnetic techniques were limited by sample size and paper chromatography was ineffective at

separation. In general, cation exchange chromatography (IEX) using alpha-hydroxyisobutyrate (α-HIB) as the eluent was the most effective separation method, but also suffered from long elution times.

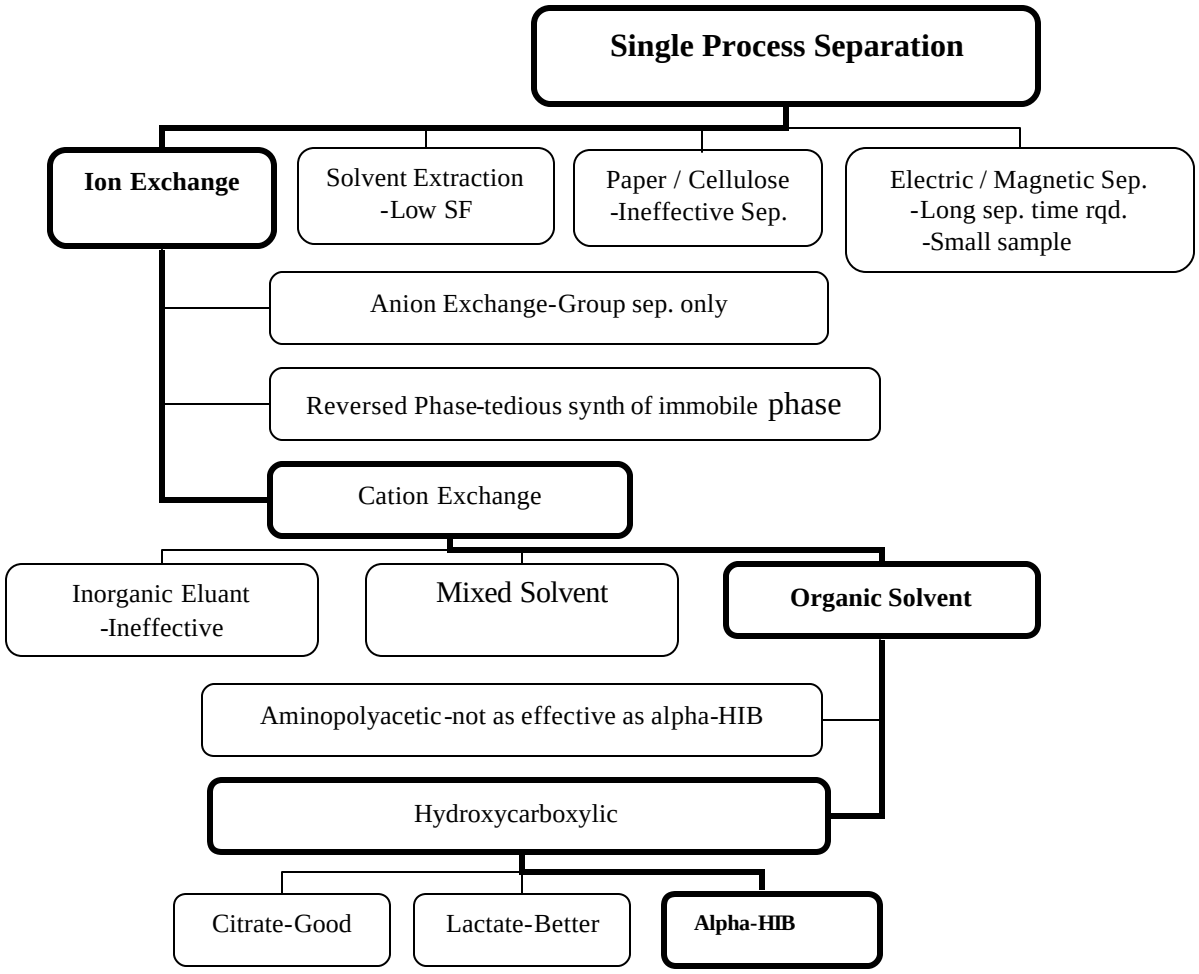

Figure 9. Single process methods used for separating mixtures of Eu and Sm.

5.2. Summary of Multiprocess Separation Methods

A multiprocess approach, where Eu(III) is reduced to Eu(II) prior to separation, requires a much less specific separation process than traditional single processes and so should provide a more effective and efficient means of separation. Figure 10 presents a flow chart of the various multiprocess separation methods. Here various reduction processes, including chemical, electrochemical and photochemical methods, were reviewed for combination with a variety of separation processes, including cation exchange (IEX), anion exchange, reversed phase chromatography (RPC), precipitation and SE. Of these, chemical and electrochemical reduction methods were most effective. Chemical reduction methods are typically easier to employ than electrochemical techniques, while electroreduction methods that use inert electrodes will introduce no contaminants to the system. Of the chemical techniques reviewed, Zn(Hg) performed better than other amalgams, various metal suspensions, metal hydrides, and nitrogenous reductors. Of the various separation processes, only precipitation and solvent extraction methods have previously been coupled with an initial reduction step. There are issues of concern with both methods relative to this work. Precipitation as the sole separation step is not capable of obtaining >99% purity of the final product. Solvent extraction produces mixed waste and effective separation is dependent upon the initial concentration of the Eu relative to the Sm. However, the amount of waste produced using a solvent extraction method might be minimized to a few milliliters by thoughtful design. In addition, separation techniques such as ion exchange or reversed phase chromatography that have not yet been employed in a multiprocess separation for mixtures of Eu and Sm hold great potential for developing a highly selective and high yielding method that also reduces waste over traditional solvent extraction.

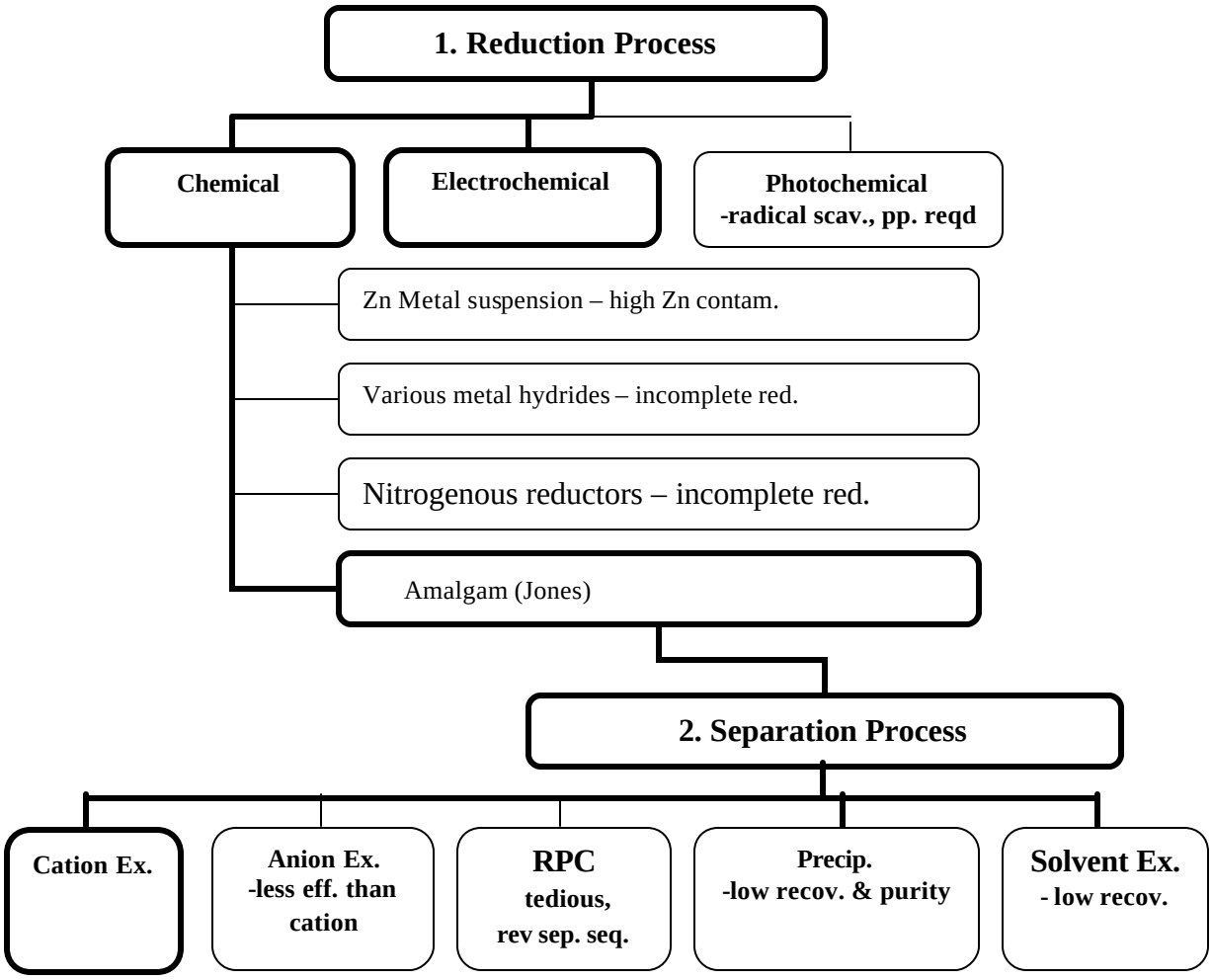

Figure 10. Multiprocess methods used for separating mixtures of Eu and Sm.

