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The Isolation of Lutetium from Gadolinium Contained in Purex Process Solutions

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IN PUREX PROCESS SOLUTIONS

D. T. Bostick, D. O. Vick, M. P. May, and R. L. Walker

Analytical Chemistry Division

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ABSTRACT

A chemical separation procedure has been devised to isolate Lu from Purex dissolver solutions containing the neutron poison, Gd. The isolation procedure involves the removal of U and Pu from a dissolver solution using tributylphosphate solvent extraction. If required, solvent extraction using di-(2-ethylhexyl)phosphoric acid can be employed to further purify the sample by removing alkali and alkali earth elements. Finally, Lu is chromatographically separated from Gd and rare earth fission products on a Dowex 50W-X8 resin column using an alpha-hydroxyisobutyrate eluant.

The success of the chemical separation procedure has been demonstrated in the quantitative recovery of as little as 1.4 ng Lu from solutions containing a 5000-fold excess of Gd. Additionally, Lu has been isolated from synthetic dissolver samples containing U, Ba, Cs, and Gd. Thermal emission MS data indicated that the Lu fraction of the synthetic sample was free of Gd interference.

INTRODUCTION

International safeguards procedures, established under the International Nuclear Non-Proliferation Treaty, require the independent measurement of fissile materials content in holding tanks at selected points within the nuclear fuel cycle. To accomplish this task, holding tank volume, as well as the heavy metal content of the tank solution, must be accurately measured. The complex geometry of existing holding tanks, the presence of entrained solids in the tank solutions and factors such as mixing times, tank sampling, and tank port biases, can compromise the accuracy of conventional tank volume determinations.

A double-spike chemical tracer technique using lutetium has been proposed to improve the measurement precision and accuracy of tank solution volume and mass.^{1,2} In the procedure, a known amount of a natural lutetium spike is added to the contents of a holding tank. After thorough mixing to ensure a uniform distribution of the first spike, a measured aliquot of the tank solution is withdrawn. A second spike containing a known quantity of enriched Lu-176 is added to the aliquot such that the final ratio of Lu-175/Lu-176 is approximately 1.0. The mass spectrometric (MS) measurement of the Lu isotopic ratio in the aliquot, when compared to the same ratio in the first spike, allows the calculation of the concentration of the natural lutetium spike in the tank in units of micrograms of Lu per gram of solution. The solution mass in the holding tank is then determined by dividing the original quantity of natural Lu spike added to the tank by the calculated tank concentration.

An early evaluation of the lutetium tracer technique was performed using a relatively large addition (16.5 $\mu\text{g/g}$) of natural Lu as the first spike to a uranium feed tank.² Because the quantity of added Lu was large and few contaminants were present in the solution, no further chemical clean-up of the double-spiked aliquot was required prior to MS analysis.

The tracer technique also has been evaluated for the calibration of output tanks, for which only low levels of Lu are permissible in the product solution.³ A calibration exercise has been performed on a plutonium nitrate holding tank using a Lu spike level of 200 ng Lu per gram of solution. To eliminate the effects of relatively large quantities of plutonium on the MS analysis of Lu, the plutonium was removed by passing the double-spiked aliquot through an anion exchange column. The eluant was then loaded onto a column containing di-(2-ethylhexyl)phosphoric acid (HDEHP) immobilized on an inert support. Eight normal HNO_3 was used to elute Lu, separating it from other rare earth elements and americium which remained on the column. MS analysis was then carried out on the column eluant.

This report describes the chemical purification procedures required to extend further the lutetium double spike technique to spent fuel dissolver tank solutions containing gadolinium as the neutron poison. Lu analysis in the head-end solution of the recycle process is complicated by the presence of uranium, plutonium, and fission products. The presence of Gd at levels of 5 g/L also interferes with Lu analysis by producing the GdO^+ ion at 176 amu in the mass spectrum. A sample preparation scheme for dissolver solutions has been devised in which the majority of the uranium and plutonium is first extracted from the aliquot. Lu can then be separated from alkali metals by a second solvent extraction before being isolated from rare earths on a cation exchange column prior to MS analysis.

REAGENTS AND EQUIPMENT

The chemical purification procedure was evaluated using 99.9% natural lutetium oxide (Atomergic Chemetals Corp.) and gadolinium oxide (Michigan Chemical Corp.) dissolved in reagent grade nitric acid (HNO_3). A depleted uranium stock solution was analyzed using the Davies-Gray potentiometric procedure. Serial dilution of this stock was used to prepare diluted uranyl nitrate standards that approximated uranium concentration in dissolver solutions. Barium and cesium stock standards were purchased from SPEX Industries, Inc. and appropriately diluted to simulate alkali metal contaminations in dissolver solutions. Tributylphosphate (Baker Analyzed) was diluted to a 30% (v/v) concentration with n-dodecane (Fisher Scientific Co.). The TBP organic extractant was equilibrated with an equal volume of 3.2 M HNO_3 prior to use. Di-(2-ethylhexyl)phosphoric acid (Alfa Products) was diluted with n-dodecane to prepare a 0.75 M (25% v/v) extractant concentration.

