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# ANALYTICAL-SCALE SEPARATIONS OF THE LANTHANIDES: A REVIEW OF TECHNIQUES AND FUNDAMENTALS

Kenneth L. Nash[a]; Mark P. Jensen[a]
[a] Chemistry Division, Argonne National Laboratory, Argonne, Illinois, U.S.A.

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# ANALYTICAL-SCALE SEPARATIONS OF THE LANTHANIDES: A REVIEW OF TECHNIQUES AND FUNDAMENTALS

**Kenneth L. Nash and Mark P. Jensen**

Chemistry Division, Argonne National Laboratory,
9700 S. Cass Ave., Argonne, Illinois 60439-4831

## ABSTRACT

Separations chemistry is at the heart of most analytical procedures to determine the rare earth content of both man-made and naturally occurring materials. Such procedures are widely used in mineral exploration, fundamental geology and geochemistry, material science, and in the nuclear industry. Chromatographic methods that rely on aqueous solutions containing complexing agents sensitive to the lanthanide cationic radius and cation-exchange phase transfer reactions (using a variety of different solid media) have enjoyed the greatest success for these procedures. In this report, we will briefly summarize the most important methods for completing such analyses. We will discuss in some detail the basic aqueous (and two-phase) solution chemistry that accounts for separations that work well and offer explanations for why others are less successful.

## INTRODUCTION

The general topic of analytical separations of the rare earths has been reviewed a number of times in the past ten years.(1–11) Some of these reviews have focused on specific, mainly chromatographic, techniques. Others have presented a broader comparison of the virtues and vices of various methods, and their suitability for specific analytical tasks. Reviews have appeared in several languages, indicating that important research is being done around the world on both lanthanide science and technology in general, and on analytical methods development for lanthanides. The most recent of the broad-based English language reviews was published in 1994, discussing the literature through 1992.(9)

To complement these fine resources, the present report will focus on providing a basic chemical thermodynamic overview of the fundamental chemistry that underpins contemporary analytical separation techniques for lanthanides. We intend that this approach will provide the reader with an improved understanding of the advantages and disadvantages of the mainstream separations-based methods for lanthanide analysis, and thus help the analyst identify the optimum techniques for any particular analytical problem in rare earth analysis. Some portion of this discussion will address developing trends in lanthanide analytical science. We will outline some of the important interfaces between the separations methods and the detection/quantitation techniques employed.

## DESCRIPTION OF THE METHODS

Analysis of lanthanide samples is typically a destructive process. Most commonly, the sample (rock, ceramic, metal/alloy, metal oxide etc.) is subjected first to a digestion process that completely dissolves the sample. Selective dissolution of the rare earths from the sample is seldom possible. For analysis of the rare earth content of the digested sample, two separations are important: 1) separation of the rare earths as a group from the matrix elements, and 2) separation (and quantitation) of the individual members of the series. The former (group) separation serves both to remove metallic species that may interfere with the lanthanide analysis and to preconcentrate the sample to increase sensitivity. The latter is one of the greatest challenges in the separation of metal ions due to the chemical similarities of the rare earths and the existence of most of these metal ions in only the trivalent oxidation state.

Though element-specific detection methods like neutron activation analysis or mass spectrometry are sometimes adequate for lanthanide analysis (and can eliminate the need for separations of the individual members of the series), chromatographic techniques are most commonly applied for this purpose. Chromatography is popular partly for its low cost, but also for its sensitivity, particularly when it is applied with a “preconcentration” separation that isolates the lanthanides from matrix elements.

Among the analytical-scale separations techniques for lanthanide analysis, the most widely used (and generally successful) methods are ion exchange (for isolation from the matrix) and liquid chromatography (for separation of individual members of the series). However, most available chromatographic methods have been tested for analysis of rare earth elements, achieving variable success. Solvent extraction has been applied for preconcentration of rare earths from the matrix elements, though it has not been used as successfully as for hydrometallurgical production of rare earths. Adaptation of solvent extraction reagents to chromatographic applications has had a more substantial impact in analytical chemistry of the rare earths. Two examples of these techniques are extraction chromatography and centrifugal partitioning chromatography. Precipitation techniques have been applied for preconcentration of lanthanides from certain matrices, but are of little value for analytical separation of series members. Neither gas chromatography nor supercritical fluid chromatography has had substantial impact in rare earth analysis.