5.3. Preliminary Experimental Results

To date, three multiprocess separation methods have been developed and investigated for their ability to efficiently and effectively separate mixtures of Eu and Sm. These new methods are:

A. **Zn(Hg)/Column-IEX(a-HIB) –** Employs a cation exchange resin (BioRad AG MP-50) in a column (Column-IEX) coupled to a Jones Reductor containing 0.5% (w_{Hg}/w_{Zn}) amalgam (Zn(Hg)). A 0.5 M α-HIB solution at pH 4.5 is used as the eluant.

B. **Zn(Hg)/Batch-IEX(a-HIB)** – Chemical components used in this method are identical to those used in method "1" (i.e., identical resin, use of 0.5% Zn(Hg) as reductant, and 0.5 M α-HIB solution at pH 4.5 as the eluant). The only difference being that reduction and separation are performed simultaneously within a batch reactor rather than in series within columns.

C. **Zn(Hg)/SE(TTA)** Couples a Jones Reductor (Zn(Hg)) in series with solvent extraction (SE(TTA)) separation step using 0.1 M TTA in benzene.

Studies investigating the ability of these methods to effectively separate Eu and Sm employed a number of stable analogs and radioactive tracers. Stable analogs were analyzed using either ICP-AES, Atomic Fluorometry, or by direct observation of a precipitate. The radiotracers employed emit ?-radiation when they undergo decay. These tracers were analyzed using a high purity P-type germanium detector and calibrated using a multi-nuclide standard.

5.3.1. Zn(Hg)/Column-IEX(a-HIB)

The proposed method for separating Eu and Sm mixtures by combining a Jones Reductor column with ion exchange chromatography shown in Figure 11. Briefly, 7.5 ml of a ~31:1 mixture of Sm and Eu was loaded onto a Jones Reductor column in dilute HNO_3 (pH~3). Eu(III) is reduced by the Zn(Hg) in transit to the ion exchange column, while both Eu(II) and Sm(III) immediately exchange for NH_4^+ ions upon contacting the resin (Step 1 in Figure 11). Forty ion exchange CVs (CV ~ 0.5 ml) of 0.5 M a-HIB at pH 4.5 are run through the series of columns to elute the Ln(III), while not disturbing M(II) ions (which includes Zn contamination from the Jones Reductor) exchanged on the resin (Step 2). Up to this point, the connection between the Jones Reductor and the ion exchange column is maintained to enhance the stability of the Eu(II) oxidation state. Once Sm(III) has been separated from Eu and Zn, Eu is re-oxidized by removing the Jones Reductor and rinsing the ion exchange column with 0.1 M HNO_3 (Step 3). This is followed by another extraction with 0.5 M α-HIB in order to elute Eu(III) and separate it from contaminant Zn (Step 4).

Results of several experiments designed to investigate the capability of the proposed multiprocess cation exchange column method for effectively separating Eu from Sm are summarized in Figure 12. Here, elution patterns for Eu and Sm are shown as a function of column volumes for the various eluants used during the procedure. The elution pattern for Ba (an analog for Eu(II) behavior) derived from a preliminary experiment was included to illustrate

where Eu elution was expected. From this figure it is evident Sm and Eu were not effectively separated and Eu eluted in the region where Ln(III) ions would be removed from the resin. These results suggest two possible conclusions with regards to the inability of the proposed method to separate Eu and Sm: (1) either the Jones Reductor was ineffective at reducing the Eu(III) initially or (2) Eu(II) re-oxidized sometime after passing through the Jones Reductor and prior to or during the initial α-HIB elution step (Step 2 in Figure 11). Additional batch experiments were planned and executed to further identify why this method was unsuccessful.

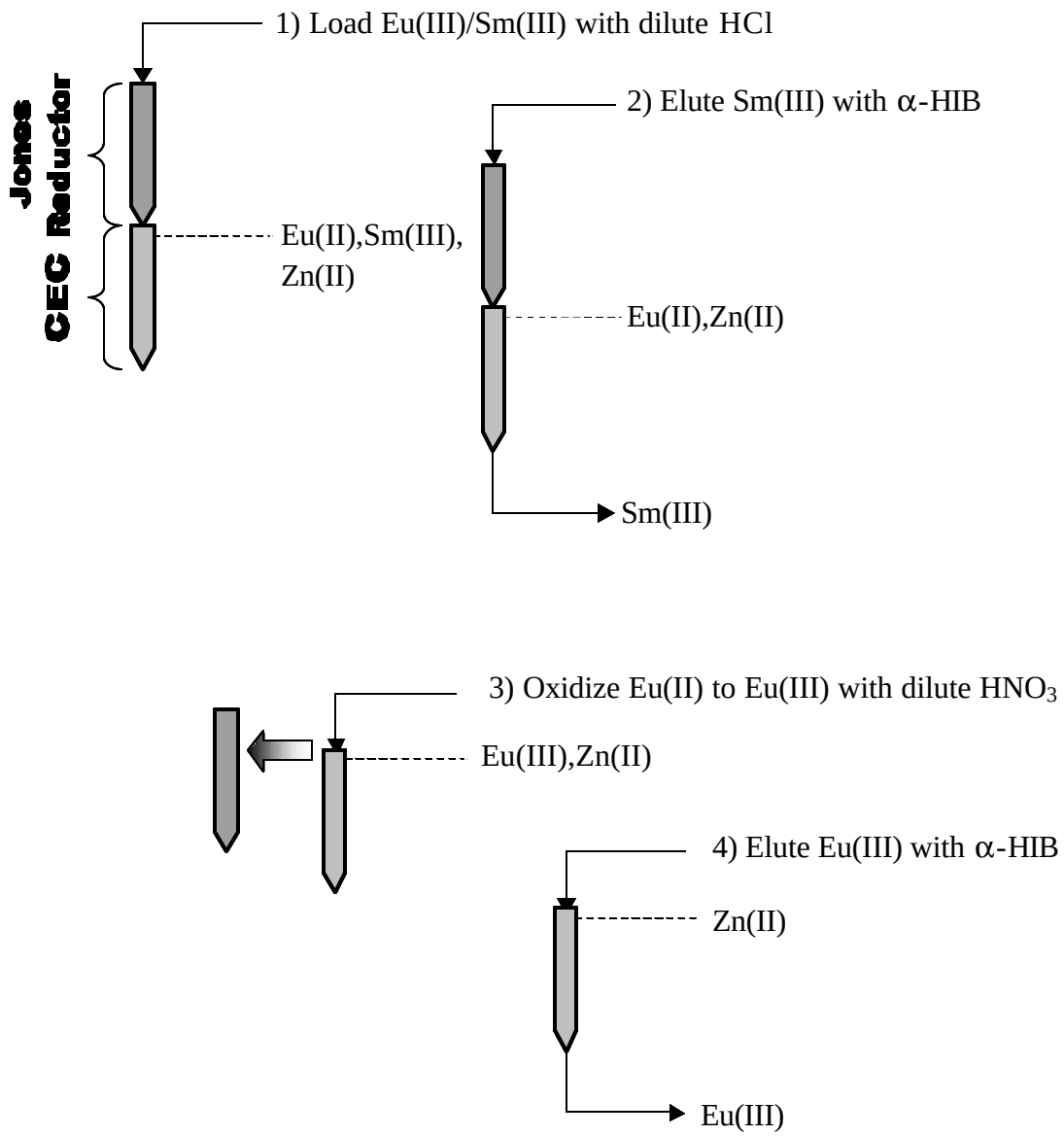

Figure 11. Principle behind the proposed multiprocess column ion exchange method, Zn(Hg)/Column-IEX(α-HIB), for separating mixtures of Sm and Eu.

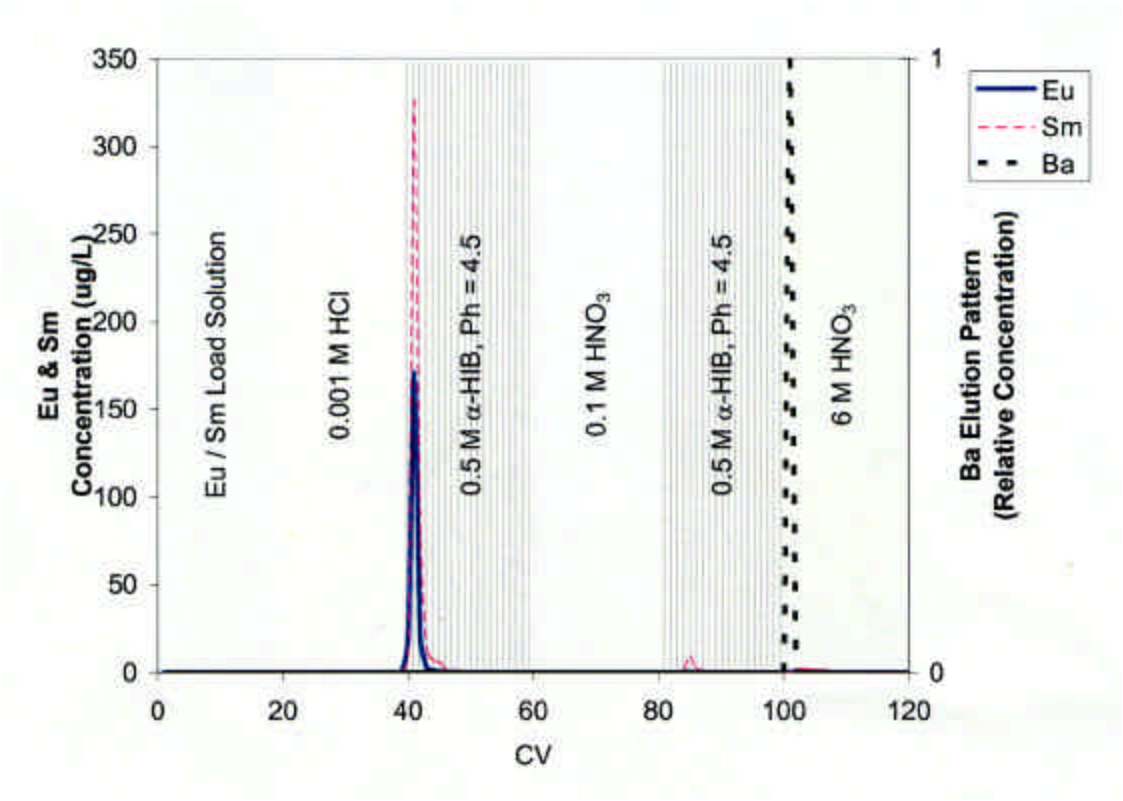

Figure 12. Elution curves for Eu, Sm, and Ba measured during the Zn(Hg)/Column-IEX(α-HIB) experiment.