Rare earth metal separations were made using a modification of a cation resin procedure developed by R. D. Baybarz et. al.⁴ Metals were separated on a column containing AG 50W-X8 cation exchange resin having a minus 400 mesh size (BIO-RAD). The resin was cleaned by loading an aqueous slurry of the resin in the hydrogen form into a 1 cm i.d. by 8 cm long glass column. After the excess water was drained from the column, two 10-mL volumes of 6 M HCl were passed through the 25 mL resin bed to remove any trace metals. Finally, distilled water was passed through the column until the pH of the eluant was greater than 4. The cleaned resin was then stored as an aqueous slurry.

The rare earth separation column was prepared by first placing a plug of acid-leached quartz wool at the exit of a water-jacketed glass column (Figure 1). A circulating water temperature of 50.5°C was used to equilibrate thermally the glass column during resin loading and sample separations. Approximately 2.5 mL of the cleaned AG 50W-X8 resin was used to fill the 5 mm i.d. inner separation column to a height of about 12 cm. A second plug of cleaned quartz wool was then placed at the head of the resin column. Due to the small mesh size, a positive pressure of 8-10 psi N_2 was required to force fluid through the resin bed. A flow rate of 0.35 mL/min is possible with this pressure without unduly compressing the resin bed.

Five mL of 3 M HNO_3 were added to the reservoir of the resin column to remove final traces of alkali metals from the prepared column. Additional volumes of distilled water were then added to the head of the column until the final acidity of the eluant was approximately pH 5. The resin bed was allowed to equilibrate at 50.5°C for 1.5 hours before metal samples were loaded onto the separation column.

To take advantage of the greater affinity of metals for the hydrogen form of the resin and to reduce the possibility of metal hydrolysis, samples were loaded onto the separation column prior to converting the resin to the ammonium counterion form. Once the metal sample had been deposited at the head of the column, the column reservoir was rinsed with three 0.5 mL additions of distilled water to completely transfer the sample onto the resin bed. Counterion conversion was then accomplished by washing the column with 0.3 M NH_4NO_3 until the pH of the eluant was greater than 4.5. Column conversion to the ammonium form was usually complete after the addition of 10-12 mL of the NH_4NO_3 wash. Multiple additions