The most useful column chromatographic techniques that have been applied for lanthanide analysis are the following:

- Adsorption and partition chromatography relies on the uptake of lanthanide ions by silica or alumina as a solid phase transfer medium. Aqueous chelating agents are employed for partitioning.
- Ion-pair chromatography (also called dynamic ion exchange or ion interaction chromatography), as applied for lanthanide analysis, consists of the use of silica phases with long-chain alkyl groups covalently bonded to the silica, creating a hydrophobic layer on the solid sorbent. The eluting solution is an aqueous medium containing a mixture of hydrophilic chelating agent(s) and a sulfonic acid surfactant. The hydrophobic silica column is preconditioned by passage of an aqueous medium containing the sulfonic acid surfactant. The organic tail of the surfactant interacts strongly with the lipophilic layer of the silica immobilizing the sulfonate group to form a solid material somewhat similar to cation exchange resins. Metal ions are sorbed to the sulfonate groups and separated based on their relative affinity for the chelating agent in the aqueous medium. This method is one of the most consistently successful analytical methods for lanthanide quantitation. The general characteristics of the method and their application for the analysis of nuclear fuels have been summarized by Cassidy et al..(12)
- Cation exchange chromatography is based on cation exchange resins, principally sulfonated polystyrene-divinylbenzene copolymers, as the phase transfer medium, and aqueous complexants as the eluant. Anion exchange is the comparable technique in which anionic mobile solutes interact with immobile cation sites in the resin phase. Anion exchange is employed less frequently in lanthanide analysis. Ion exchange using resins containing chelating functional groups, which can exhibit greater cation specificity, also has been investigated.

- Ion chromatography is distinguished from cation exchange chromatography by the application of continuous conductivity detection, and the use of two ion exchange columns in series. Separation of the analyte solution is achieved in the first column while the second sorbs counter ions that interfere with the conductivity detection system. Recent developments have reduced the need for a secondary (suppression) column, thus blurring the distinction between cation exchange and ion chromatography.
- Extraction chromatography is the application of conventional solvent extraction chemistry in a chromatographic mode. The lipophilic solvent extraction solution is immobilized on a solid support and an aqueous solution containing the analytes is passed through the column. The extraction chromatographic material may serve as a phase transfer medium only (much like cation exchange resin, exhibiting minimal selectivity) or may engage in selective sorption of lanthanide ions thus achieving separation without the addition of water-soluble chelating agents. Acidic organophosphorus extractants are the most typical reagents for lanthanide analysis by extraction chromatography.

In addition to these techniques, applications of capillary electrophoresis for lanthanide analysis have appeared recently.(13,14) Capillary electrophoretic separations rely on differences in the electrophoretic mobility of analyte species in an electrolyte buffer while under the influence of an applied electric field. For lanthanide analysis, the mobilities of the aquo cations are not adequately differentiated for an effective mutual separation, though separation from transition metals or alkali/alkaline earth metals should be readily accomplished. Introduction of chelating agents that form complexes with the ions leads to improved separation. Vogt and Conradi (14) have described the relationship between complex formation and electrophoretic mobility. Robards et al.(11) also described lanthanide separations by the related techniques of zone electrophoresis and isotachophoresis, both based on the electrophoretic mobility of lanthanide complexes. Other common chromatographic techniques (thin-layer methods, gas, supercritical fluid) have not achieved much success in rare earth analysis, as will be discussed below.