5.3.2. Zn(Hg)/B-IEX(α-HIB)

Based on the results of the column separation experiments, Zn(Hg)/Column-IEX(α-HIB), it was hypothesized that as Eu(II) traveled out of the Jones Reductor and into the ion exchange column it most likely became unstable and oxidized in the absence of reductant. This lead to the design of a batch method that provided a constant source of reductant for Eu throughout the separation process. Figure 13 illustrates the principle behind the proposed Zn(Hg)/B-IEX(α-HIB method.

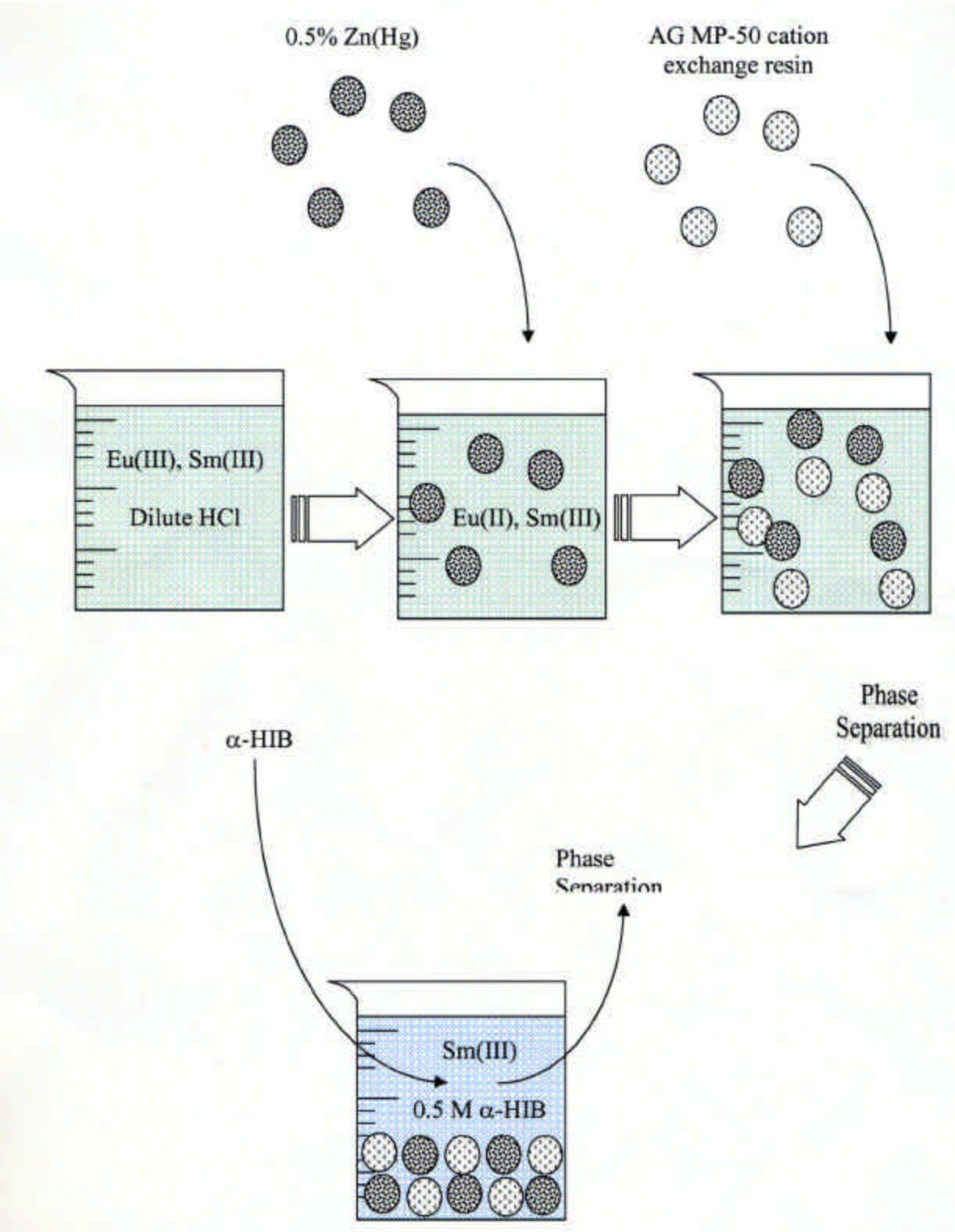

Figure 13. Illustration of the proposed Zn(Hg)/B-IEX(α-HIB) method for separating Eu and Sm mixtures.

The proposed batch separation method, Zn(Hg)/Batch-IEX(α-HIB), starts with 30 ml of slightly acidic (0.001 M) HCl solution containing a mixture of Eu and Sm. An excess (5 g) of solid 0.5% Zn(Hg) is then added to the mixture to reduce Eu(III) to Eu(II), which is followed by the addition of 5 g of 50-100 mesh MP-50 cation exchange resin to sorb both Eu(II) and Sm(III). Solid phases are separated from the dilute acid and added to 25 ml of 0.5 M α-HIB at pH ~4.5. It was expected that Sm(III) would be preferentially desorbed from the ion exchange resin and stabilized in solution by α-HIB, while Eu(II) remained on the resin. A subsequent phase separation of the α-HIB solution and the resin/Zn(Hg) solids would effectively separate Sm and Eu.

Results of the batch Zn(Hg)/Batch-IEX(α-HIB) experiment are shown in Figure 14 and indicate this method was only partially successful at separating Eu from Sm. Results show that during the first 2 minutes after adding α-HIB up to 65% of the Eu remained on the resin (likely as Eu(II)). After this period, however, 80% of the Eu had desorbed and stabilized by the α-HIB within solution as Eu(III). Redox potential measurements of the various solutions help elucidate the behavior of the Eu during this attempted separation (Figure 15). While the potentials of the solutions containing Eu and Zn(Hg), and Eu, Zn(Hg), and resin indicate Eu(II) was stable with respect to Eu(III) within these systems, the addition of α-HIB oxidizes and re-stabilizes Eu to the trivalent state. This kinetically limited re-oxidation of Eu(II) by α-HIB is of limited use for this work but could potentially find application where a fast, less efficient, separation method is needed.

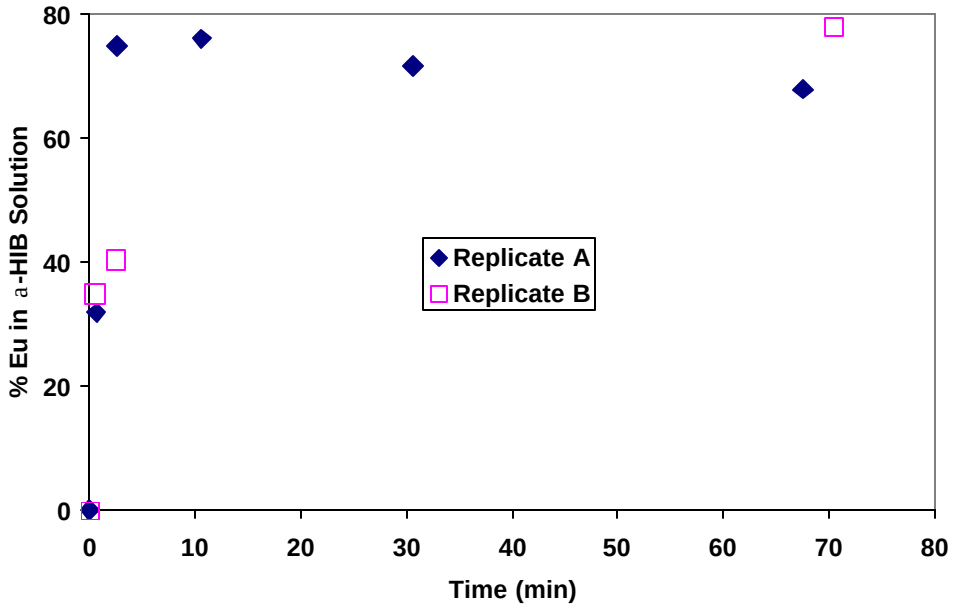

Figure 14. Percent of the total Eu in solution as a function of time during the Zn(Hg)/ Batch-IEX(α-HIB) experiment.