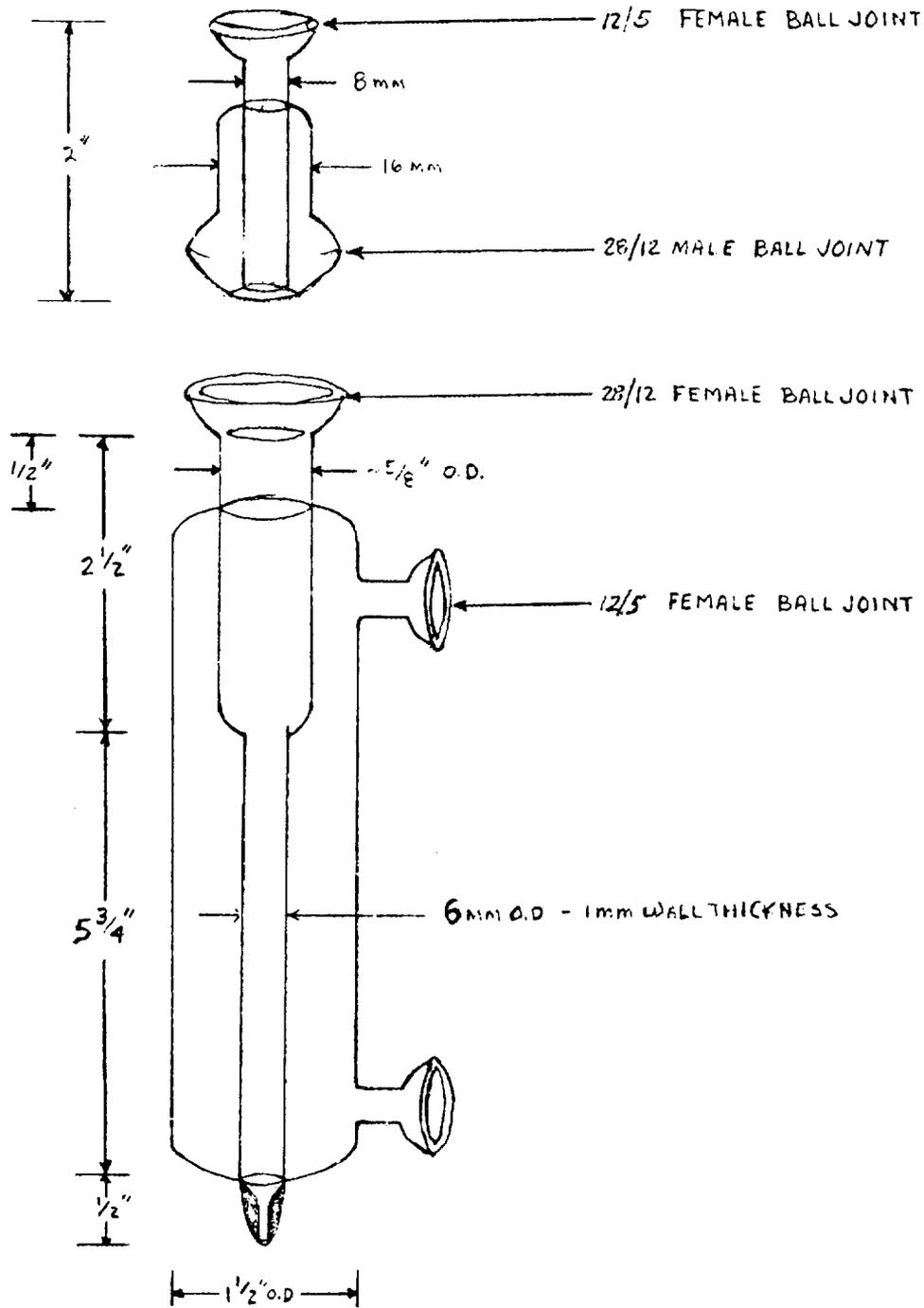


Figure 1. Hot Water-Jacketed Ion Exchange Column No. 1⁴

of distilled water totaling 5 mL of rinsate were then used to remove excess NH_4NO_3 from the resin.

Rare earth metals were eluted from the separation column using 0.25 M α -hydroxyisobutyric acid (AHIB). The reagent was prepared by dissolving 13 g AHIB (Eastern Chemical Co.) in 500 mL of distilled water. Because the solution pH of 2.3 retards bacterial growth in the reagent, only a 125 mL aliquot of 0.25 M AHIB is withdrawn and adjusted to $\text{pH } 4.15 \pm .01$ with approximately 20 drops of concentrated NH_4OH just prior to use. The container of pH-adjusted AHIB was placed in the 50.5°C water bath to equilibrate its temperature with that of the separation column. Four-milliliter aliquots of the AHIB were added to the reservoir of the column to begin sample elution. Typically, column eluant was collected in 5-drop fractions (~ 0.04 mL/drop) for the first seven fractions. Beyond this volume, eluant fractions contained 1-2 mL.

During initial procedure development, metal elution from the column was followed using scanning ICP-OES. Sample fractions were diluted to a 5 mL volume with 1 M HNO_3 and introduced into the ICP without further treatment. Detection limits for Lu, Gd, and Ba were 20 ppb, 50 ppb and 10 ppb, respectively. Analysis of the Cs content in the samples was not possible by this method due to the ease of Cs ionization in the plasma.

Isotope dilution mass spectrometry (IDMS) was used to analyze lutetium recovery in final rare earth separation experiments. One microliter of a column fraction was dried on a rhenium filament. One μL (0.8 ng) of an enriched lutetium-176 spike (1.4836% Lu-175 and 98.5164% Lu-176) was then dried on the same MS filament. The Lu-175/Lu-176 ratio in the spiked sample was measured using a two-stage instrument with two 30 cm-radius, 90° -sector magnets.⁵ The spectrometer is equipped with a pulse-counting detection system and an ion source designed in-house,⁶ making possible analysis of subnanogram samples. Sample filaments were heated to 1300°C initially to remove Ba from the sample; lutetium data were collected at a filament temperature of 1350°C .

RESULTS AND DISCUSSION

The proposed scenario for the calibration of the dissolver tank volume would begin with the addition of sufficient natural Lu to the tank such that the final concentration in the equilibrated tank solution is approximately 10 $\mu\text{g/mL}$. To reduce operator radiation exposure, an aliquot would be withdrawn from the tank and diluted 200-fold with 5 M HNO_3 . Enriched Lu-176 spike would be added to a portion of the diluted aliquot to produce a Lu-175/Lu-176 ratio of approximately one. The double-spiked sample would then contain about 100 ng/mL total Lu, 1 mg/mL uranium, 10-500 $\mu\text{g/mL}$ plutonium, 25 $\mu\text{g/mL}$ gadolinium, 2 $\mu\text{g/mL}$ alkali metals and 1 to 5 $\mu\text{g/mL}$ rare earth fission products.

Direct analysis of the diluted dissolver solution by thermal ionization IDMS is not possible due to the high levels of fission products. Fluorides, oxyfluorides, and oxides of rare earth and alkali metal elements are generated during thermal ionization of the dissolver sample in the mass spectrometer. Barium-138 fluoride (BaF_2^+), ytterbium-176, Ce-140 oxyfluoride (CeOF^+) and gadolinium-160 oxide (GdO^+) all have a mass-to-charge ratio of 175 or 176, equivalent to one of the Lu isotopes. In addition, the low ionization potential of

plutonium would prevent efficient ionization of Lu in the sample if the heavy metal were present in large quantities.

A chemical separation procedure will therefore be required to isolate Lu from the dissolver solution matrix. The aforementioned lutetium isolation procedure employed for plutonium product solutions is not directly applicable to dissolver samples containing gadolinium at concentrations as great as 5000 times higher than that of Lu. Hence, a sample preparation scheme for dissolver solutions has been devised in which the majority of the uranium and plutonium is first extracted from the aliquot. Lutetium then is separated from alkali metals in a second solvent extraction step prior to isolation from other rare earths on a cation exchange column.

Liquid-Liquid Extraction of Heavy Metals

The method selected to remove uranium and plutonium from the diluted dissolver sample is liquid-liquid extraction using 30% TBP in dodecane. Conventionally, uranium and plutonium nitrates are extracted with greatest efficiency from aqueous dissolver solutions containing 3-4 M HNO₃. Fortunately, loss of Lu to the organic phase under these extraction conditions is not significant. Loss of Lu becomes significant only if the concentration of TBP in the organic phase is markedly greater than 30%.⁷

The extraction characteristics of rare earths in TBP also aid in the isolation of Lu from Gd by reducing the amount of Gd in the extracted double-spiked aliquot. This observation is supported in an earlier investigation made by Peppard et. al.⁸ At acidities below 5 M HNO₃, the distribution coefficients in TBP were found to decrease as Z increased for lanthanide elements with an atomic number (Z) between 64-71. In more extensive studies,^{4,6} Gd (and lighter lanthanides) exhibited a maximum distribution coefficient when the aqueous phase contained between 3-4 M HNO₃. The extraction of Lu, and other odd-Z lanthanides heavier than Gd, exhibits a similar but more pronounced dependence with Z below 5 M HNO₃. This difference in behavior results in an increasingly larger separation factor of Gd from Lu as the acidity of the aqueous phase decreases. The corollary to this behavior is that the total amount of either rare earth element extracted into TBP is reduced at lower aqueous phase acidities. It would thus appear that the optimum aqueous acidity for the removal of U, Pu, and Gd from the double spiked-aliquot would be between 3-4 M HNO₃. This acidity would allow maximum actinide decontamination, as well as provide a partial extraction of Gd from the aqueous phase without undue loss of Lu.

The actual loss of Lu during the TBP solvent extraction was investigated by analyzing a synthetic sample simulating a 100-fold dilution of a dissolver solution. The synthetic sample contained 1.50 mg U, 50 µg Gd, 160 ng Ba, 160 µg Cs, and 100 ng Lu per mL in 5 M HNO₃. A volume of the sample was shaken for five minutes with an equal volume of acidified 30% TBP. The following recoveries were found in the separated aqueous phases at the completion of a single and a double TBP extraction procedure, respectively:

Table I. Percent Aqueous Metal Recovery

	U	Lu	Gd	Ba
Single extraction	3	98 \pm 5	77 \pm 4	106
Second extraction	trace	99 \pm 4	78 \pm 8	99 \pm 17

The single extraction recoveries represent data from two trials; the second extraction results are based on data from four trials. Quantitative recovery of Lu is observed following TBP extraction; better than 20% of Gd content is removed from the aqueous phase. One would expect a similar reduction in Gd after a second TBP extraction of the sample. Apparently further Lu/Gd separation is not accomplished with a second TBP extraction; this may be the result of the limited precision of ICP analysis in samples containing the metals at close to the metal detection limits of the ICP. A second solvent extraction is required to remove the majority of uranium, and, by inference, plutonium from the aqueous aliquot. Barium (and presumably other alkaline and alkaline earth metals present in a dissolver sample) is not removed from the aqueous phase. The large standard deviation in Ba data probably reflects the difficulty in controlling Ba contamination in reagents and laboratory glassware.