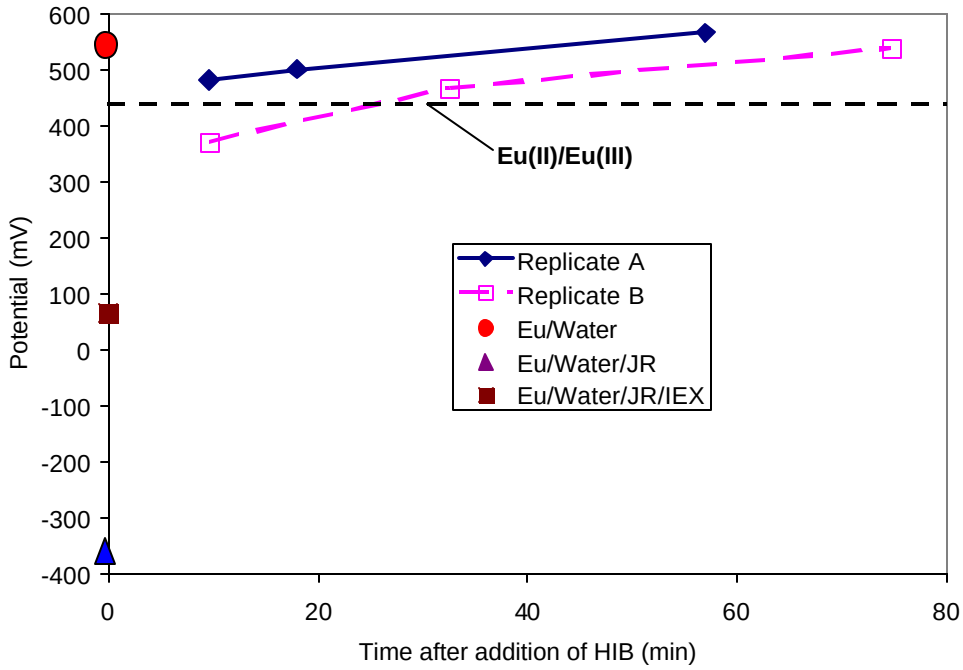

Figure 15. Measured oxidation potential within various systems containing Eu and during the Zn(Hg)/Batch-IEX(α-HIB) separation. The dashed black line indicates the potential at which [Eu(II)] = [Eu(III)]. Below this line, [Eu(II)] > [Eu(III)]. Above this line, [Eu(II)] < [Eu(III)].

5.3.3. Zn(Hg)/TTA-SE

A third experiment, Zn(Hg)/SE(TTA), couples a Jones Reductor (Zn(Hg)) in series with solvent extraction (SE(TTA)) separation step using 0.1 M TTA in benzene. Figure 16 illustrates a proposed multiprocess method for separating Eu and Sm mixtures utilizing TTA-solvent extraction. A separatory funnel is connected to either a Jones Reductor (0.5% Zn(Hg)) for loading aqueous solutions or a syringe for injecting solvent. A separate injection port was required for the TTA solvent as preliminary experiments indicated that TTA was degraded when allowed to come into contact with Zn(Hg). Mixtures within the separatory funnel were continuously bubbled with $N_{2(g)}$ to prevent re-oxidation of Eu(II) by atmospheric oxygen. Initially, 15 ml of a 0.1 M HCl solution containing Eu-152 tracer was introduced into the separatory funnel either directly to test Ln(III) separation or via a Jones Reductor to study the behavior of Ln(II). In the case of Ln(II) studies, the Jones Reductor was replaced with a syringe at the top of the funnel where 0.1 M TTA in Benzene was introduced after loading the aqueous solution. The aqueous/TTA solutions were separated after 0 to 30 minutes of vigorous mixing by bubbling action. In principle, solvent containing TTA should strip Ln(III) preferentially from Ln(II) ions in the aqueous solution. Upon Ln(III) extraction, the organic phase is then collected, stripped of Ln(III) using strong nitric acid (> 6 M), and reused in subsequent extraction steps to minimize the volume of mixed waste generated.

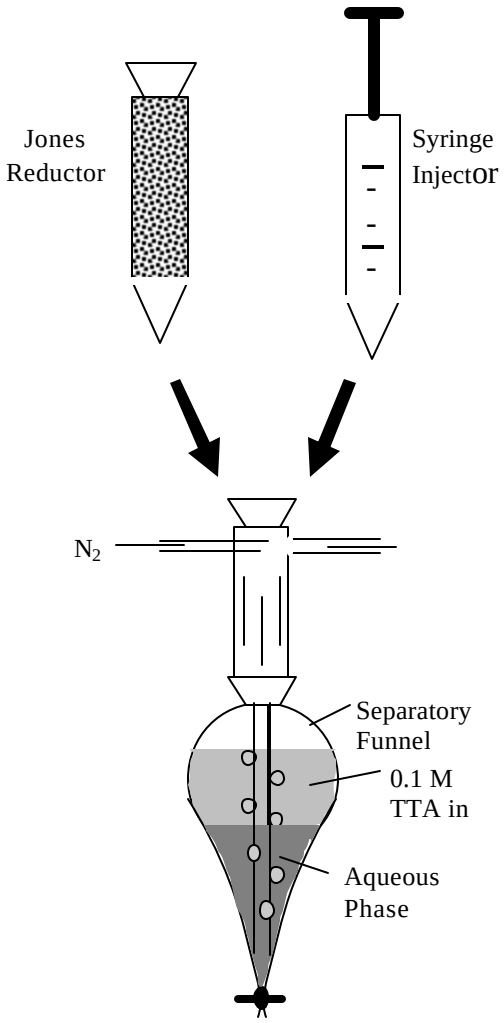

Figure 16. Experimental apparatus for the proposed Zn(Hg)/TTA-SE separation method.

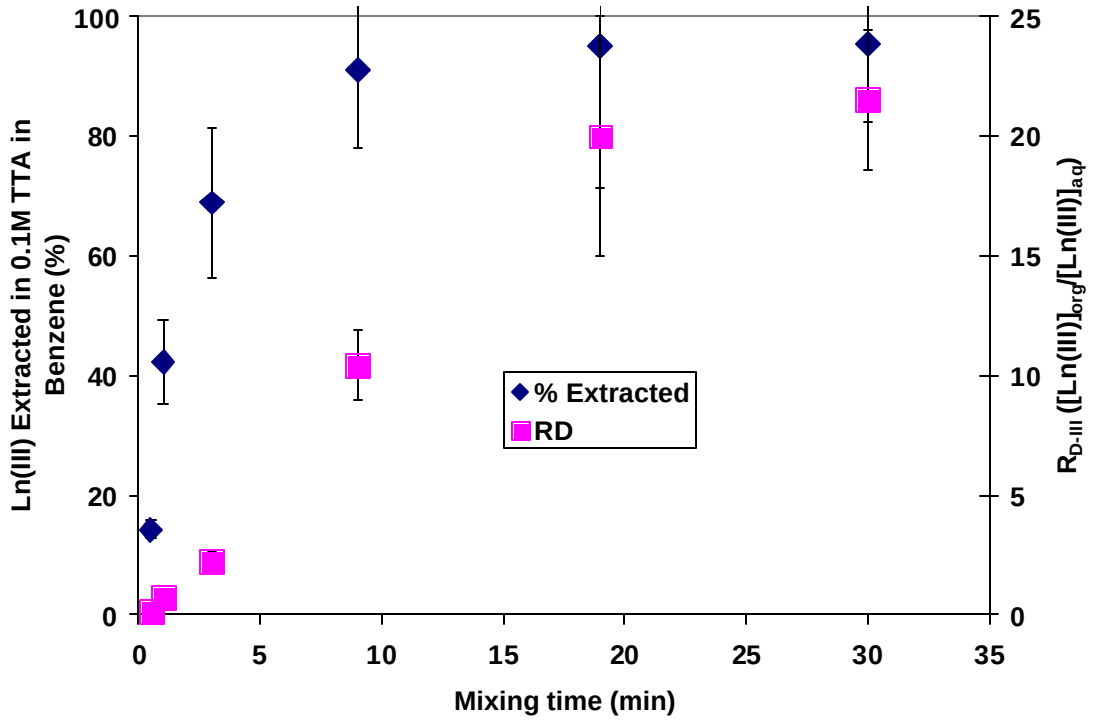

Figure 17. Percent of Ln(III) extracted and R_{D-III} from 0.1 M HCl by 0.1 M TTA in Benzene as a function of mixing time between organic and aqueous phases.

Figure 17 illustrates the extraction of Ln(III) ions as a function of time from dilute HCl using 0.1 M TTA in Benzene. Maximum extraction of Ln(III) into the organic phase is reached somewhere between 10 and 20 minutes. However, reaction time must also be minimized to limit the potential for the restabilization of Eu(III) during separation. Therefore, a reaction time of 15 minutes was chosen for the Zn(Hg)/TTA-SE separation method. A small distribution coefficient for Ln(II) (R_{D-II}) and large value for R_{D-III} results in the maximum overall yield and effectiveness of the proposed separation procedure. While R_{D-III} was relatively constant during repeat cycles of the solvent extraction, R_{D-II} increased as a function of solvent extraction cycle (Figure 18). This behavior was attributed to the decreasing effectiveness of the Jones Reductor and possible degradation of the TTA as a result of regeneration. Values for R_{D-II} and R_{D-III} during the first extraction using fresh a TTA organic phase were 0.03 and 21.6, respectively. During the second and third extraction cycles, however, R_{D-II} values increased to 0.18 and 1.3, respectively. This corresponds to purities for an initial 1:20 mixture of Eu to Sm of 52.3%, 95.45%, and 99.5%

measured for the first, second and third solvent extraction cycle, respectively. While the Zn(Hg)/TTA-SE method was able to achieve the design criteria for purity of > 99% after the third extraction cycle, the corresponding yield was poor. Yields for the series of extractions were 97.1%, 82.3%, and 35.8%, respectively. A negative aspect to using Zn(Hg) is the introduction of Zn contamination into the system, which requires additional purification steps, resulting in more mixed waste generation, and may be related to the eventual degradation of the TTA solvent. If this is the case, coupling a solvent extraction with a reduction step that does not introduce significant contamination may significantly enhance the performance over that reported here for Zn(Hg)/TTA-SE.