Column Separation of Rare Earth Elements

Although Lu separation from Gd might be enhanced by reducing the acidity of the aqueous phase from 5 to 3 M HNO₃, the primary function of the TBP extraction is to remove the heavy metals while requiring a minimum of laboratory operations with a highly radioactive sample. Rare earth metal separation is accomplished more efficiently by passing the extracted aqueous phase through an ion exchange column.

A significant body of literature is available describing rare earth separations using cation exchange resins. Attempts to isolate rare earths by elution with inorganic acids have been explored but were not very successful.^{10,11} The separation factors between adjacent elution peaks were poor because the affinities of rare earth elements for cation exchangers are very similar. However, very good results have been obtained using complexing eluants, such as citrate,¹² lactate,¹³ ammonium alpha-hydroxyisobutyrate (AHIB)^{14,15} and ethylenediaminetetraacetic acid (EDTA).^{16,17}

Of the complexing eluants, AHIB has essentially supplanted other complexing agents as the eluant of choice for rare earth separations on cation resins. Both citrate and lactate eluant systems require a significant elution time, as compared to EDTA or AHIB complexation, to separate adequately Lu from other rare earths. The major application of EDTA has been for large scale production of rare earth compounds. Separation factors for small-scale rare earth separation are quite poor for EDTA in comparison with other complexing agents.

Rare earth separation factors on the AHIB column are superior to other complexing eluants. With proper selection of column parameters, milligram or smaller quantities of rare earth mixtures can be discretely separated into individual metal fractions. A characteristic of the AHIB column that is particularly advantageous for the present application is the order in which rare earths elute from the cation resin column. Rare earth element elution is in the order of decreasing Z. Lu, therefore, is eluted from the cation exchange column in the first eluant metal peak. Further column separation of the dissolver sample is unnecessary; the remainder of the rare earths need not be eluted. Thus, considerable laboratory time is saved using this particular separation scheme for dissolver solutions.

Selection of the optimum column parameters for Lu/Gd separation on an AHIB column is based on a number of literature studies. The concentration of the complexing anion in the AHIB eluant is the primary parameter governing the separation and elution volume of each rare earth from the cation resin column. The relative elution volumes of the rare earths as a function of free anion concentration have been defined in several reports.^{4,17-20} Typically, the eluant concentration ranged from 0.1-0.5 M AHIB and pH varied between 3 and 4.5. The optimum alpha-hydroxybutyrate ion concentration appears to be greater than 0.15 M. At this free anion concentration, the Lu will rapidly elute from the resin column and Gd will be effectively retained. Much below this free anion concentration, elution volume of high Z elements becomes sensitive to slight variations in alpha-hydroxybutyrate ion concentration.¹⁸ An operating pH of 4.15 was selected for the current application. Using an ionization constant for AHIB¹⁵ of 1.04×10^{-4} , the comparable concentration of AHIB at pH 4.15 is 0.25 M to achieve a free anion concentration of 0.15 M.

Separation of rare earth elution peaks is also governed by cation resin characteristics, such as the percentage cross-linkage and the resin size. The extent of cross-linkage controls the number of available active sites in the resin bead and the extent to which the bead volume changes with acidity. Resin bead volume, in turn, defines the peak shape and resolution of adjacent elution peaks. Typically, sulfonic acid resins with a 4-12% cross-linkage are used for removal of cations and metal separations. Initial rare earth separations were performed using a 12% cross-linkage. A heated (87°C) AHIB eluant was required with a highly cross-linked resin in order to obtain resin-solution equilibrium rapidly.¹⁸ Heated columns are not required if a lower cross-linkage is used.¹⁵ An 8% cross-linked resin for the current Lu/Gd separation was viewed as a compromise between low cross linking and low swelling during Lu/Gd separations. The column was operated at 50°C to improve the resolution of the elution peaks. A resin size of either 200-400 mesh (nominal 74 to 37 microns) or "minus" 400 mesh (nominally 62 to 23 microns) has been used for the separation of adjacent rare earth metals. A comparison of rare earth elution profiles has been made as a function of resin bead size.²¹ As expected, the more uniform and finer the bead volume, the more resolved the elution peaks. The disadvantage to using smaller resin beads is the reduced eluant flow through the column, resulting in extended separation times. A minus 400 mesh Dowex 50W-X8 resin was selected for the separation of Lu from Gd in dissolver samples. External nitrogen pressure (8-10 psi) is required to maintain an eluant flow of 0.35 mL/min.

Table II summarizes results obtained in six experiments using the column operating parameters described above. Lutetium and Gd standard solutions contained in 0.4 M HNO₃

were added to the column in total volumes of less than 1 mL. The ratio of Gd/Lu in the experiments ranged from 66 to 5457; quantities as great as 1.5 mg total rare earth metal were loaded on the column during a single run. Experimental results indicate that the majority of Lu elutes within the second half-milliliter of eluant volume. Taking into account the eluant fraction size collected in each separation run, the Lu elution volume does not appear to vary significantly with either the total heavy metal loaded on to the column or the ratio of Gd/Lu in the sample. The Gd elution volume occurs between the fifth through ninth milliliter of AHIB eluant. Within experimental error, both the Lu and Gd are recovered quantitatively. Recoveries greater than 100%, again, reflect the imprecision of the metal analysis near the instrument detection limit.

Table II. ELUTION VOLUME OF LU AND GD FRACTIONS

RUN #	METAL LOADING		FRACTION SIZE	ELUTION VOLUME		METAL RECOVERY	
	Lu	Gd		Lu	Gd	Lu	Gd
1	23	1529	4	0-4	4-8	150%	110%
2	1.43	152.9	1	0-2	4-8	97%	100%
3	0.143	15.3	1	0-1	5-8	92%	99%
4	0.0143	7.64	1	0-1	5-7	104%*	100%
5	0.0014	7.64	1	0-2	6-9	112%*	100%
6	0.143	152.9	0.18	0.6-1	---	103%*	----

Volume in units of mL; metal loading in units of μg .

*Lu analysis based on thermal ionization MS; Gd and remaining Lu results based on ICP analysis.

Lu analysis in runs 4-6 was performed using thermal ionization MS. All eluant fractions could be loaded directly onto MS filaments; the 0.25 M AHIB eluant did not interfere with Lu ionization or produce a significant ion background. Traces of Ba were observed in the samples. However, the Ba contamination was easily removed by heating the filament at a temperature lower than that required to ionize Lu prior to MS analysis. In fact, the column in Run #6 was also loaded with 7 μg Ba, in addition to Lu and Gd. Although Ba was observed in the MS profile, the contaminant could be burnt off if the MS filament was heated at slightly less than 1350°C for 0.5 hr.

**TABLE III. SEPARATION EXPERIMENTS WITH A
SYNTHETIC DISSOLVER SAMPLE**

RUN	LU (ng)	GD (μ g)	INITIAL GD/LU	LOADING		ELUTION		FINAL GD/LU
				VOL (mL)	[HNO ₃] (M)	LU VOL (mL)	GD VOL (mL)	
7 ^B	206	82	398	2	5	0.6-1.2	0.8-7.6	9 U(VI)
8 ^B	205*	75*	366	4	2.5	0.6-1.0	0.6-3.6	52 Trace U
9 ^B	195*	85*	436	12	0.83	0.8-1.4	4.6-8.6	No Gd No U
10 ^B	182*	86*	473	12	0.83	0.6-1.2	5.6-8.6	No Gd Trace Ba

*Rare earth element masses are those obtained after double extraction of 5 mL synthetic sample with 30% TBP.

B indicates that 0.35 μ g Ba(II) was contained in the synthetic sample.

Pre-column Sample Preparation Procedures

Sample acidity alters Lu/Gd column separations if the loading acidity is too great. These loading conditions apply when an extracted synthetic dissolver sample is loaded either directly onto the column or is diluted by a factor of 2 prior to column loading. Table III summarizes the elution characteristics of a synthetic dissolver sample. As is evident in the final Gd/Lu found in the Lu column fraction of runs 7 and 8, Gd migrates down the resin column when the loading acidity is 2 M HNO₃ or greater. Lu and Gd coelute when AHIB is then used to remove the rare earths from the column.

The correct acidity for sample loading was determined in a series of experiments in which a sample simulating the 1:200 diluted dissolver synthetic solution was treated batch-wise with cation exchange resin. The acidity of one mL of the TBP-extracted sample was varied; a 1:10 dilution of the treated sample was shaken with 0.25 g resin for 20 minutes. The percent metal adsorbed on the resin was determined by analyzing the resulting aqueous sample for the final metal content. Table IV summarizes the percent of Lu, Gd, and Ba retained on AG 50W-X8 (50-100 mesh) resin after being contacted with treated synthetic sample with varying HNO₃ content.

TABLE IV. RARE EARTH AFFINITY ON AG 50W-X8 RESIN

SAMPLE ACIDITY [HNO ₃]	% ADSORBED		
	Lu	Gd	Ba
0.50	100	99	86
0.66	100	97	81
0.85	90	94	74
1.0	93,100	95,86	61,80
1.3	84	87	
3.51	34	24	