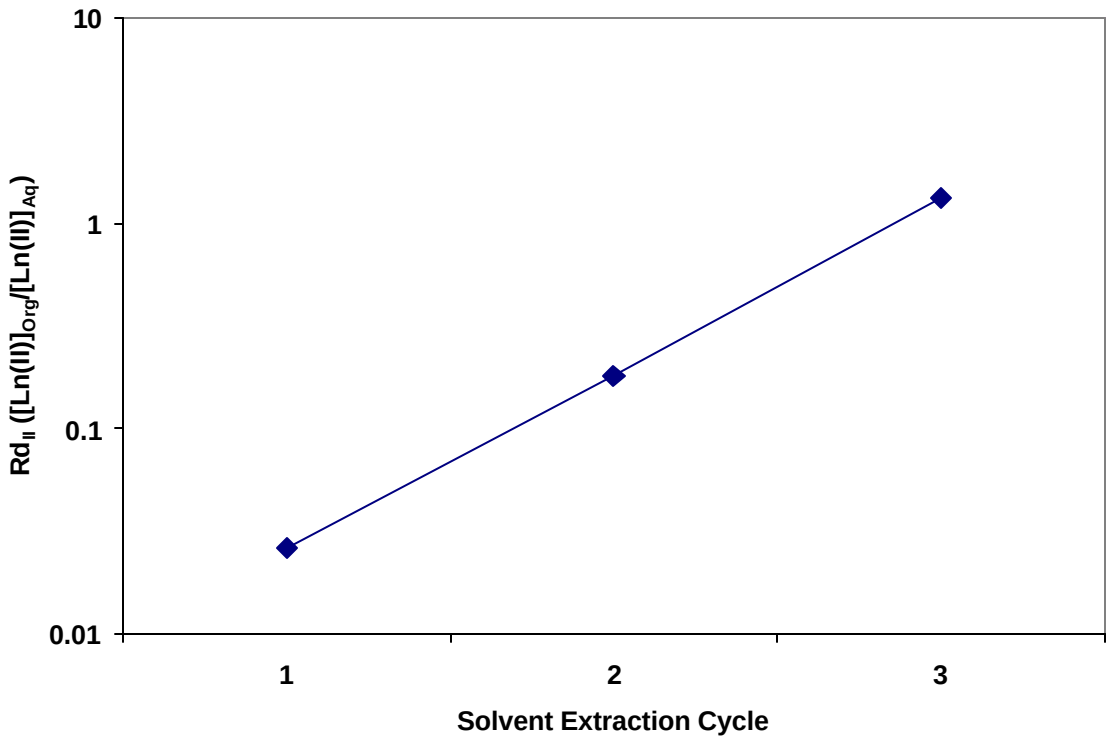

Figure 18. The distribution coefficient for Ln(II) ($R_{D\text{-}II}$) between 0.1 M TTA in benzene and 0.001 M HCl.

6.0. PARTICIPATION IN DATA ACQUISITION AT DANCE

A PhD student from the group, Charles M. Folden III, has visited the LANSCE facility, participated in several parameter checks of the DANCE, and acquainted himself with the data acquisition system. During these initial experiments, data were collected and brought back to UC Berkeley for future analysis.

7.0. FUTURE RESEARCH

Much of the work planned for this project in the near term will focus on developing improved techniques for separation of Eu from Sm. Alternatives to the initial reduction and final separation steps of the multiprocess approach will both be investigated. An electrochemical reduction process that uses a potentiostat and an inert electrode will be studied as a potential replacement to Zn(Hg), the chemical reductant currently used. For example, an electrochemical technique using a glassy-carbon electrode shows promise for providing a cleaner and more reliable process for reducing Eu.

TTA and other similar complexants of Ln(III) ions provide great promise with respect to developing a fast, high-yield, high-purity separation process for Eu and Sm mixtures. These complexants are traditionally used within an organic phase during solvent extraction, meaning a disposal pathway and added waste resources are needed for dealing with the generation of mixed wastes. To alleviate waste issues related to solvent extraction, future investigations will focus on the production and application of complexing agents for Ln(III) that have been immobilized on a surface resin rather than dissolved in an organic solvent. Experiments will examine multiprocess separations that use a number of reversed phase resins. Longer term research on the Nd/Pm and Er/Tm systems will be initiated and will probably require high pressure ion exchange chromatographic techniques.

Another research objective of this project includes direct participation in the acquisition and analysis of the data generated during the experimental measurements at DANCE. In preparation for analysis of the experiments on the already prepared Eu targets and future actinide targets, researchers at UCB/LBNL will become familiar with the data acquisition and analysis software package, MIDAS (Maximum Integrated Data Acquisition System), and the software package ROOT used to retrieve and analyze stored data. as well as the base languages of these programs,

8.0. REFERENCES

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APPENDIX: LITERATURE REVIEW OF SINGLE PROCESS AND MULTIPROCESS SEPARATIONS

Historical approaches to separating Eu from neighboring rare earth element, Sm, may be grouped into one of two categories: single and multiprocess methods. A single process method uses a single technique to separate the mixture, while multiprocess methods first reduce Eu(III) to Eu(II) prior to separation.

A.1. SINGLE PROCESS SEPARATION

A review by Stevenson and Nervik[8] reports that of a number of different single process separation methods only those using cation exchange or reversed phase partition chromatography adequately separated individual REEs from each other. Specifically, anion exchange, solvent extraction, and paper and cellulose chromatography methods used alone were not capable of effective separations of individual REEs. Also, electric and magnetic field separation procedures were less effective than cation exchange, suffering from long elution times, bad separation between adjacent REs, and were limited by sample size.

A.1.1. Anion Exchange Chromatography

The use of anion resin for REE separation is limited since this group of elements, under most circumstances, does not form complexes that stick to anion exchange sites. However, anion exchange has been used to purify REEs from other ions that do exchange with these resins. For instance, lanthanides may be separated from actinides, which are retained by the column, by loading the mixture to hydroxide form Dowex-1 resin and eluting with 6 M HCl[9-11], 3-4.4 M $LiNO_3$ [12,13] or 2 M [14] and 5 M [15] NH_4SCN. Further improved lanthanide-actinide separations were accomplished using eluants such as 10 M LiCl in 0.1 M HCl [16]. Various forms of anion resins were also studied. Bunney et al.[17] reported sulfate forms were of limited use for separating individual REs from the group. In addition, F^-, oxalate, and OH^- forms were also not useful due to their low solubilities with REEs.

A.1.2. Solvent Extraction

Solvent extraction has limited application in single process separation methods due to rather low separation factors (SFs) for adjacent REEs[2]. For instance, SFs were estimated to be 1.4 or 1.5 for an extraction from a chloride or nitrate solution into various alcohols, ethers and ketones[18,19]. Even lower SFs (10^{-3}) were estimated for $LiNO_3$ solutions in ether or n-pentanone-2[20]. Thiocyanate in a variety of solvents was also investigated [21]. Here, SFs on the order of 1 and 0.3 were attained in isopropanol and tert butyl alcohol, respectively, while separation was largely ineffective within glycols, ketones, esters, ethers, and halogenated solvents.

Higher SFs are obtained using tributyl phosphate (TBP) or organophosphorous compounds rather than simple salt solutions. In 100% TBP and 15.6 M HNO_3, a SF of around 1.9 was obtained by several authors [22-25]. Others have noted improvements to this value at lower acidities

[26,27]. For instance, a SF of greater than 3 was obtained for a HNO_3-NH_4NO_3 solution with a TBP-kerosene mixture containing thenol trifluoroacetone (TTA) [27].

The use of organophosphorous compounds to separate REEs was first suggested by Cunninghame et al.[28]. Peppard et al.[29] demonstrated the usefulness of such compounds with 0.75 M di-(2 ethyl hexyl) orthophosphoric acid (HDEHP) in toluene and 0.5 M HCl. Results from this study indicated that a SF of 2.5 was possible.

Assuming a liberal SF of 3, an extraction yield of 90% and an initial mixture of Eu and Sm at a ratio of 1:1, solvent extraction would need to be applied over six times in series to attain >99% purity and would result in an overall separation yield of 59%.

A.1.3. Cellulose and Paper Chromatography

A few studies have been conducted on the feasibility of using cellulose or paper chromatographic methods for separating REEs. Lederer[30,31] used paper saturated with 10% ethanol and 2 M HCl as an eluant. Another study utilized cellulose with an ethyl ether-NO_3 solvent[32]. In all cases, separation of individual REEs from each other was not possible.

A.1.4. Electric and Magnetic Field Separation

Using filter paper moistened with 0.1 M lactic acid, Sato et al.[33] reported that electrophoretic means were not capable of separating individual REEs from each other. However, Clusius and Ramirez[34] found that individual separation was possible after two weeks of separation time using a solvent flowing counter to the flow of cations. Others have studied electromigration of REEs in citrate and report that separation of the lighter elements is possible in 3 to 6 hours, while separation of heavier group elements remained poor [35-38]. All of these methods were limited to sample sizes of 10-100 micrograms of mixed REE material.

A.1.5. Reversed Phase Chromatography

This method involves the saturation of a column of inert absorbent with an organic solvent in which the REs are soluble, followed by elution of the REEs from the column using a strong acid. Siekierski and Fidelis[39] first applied reversed phase chromatography to REs using TBP as the solid phase and HNO_3 as the eluant. REEs were eluted in order of increasing atomic number or in reverse order compared to traditional cation exchange methods. Despite the successes of Siekierski and Fidelis, more recent published works regarding the use of reversed phase chromatography to separate REEs are lacking from the literature likely due to the fact that preparation of these columns is labor intensive and commercially available reversed phase resins are expensive. For the purpose of eluting relatively small amounts of the heavier element, Eu, from larger amounts of the lighter element, Sm, a method that retains Eu and elutes Sm is preferred.

A.1.6. Cation Exchange Chromatography

The most common cation exchanger is a polymeric type resin[40]. This type is typically produced via copolymerization of styrene with a small percentage of divinylbenzene, which may be varied in order to produce differing degrees of cross-linking. Higher cross-linked resin is less vulnerable to swelling, while fewer cross-links increase porosity and ion accessibility to exchange sites. The final matrix is then treated in different ways to introduce different functional groups. As an example, sulfonic groups give rise to strong, monofunctional cation exchangers, while carboxylic and phosphoric acid groups have weak acidic properties.

A.1.6.1. Inorganic Eluants

Although successfully used in the past for separating the REE group from other contaminants, inorganic eluants such as HCl, $HClO_4$, and ammonium thiocyanate, provide poor separation of the REs on cation exchange resin[14,41-43]. One exception to this, the eluant sodium tripolyphosphate successfully separated individual REs from each other[44].

A.1.6.2. Mixed Solvent Eluants

Mixed solvent eluants have also been investigated for purposes separating individual REEs from each other. Ionescu et al.[45] used 20% conc. HCl-65% acetone-20% water mixture as an eluant and reported SFs on the order of 3. However, these mixtures were found to be inferior to various organic solvents.

A.1.6.3. Organic Eluants

Two significant groups of organic complexing agents, hydroxycarboxylic and aminopolyacetic acids, have been used to separate individual REEs from each other. The hydroxycarboxylic acids include: citric acid, lactic acid, alpha hydroxylisobutyric acid (α-HIB), and glycolic acid among others. Citric acid has been used for individual RE separations in the past [46-54], however, SFs using citrate are typically lower than those obtained using lactate or α-HIB. Citrate separations are also plagued by rather long separation times on the order of 90 to 100 hours [48-50].

Lactic acid provides better RE separations of individual members of the group than citric acid[55]. Although some overlapping of peaks have been reported for Gd/Eu and Tm/Yb pairs when using lacate[56], several authors report success in separating 10-20 mg mixtures of light REs from each other with this eluant[57-59]. Methods for separating smaller amounts of material have also been successful [60,61]. In most of these cases, separation was conducted at higher temperatures, which produced sharper peaks and better SFs (a characteristic that has not been observed using α-HIB). More complex procedures utilized continuous or stepwise gradients of pH or ligand concentration for enhanced separation[62-65] within 10 hours time[64-66]. Bruchner and Szarvas[66,67] separated RE mixtures using a column of Dowex 50 x 8 (hydrogen form) with 0.002 M EDTA-0.4 M lactate as the eluant. The pH was increased from 3.0 to 3.5 during the

separation and SFs were greater than with α-HIB. Although the use of lactate enhances SFs over that of citrate, there are two main drawbacks for its use, including: (1) susceptibility to attack by bacteria; and (2) the potential for forming dimers during experiments, which may affect reproducibility of distribution coefficients.

Alpha-HIB is considered to be the best performing hydroxyacid for separating individual REEs. Choppin and Silva[68] were the first to use α-HIB for this purpose. These authors used a 0.2 M – 0.4 M α-HIB solution of pH 4.0-4.6 on Dowex-50 resin at a temperature of 87^0C. Alimarin et al.[69] later separated traces of Dy, Eu, Sm, and Gd from each other on a KU-2 colum with 0.17 M α-HIB in 120 drops. A mixture of Y, Gd, Eu, Sm, Nd, Pr, Ce, and La was also separated by Wolfsberg[70] in 30 hours time with peak to valley ratios of 1/1000 using α-HIB. The column consisted of Dowex 50 Wx4 (62.5cm x 8 mm), using an initial eluant of 0.5 M α-HIB at pH 3.4, which was increased at a rate of 0.025 pH units per hour. This method has been applied with success by other researchers as well[71,72]. Unlike lactate, when α-HIB is used as the eluant, SFs for neighboring REs have been observed to decrease when experiments were conducted above room temperature[73].

For complex mixtures of REEs, gradient elution is typically used. Massart[73] provides an extensive review of optimization techniques and various gradient elution methods developed for α-HIB and some points made in this review are noteworthy here. The use of small, spherical and homogeneous-diameter resins enhanced SFs by 3 to 4 orders of magnitude[74]. Zeman et al.[75] studied the effects of resin type, size and cross-linking and α-HIB concentration on RE separations and reported that Dowex 50 Wx8 100-200 mesh was the optimal choice for these separations. Dowex 50 Wx12 gave larger SFs but more diffuse peaks than Dowex 50 Wx4. Also, 0.5 M α-HIB gave slightly better results than 0.1 M. Optimizations for separating mixtures of REs where one is present at large quantities and the other at trace quantities is also discussed[33]. Noteworthy was that the width of peaks for milligram quantities increased much more rapidly with increasing flow rates than for tracer peaks.

Several important aminopolyacetic acids have been examined for use in separation of individual REEs including, ethylenediaminetetraacetic acid (EDTA), N-hydroxyethylenediaminetetraacetic acid (HEDTA) and nitrilotriacetic acid (NTA). EDTA shows larger SFs than citrate[48], however, the elution characteristics were poorer than with citrate[76]. This latter point is the reason why EDTA or similar eluants have not been widely used in radiochemical separations.

A.1.7. Summary of Single Process Separation

Figure A-1 presents a flow chart of the various single process separation methods. Problems were associated with each of these methods. For instance, relatively low separation factors (SF<2) were associated with solvent extraction (SE). While, electrochemical and magnetic techniques were limited by sample size and paper chromatography was ineffective at separation. In general, cation exchange chromatography (IEX) using alpha-hydroxyisobuterate

(α-HIB) as the eluent was the most effective separation method, but also suffered from long elution times.

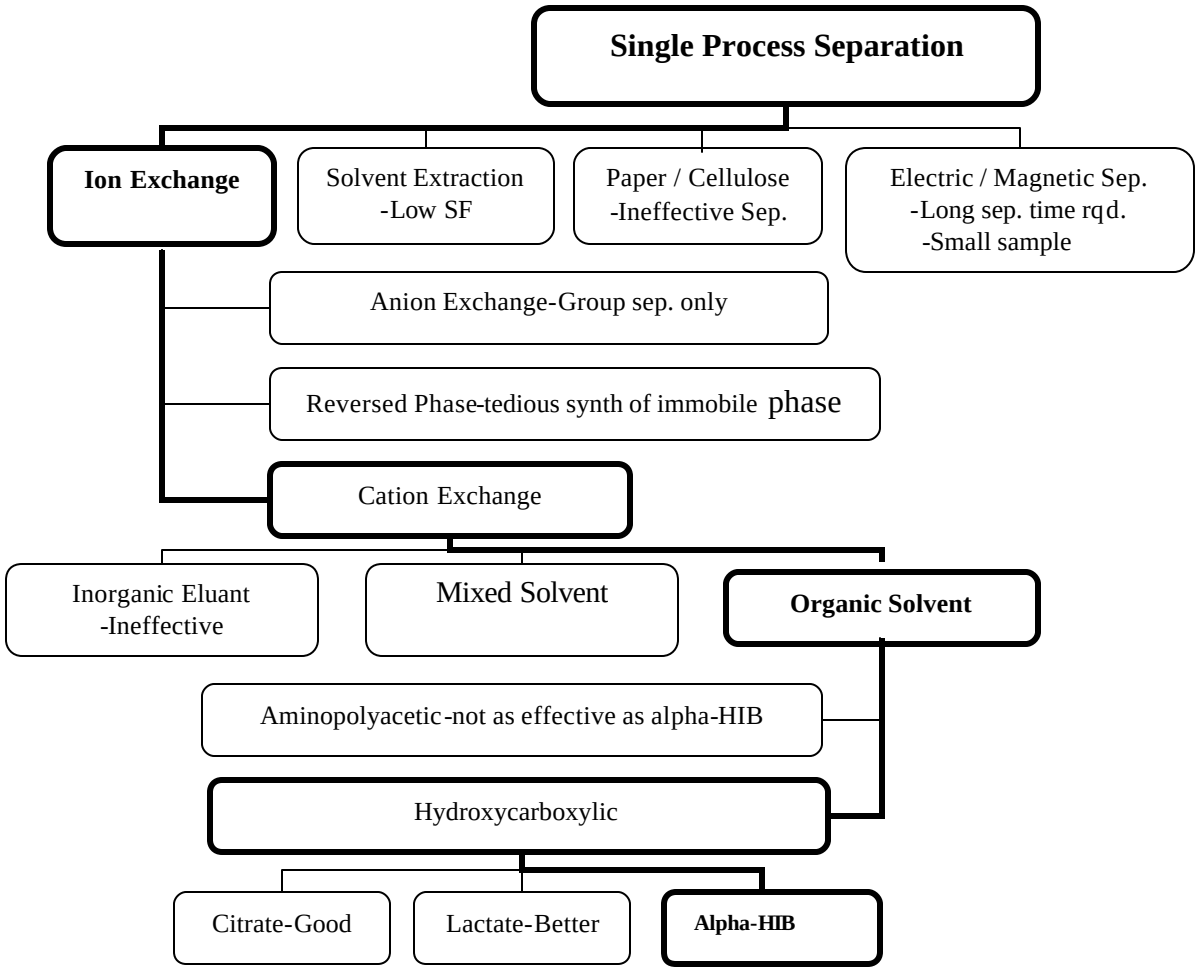

Figure A-1. Published single process methods used for separating mixtures of Eu and Sm.