To prevent migration of rare earth metals down the separation column, it can be concluded that the loading acidity of the sample on the column must be less than 1 M HNO₃. In addition, it is evident that a portion of the Ba contamination can be removed from the column by rinsing the loaded resin with a small volume of 1 M HNO₃ after sample application. Runs 9 and 10 in Table III present separation results in which 2 mL of a TBP-extracted synthetic sample were diluted to 12 mL such that the final acidity of the sample was 0.83 M HNO₃. The diluted sample was loaded onto the separation column, and the column rinsed with 5 mL of either 0.4 or 0.9 M HNO₃ in Runs 9 and 10, respectively. The column was then rinsed with 4 mL H₂O to remove the excess acid before rare earth separation was initiated with AHIB. Based on ICP-OES analysis, 99% of Lu was recovered in the 0.8-1.4 mL of AHIB column effluent in Run 9. The Lu fractions were not contaminated with Gd. Column fractions analyzed by IDMS indicated that 90% of the loaded Lu was recovered in the eluant of Run 10. Gd was not found in Run 10 Lu fractions. However, significant quantities of Ba in the samples required a 0.5 hr preheating before Lu results could be acquired by the MS.

Extraction of Alkali and Alkali Earth Metals

To overcome the Ba interference in IDMS analysis, it may be possible to separate the elution peak of Ba from that of Lu by reducing the concentration of the alpha-hydroxyisobutyrate ion in the column eluant. The reduced complexing ability of the column eluant would increase the retention of Lu (and remaining rare earths) on the column, without affecting the elution position of non-retained metals such as Ba.

If the sample contains a significant quantity of alkali and alkali earth metals, it may be necessary to remove them from the TBP-extracted sample prior to column loading. Isolation of Lu from fission product contaminants has been accomplished in the past by solvent extraction using di-(2-ethylhexyl) phosphoric acid (HDEHP).^{22,23} HDEHP strongly extracts penta- and tetra-valent metal species and retains them in the organic phase. Trivalent species are less strongly extracted and thus can be stripped from the organic phase. Di- and monovalent species are extracted only at very low acidities.

HDEHP has been successfully applied in the current studies to the separation of sub-microgram quantities of Lu contained in 0.5 M NaNO₃ prior to IDMS analysis. Because rare earth extraction is more efficient with a hydrocarbon diluent,²⁴ HDEHP was prepared in n-dodecane. The HDEHP reagent was used as received, although the literature suggests that mono-ester phosphates contained in the extractant be removed to improve the reliability of the extraction process for samples containing low concentrations of rare earths.²² The HDEHP was prepared at a concentration of 0.75 molar. This concentration of extractant is sufficient for most applications to maintain a ratio of HDEHP to extracted metal concentration above the solvent saturation level of 6:1.²⁵ Because of the strength of the HDEHP-Lu bond, use of any higher concentration of HDEHP would limit the recovery of Lu from the organic phase during the stripping procedures.

The type of mineral acid in the aqueous sample has little influence on the extraction behavior of rare earths. The dominant factor in the selection of the mineral acid is determined by the quantity and the type of transition metal contaminants that may also be present in the Lu sample. A review of the extraction behavior of fission product metals in several mineral acids has been made²⁴ for reference. Because the presence of alkali metals was the only concern in the present application, Lu was extracted from an HNO₃ matrix.

The distribution coefficients of rare earths at a given HDEHP concentration are greatest at HNO₃ concentrations less than one molar. The lower limit of acid concentration in an aqueous sample is set by the possibility of metal hydrolysis and metal adsorption on vessel walls.²⁶ The aqueous acidity should be greater than 0.05 M HNO₃ to prevent loss of rare earths, as well as to eliminate alkali metal extraction. Above 1 M HNO₃, the extraction efficiency of all rare earths except Sc, Yb, and Lu decreases precipitously. From 3-11 M HNO₃, the rare earths lighter than Tb are not significantly extracted with HDEHP. Selection of an aqueous phase acidity within this range could provide a means to reduce significantly the Gd content of a dissolver solution sample prior to AHIB column separation. At approximately 9 M HNO₃, the distribution coefficients of all rare earths in HDEHP increase.²⁴ The mechanism for extraction of the rare earths above this acidity becomes dominated by both the neutral HDEHP molecule as well as the dissociated DEHP ion.²² The complicated extraction mechanism would suggest that aqueous acidities be kept below 9 M HNO₃ to ensure reproducible results.

In the practical application of the HDEHP extraction procedure, the acidity of the aqueous samples containing Lu was adjusted to 0.2 M HNO₃. Volume ratios ranging from 1 to 10 (aqueous to organic phase volume) were shaken for 5 minutes. Literature citations indicate that extraction equilibrium is rapidly attained²⁴ so that extended mixing times are not required. After centrifugation and phase separation, the organic phase was washed with 0.2 M HNO₃. The Lu was stripped from the organic phase with twice the volume of 8 M HNO₃. Four stripping steps were required to obtain a 75% recovery of added Lu; a fifth strip of the HDEHP yielded an 83% Lu recovery.