A.2. MULTIPROCESS SEPARATION

Recent procedures developed for separating Eu from other REEs typically take advantage of the redox active nature of Eu by selectively reducing the element prior to its separation. Such methods are referred to in this review as "multiprocess" separations. The initial process for all multiprocess separations is always reduction of Eu, while subsequent processes that separate Eu(II) from other members may include one or a number of the following: ion exchange chromatography, precipitation, and / or solvent extraction.

A.2.1. Reduction: Initial Process

Various methods have been used to selectively reduce Eu from a solution of REEs including, chemical reduction[7,77-82], electrochemical reduction[83-94], photochemical reduction[95-102], and radiochemical reduction [103,104].

A.2.1.1. Chemical Reduction

Chemical reduction methods are both reliable and relatively simple to employ. For these reasons, a number of multiprocess separations utilizing a variety of chemical reduction methods have been developed including the use of various metal (Eu, Zn, Na) amalgams[7,105], a suspension of metal (Mg, Zn) dust[7], the use of metal hydrides ($NaBH_4$) and nitrogenous (N_2H_4 and NH_2OH) reductants[7], or a solution of chromous chloride at low pH's[106].

A review of various chemical reductants revealed that Zn amalgam might be effectively used to reduce Eu as part of a multiprocess separation method[1]. Zinc and Eu amalgams selectively reduced Eu in the presence of Sm, however, using a Eu amalgam to purify a Eu sample adds unwanted contaminant that is hard to separate from the original sample. A Na amalgam reduced both Sm and Eu to zero valent metals, a feature that might be of use in separating these elements from complex mixtures of other REEs, but is not useful for separating Sm from Eu. Zinc metal was also capable of effectively and selectively reducing Eu within a mixture of REEs, however, Mg metal was much less effective (~70%) at reducing Eu[7]. Unfortunately, it is tedious to separate these metals from the sample following reduction. Chromous chloride reduced Eu but also required additional steps to separate Cr from the Eu. Metal hydrides and nitrogenous reductants were found to be largely ineffective at reducing Eu[7].

A common application of Zn amalgam is in the form of the Jones Reductor, which consists of a glass tube containing a filter pad upon which rests a column of amalgamated zinc (Figure A-2). Only the Eu from a lanthanide solution will be reduced within the Jones Reductor. Since the reductant is contained within a column, contaminants introduced to the sample during reduction are kept to a minimum.

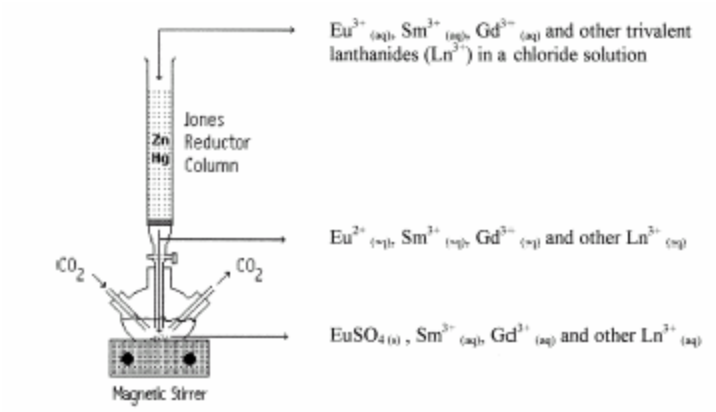

Fig. 1. Schematic diagram of the Jones reductor column.

Figure A-2. Schematic diagram of the Jones reductor column[81].

A.2.1.2. Electrochemical Reduction

A potentiostat and appropriate electrodes may be employed to electrochemically reduce Eu as an initial step of a multiprocess separation method. If inert electrodes are used, these techniques are relatively clean in comparison to other reduction methods. To date, the use of electrochemical reduction has always accompanied the use of a precipitation step, such as depositing $Eu(II)SO_{4(s)}$ from a sulfate solution, for separating Eu and Sm [1,75,82,88]. These methods take advantage of relatively slow redissolution kinetics of the highly insoluble $Eu(II)SO_4$, allowing the divalent Eu to be easily stabilized within the system. The disadvantage of using precipitation as a separation mechanism is that purity of the initial precipitate and the recovery are typically low (<90% and ~80%, respectively[2,75,93,112]). Subsequent re-dissolution and re-precipitation steps can be used to enhance purity, however, at the price of overall recovery. As an initial step in a multiprocess separation method, electrochemical reduction of Eu shows promise. However, separation processes that may be incorporated with elecroreduction other than precipitation need to be investigated.

A.2.1.3. Photochemical Reduction

Adsorption of a photon can stimulate electron transfer within an inorganic complex or molecule[99]. As an example, Eu may be reduced photochemically by electron transfer from a binding ligand such as water in its charge-transfer band.

$$Eu^{3+} + H_2O \rightarrow Eu^{2+} + H^+ + OH^\bullet \qquad (3)$$

In this case the radical ($OH^\bullet$) must be scavenged immediately to avoid the reverse reaction. Also, Eu^{2+} can be photo-oxidized by the reaction:

$$Eu^{2+} + H_2O \rightarrow Eu^{3+} + OH^- + H^\bullet \qquad (4)$$

Reaction 4 may be suppressed by the removal of Eu(II) from solution as a sulfate solid.

Various light sources have been successfully utilized to effect reduction of Eu within solution including both low and high pressure mercury lamps (LPML or HPML)[96,99] or an ArF excimer laser[103]. 2-propanol was found to be a more effective radical scavenger than either isopropyl formate or formic acid during the photoreduction process of Eu[99]. Donohue[96] proposed the following reaction scheme for radical scavenging by 2-propanol in the presence of Eu(III).

$$OH^{\bullet} + CH(CH_3)_2OH \rightarrow C(CH_3)_2OH^{\bullet} + H_2O \qquad (5)$$

$$Eu^{3+} + C(CH_3)_2OH^{\bullet} \rightarrow Eu^{2+} + (CH_3)_2C = O + H^{+} \qquad (6)$$

Problems associated with the photoreductive separation of Eu include: (1) the requirement of a precipitation separation process directly following reduction; (2) contamination of the solution with organic radical scavengers; and (3) the necessity of rather long (> 24 hours) irradiation times[99].

A.2.1.4. Radiochemical Reduction

Gamma ray irradiation has also been proposed as a method for reducing Eu within solution[99,100], however, this technology is still in the early stages of development. Therefore, a review of this method was not warranted here.

A.2.2. Separation: Secondary Process

A.2.2.1. Cation Exchange

Cation exchangers have not been employed within multiprocess methods for separating Eu from other REs in the past. With that said, several authors have used cation exchange for separating Ba^{2+} from Ln(III) elements[107-111]. Since Ba is a chemical analog of Eu(II), these cation exchange methods might well be suitable for use within a multiprocess separation procedure.

Fourcy et al.[107] reports on the use of cation exchange to separate Ba from REEs. The mixture was loaded onto a column containing Dowex-50 (200x400 mesh) resin using dilute HCl. Subsequently, +3 REEs were eluted from the column using 45 ml of 0.5 M α-HIB at a pH of 4.8. The elution of Ba was followed using 45 ml of 4 M HCl. Several authors also report on the separation of Ba from La or Ce using cation exchange resin. Fritz et al.[108] loaded a solution containing the Ba and La onto cation resin using 0.1 M HF. One molar HF eluted the Ba while the La was retained on the column. Herrmann and Strassmann[110] and Lieser and Bachmann[109] eluted La from Ba in roughly 100 minutes time using 0.5 M lactate at a pH of 4.6 and a flow rate of 0.1 ml/min. A similar method using ammonium lactate was also used for separating Ba from Ce[111].

A.2.2.2. Anion Exchange

Two reports were found discussing the use of anion exchange resin for separating Ba from La[112,113]. Bosholm[114] reports successful separation is easily accomplished in a few minutes using a nitrate form of Dowex-1 and an eluant of 3-4 M $LiNO_3$. Similar results were obtained using the hydroxide form of Dowex-1 anion resin[113]. In both cases, Ba is eluted while La was retained on the resin.

A.2.2.3. Reversed Phase Partition Chromatography

Several authors report using reversed phase partition chromatography for separating Ba from REEs[115,116]. Esser et al.[115] successfully separated Ba from REEs using a commercially produced reversed phase resin known as RE-Spec (produced by Eichrom Inc.). RE-Spec contains 1 M octyl (phenyl) – (N,N diisobutylcarbonyl) methyl phosphine oxide (CMPO) in tributyl phosphate (TBP) on Amberchrome CG-71 ms resin. Samples were loaded onto RE-Spec using 2-6 M nitric acid. Ba was eluted first using 25 Full Column Volumes (FCVs) of 2-6 M nitric acid, while the remaining REEs were eluted using 25 FCVs of 0.015 M nitric acid. Seeber et al.[116] synthesized and utilized poly (7-oxanorborn-2-ene-5,6-dicarboxylate) coated silica for their experiments. They report that at 5% nitric acid concentration Ba is not retained on the resin. Recovery and purity of the Ba was greater than 95%. While immobile phase was tedious to synthesize in the laboratory, commercially available RE-Spec was relatively expensive. Also in both cases, Ba (i.e., Eu(II)) was eluted prior to Ln(III) (i.e., Sm), a characteristic undesirable for this work. With that said, there is a distinct advantage provided by reversed phase resins in the area of waste reduction with respect to other traditional techniques. Many complexants that have been used successfully in solvent extraction for separating Ln(II) and Ln(III) metals may also be incorporated as a reversed phase resin. So, similar separation performance of traditional solvent extraction techniques might be attained with a reversed phase resin without generating hazardous mixed waste. This advantage will become increasingly important as disposal costs increase and fewer research groups have access to a disposal path that includes hazardous mixed waste.