Because HDEHP is partially soluble in the aqueous phase, entrained organic extractant must be removed from the combined strip solutions prior to IDMS analysis or before application on the AHIB resin column. Organic removal may be accomplished in one of several ways: 30% hydrogen peroxide (H₂O₂) and may be added to the stripped sample to oxidize the HDEHP. Alternatively, the strip solution may be passed through a Dowex-2

anion column to remove HDEHP.²⁶ The HDEHP may also be back-extracted from the strip solution using n-octyl alcohol.²⁷

IDMS analysis of solutions treated with H_2O_2 suggests that low molecular weight organic contaminants remain in the strip solution and compromise analysis accuracy. HDEHP removal by either an anion column or solvent extraction procedure may prove to be more effective. IDMS results also indicated that sufficient sodium had been removed from the sample by HDEHP treatment because Lu ionization was not inhibited by the presence of large quantities of alkali metal.

CONCLUSIONS

The current study suggests a series of sample separation procedures to address the need to isolate Lu from complicated solution matrices presented in the nuclear fuel cycle. The separation techniques can be used individually or in sequence depending upon the quantity and types of contaminants contained in a given sample. Solvent extraction using TBP can be used to remove uranium and plutonium from an aqueous sample. In so doing a certain degree of separation of Lu from other rare earths is also accomplished. If a reprocessing sample contains a significant quantity of fission products or alkali and alkali earth metals, solvent extraction using HDEHP can be used in a single isolation procedure or as a follow-up to the TBP extraction to isolate Lu. Finally, when a sample contains a number of rare earths, present either as fission products or as a neutron poison, chromatographic separation on an AHIB column can quickly isolate Lu for subsequent IDMS analysis. The selection of the number and type of separation procedures is ultimately dominated by the need to provide the most accurate measurement of Lu content in tank solutions.

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APPENDIX A

SAMPLE PREPARATION SEQUENCE FOR LU ISOLATION
FOR SYNTHETIC DISSOLVER SOLUTION

- I) TBP SOLVENT EXTRACTION OF U (AND Pu)
- A) Filter sample with a 0.45 μm filter if necessary
 - B) Spike sample with enriched Lu-176 and mix sample for 20 min.
 - C) Add 4 mL acidified 30% TBP/dodecane to sample; mix 5 min.; discard organic phase
 - D) Add 4 mL acidified 30% TBP/dodecane to aqueous phase; mix 5 min.; discard organic phase
 - E) Evaporate the sample to near dryness.
- II) HDEHP SOLVENT EXTRACTION OF ALKALI AND ALKALI EARTH METALS
- A) Add 100 μL 8 M HNO_3 to redissolve metal salts.
Add 4 mL H_2O so that the sample contains < 0.3 M HNO_3 .
 - B) Add 1 mL 0.75 M HDEHP to 4 mL Lu sample.
 - C) Vortex 5 minutes; centrifuge 3 minutes; discard aqueous phase.
 - D) Scrub organic phase with 4 mL H_2O ; discard aqueous phase.
 - E) Strip Lu from organic phase using 2 mL 8 M HNO_3 .
Vortex 5 min, centrifuge 3 min. Strip organic phase three more times and combine strip fractions.
 - F) Evaporate sample to dryness and bring up in 0.5 mL of 0.5 M HNO_3 .

APPENDIX A, CONTINUED

III) AHIB COLUMN PROCEDURE FOR LU ISOLATION

A) Column Preparation

- 1) Clean AG 50WX8 (minus 400 mesh) resin batchwise with 6 M HCl
- 2) Rinse resin with H₂O until eluant is neutral and store in H₂O until use
- 3) Fill water-jacketed glass column with H₂O
- 4) Add cleaned resin to column to displace the H₂O sufficiently to make an 11 cm long resin column
- 5) Equilibrate column at 50 °C for 1 hour
- 6) Wash column with 10 mL of 3 M HNO₃; rinse column with 4 mL H₂O until the eluant is neutral

B) Sample Loading

- 1) Add extracted Lu fraction to column
- 2) Rinse column with 4 mL 1 M HNO₃
- 3) Rinse column with H₂O until neutral (2 mL)
- 4) Convert column to NH₄⁺ form with 15 mL 0.35 M NH₄NO₃
- 5) Rinse column with 5 mL H₂O
- 6) Adjust 125 mL 0.25 M AHIB to pH 4.15 with concentrated NH₄OH
- 7) Add 4 mL 0.25 M AHIB, pH 4.15, and begin elution
- 8) Discard first 0.5 mL, collect next 0.5-1.5 mL for lutetium analysis
- 9) Evaporate lutetium fraction; redissolve in 5 μ L 0.05 M HNO₃

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