A.2.2.4. Precipitation

Several recent publications utilized precipitation of $EuSO_4$ in a multiprocess method for separating Eu from other REEs[7,81,88,94]. Hirai and Komasawa[88] and Yorukaglu and Girgin[94] both used a two compartment cell for the initial electroreduction of Eu. Cells were separated by a cation exchange membrane and either a Ti or Hg coated Cu electrode was used as the cathode, while either a stainless steal or Pt anode was used. Both methods utilized 0.1 M H_2SO_4 within the anode compartment, while either $(NH_4)_2SO_4$ or Na_2SO_4 solution was used within the cathode compartment. Nitrogen sparging stabilized Eu(II) and precipitation occurred at the electrode. The purity of the Eu precipitate was reported to be greater than 97% by Hirai and Komasawa[88] and greater than 94% by Yorukaglu and Girgin[94], while the recovery of the Eu was only 70 – 80%[94]. An equilibration time of roughly 24 hours was required for both experiments.

Preston and du Preez[7] and Morais and Ciminelli[81] employed precipitation as a way of separating Eu from a lanthanide mixture following a reduction process using a Jones Reductor. Preston and du Preez precipitated the reduced Eu in 100% excess $(NH_4)_2SO_4$. The Eu recovery was reported to be 97.5%. A single precipitation step yielded a 92% pure Eu solid, while dissolution and subsequent reprecipitation enhanced purity to 96.5%. Further enhancement of purity was attained using a solvent extraction step following the initial precipitation. In this case, both 0.4 M HDEHP in xylene and 1 M Versatic 10 acid improved Eu purity to 99.7%. Cyanex 925 in xylene removed 99% of the Zn that was present as a contaminant from the Jones Reductor.

Morais and Ciminelli[81] precipitated Eu(II) from a Jones Reductor within dilute sulfuric acid under a CO_2 atmosphere. Contaminant Zn was removed by redissolution using HCl and reprecipitation with Na_2CO_3. The authors noted recovery decreased when Eu concentrations in the feed solution fell below 2.5 g L^{-1} or when the acid concentration was outside 3-4 M. Purity was greater than 95% as long as the acid concentration was below 4 M. Estimates on recovery were not published.

In all of the referenced cases, precipitation alone was not be capable of attaining the >99% purity design standard as set fourth by this project. Preston and du Preez[7] and Morais and Ciminelli[81] both employed solvent extraction following two precipitation steps to reach >99% purity. A fair assumption is that the precipitation step is ~85% efficient and the solvent extraction step is ~90% efficient. This would equate to an overall recovery of the three-step separation process of roughly 65%, much lower than the estimated yield of 91% required for producing two targets of ^{155}Eu from the available stock.

A.2.2.5. Solvent Extraction

Peppard et al.[117] first reported distribution ratios for Eu(II) and Ln(III) between aqueous solutions and either 1 M di-(2 ethyl hexyl) orthophosphoric acid (HDEHP) or 0.4 M di-para-(1,1,3,3-tetramethyl butyl) phenyl phosphonate. The ratio of the distribution constants for Eu(II) and various Ln(III) ions was similar in all solvents and roughly equal to 10^6 or 10^7. Extractions were conducted in 3 to 1 mixtures of organic to aqueous solutions and required a 5 minute equilibration time. Other researchers have built upon this work, conducting solvent extractions of Eu(II) in sulfate solutions in order to cause precipitation of the Eu as a final separating step[99,118]. In both cases, separation was done following photochemical reduction of the Eu using either a LPML or a HPML in the presence of a radical scavenger (e.g., isopropyl formate). Both experiments utilized 0.2 M HDEHP in either xylene or cyclohexane in the presence of 1 M $(NH_4)_2SO_4$ at pH 5. Recovery of Eu was as high as 90% while its purity within the solid was greater than 99%. The most obvious disadvantage to solvent extraction is the generation of hazardous mixed waste as a byproduct.

A.2.3. Summary of Multiprocess Separation

A multiprocess approach, where Eu(III) is reduced to Eu(II) prior to separation, requires a much less specific separation process than traditional single processes and so should provide a more effective and efficient means of separation. Figure A-3 presents a flow chart of the various multiprocess separation methods. Here various reduction processes, including chemical, electrochemical and photochemical methods, were reviewed for combination with a variety of separation processes, including cation exchange (IEX), anion exchange, reversed phase chromatography (RPC), precipitation and SE. Of these, chemical and electrochemical reduction methods were most effective. Chemical reduction methods are typically easier to employ than electrochemical techniques, while electroreduction methods that use inert electrodes will introduce no contaminants to the system. Of the chemical techniques reviewed, Zn(Hg) performed better than other amalgams, various metal suspensions, metal hydrides, and nitrogenous reductors. Of the various separation processes, only precipitation and solvent extraction methods have previously been coupled with an initial reduction step. There are issues of concern with both methods relative to this work. Precipitation as the sole separation step is not capable of obtaining >99% purity of the final product. Solvent extraction produces mixed waste and effective separation is dependent upon the initial concentration of the Eu relative to the Sm. However, the amount of waste produced using a solvent extraction method might be minimized to a few milliliters by thoughtful design. In addition, separation techniques such as ion exchange or reversed phase chromatography that have not yet been employed in a multiprocess separation for mixtures of Eu and Sm hold great potential for developing a highly selective and high yielding method that also reduces waste over traditional solvent extraction.

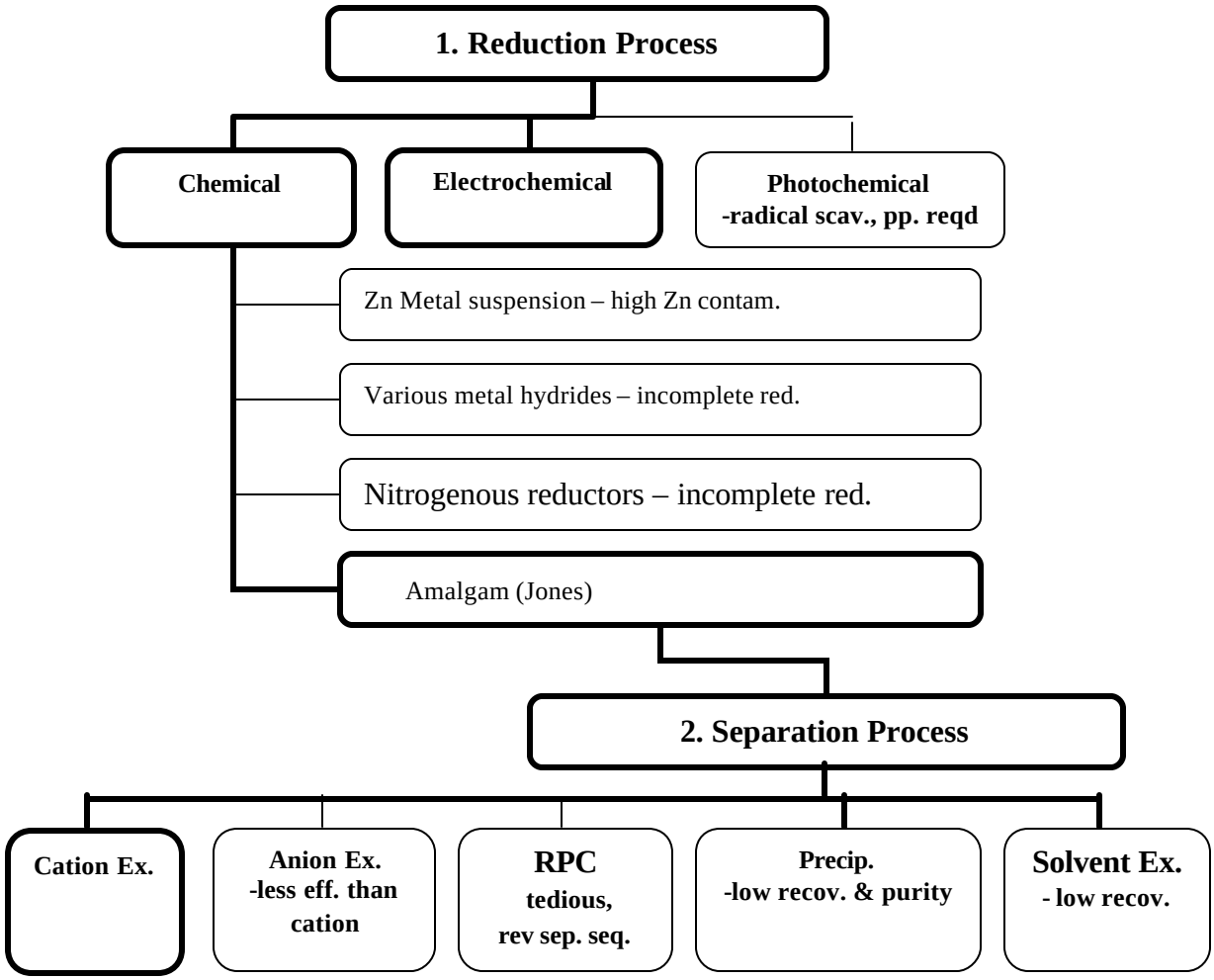

Figure A-3. Multiprocess methods used for separating mixtures of Eu and Sm.