## PRECONCENTRATION/GROUP SEPARATIONS

A commonly used approach for group separations is to apply cation exchange from concentrated mineral acid solutions. Typically, a column of Dowex 50X8 sulfonic acid resin is prepared and preconditioned by passage of nitric acid of the appropriate concentration followed by a deionized water wash. The sample is then loaded onto the column from dilute acid. The lanthanides and most polyvalent cations are bound to the column while anions and alkali metal ions pass through. A subsequent rinse with 2 M HCl or 2 M $HNO_3$ is used to elute alkaline earth metal ions and most first row transition metals. A second rinse of 4 M HCl or $HNO_3$ may be applied to remove problematic metal ions like $Fe^{3+}$. The concentrated lanthanides are eluted with 6 M HCl or 6–8 M $HNO_3$. This eluant is usually evaporated to prepare the sample for the subsequent ion-selective analysis. Depending on the exact composition of the sample being analyzed, $Fe^{3+}$, $Al^{3+}$, $Sc^{3+}$ and $Ba^{2+}$ are common contaminants that may co-elute in the group separation and can interfere with lanthanide analysis.

Some authors have used precipitation techniques to concentrate the lanthanides. The most commonly used species are oxalates and fluoride. Rare earth oxalates ($Ln_2(C_2O_4)_3$) have solubility products ranging from $10^{-25}$ to $10^{-29}$ $M^5$. Isolation of lanthanide cations as oxalate precipitates is often followed by ignition to the oxide, then acid dissolution of $R_2O_3$. This procedure can be expected to provide samples suitable for almost any type of detection/quantitation method. The solubility products of the fluorides ($LnF_3$) are found in the range of $10^{-15}$ to $10^{-19}$ $M^4$. Whether precipitation techniques can be applied is partly determined by the concentration of rare earth ions in the sample, and whether a carrier precipitation is acceptable for those samples in which the lanthanide concentration is too low. The detection method most directly impacts the viability of carrier precipitation techniques.

Solvent extraction is also suitable for group separation and preconcentration in many analyses. The basic technique can be applied in either a liquid-liquid contact mode or using extraction chromatographic techniques. When the sample is not too complex and the method of analysis is amenable to a group separation without preconcentration, the easiest approach for isolation of the rare earths is often to extract the interfering matrix components, leaving the rare earths in the aqueous phase. This approach has been applied in the analysis of rare earths in nuclear materials (15–17) and also in NAA of high purity Ni.(18) When an analysis demands preconcentration of the rare earths, a solvent extraction reagent capable of selectively extracting rare earth ions must be employed, most commonly tributylphosphate (TBP) (19), octyl(phenyl)-N,N-di-isobutylcarbamoylmethylphosphine oxide (CMPO) (20) or, most often, bis(2-ethylhexyl)phosphoric acid (HDEHP).(21, 22)

## SEPARATIONS AND ANALYSIS OF RARE EARTHS BY CHROMATOGRAPHY

Separations by extraction chromatography and centrifugal partition chromatography (also known as centrifugal countercurrent chromatography depending on the apparatus used), are, like solvent extraction, based on the partitioning of an analyte between two liquid phases. Extraction chromatography and centrifugal partition chromatography differ from solvent extraction in that one liquid phase is stationary, giving the immobile phase the characteristics of a chromatographic material. In extraction chromatography the stationary phase is fixed via sorption on an inert solid such as silica, polystyrene, or even paper. In centrifugal partition chromatography, one liquid phase is held stationary by centrifugal force either in individual partition cells (centrifugal partition chromatography) or in a spiral column (centrifugal countercurrent chromatography).

As compared to solvent extraction, the primary advantage of extraction chromatography or centrifugal partition chromatography for rare earth separations resides in the presence of multiple equilibration (extraction) stages, or theoretical plates, along the path of the mobile phase. By immobilizing one phase and using it for chromatography, the same reagents used for group separations by solvent extraction become capable of separating individual rare earth ions from each other. When the same diluents, extractants, and aqueous phases are employed, the separation factors of rare earth elements obtained by solvent extraction, extraction chromatography, and centrifugal partition chromatography are similar (Fig. 1).(23, 24) Generally, the number of theoretical plates in an extraction chromatographic column or a CPC apparatus is moderate compared to those encountered in conventional chromatography, between 10 and 500 vs. 10,000. Nevertheless, separations based solely on the affinity of an extractant for the individual rare earths have been demonstrated with these systems. Moreover, Kitazume et al.(25) report a high-speed counter-current chromatographic separation of the lanthanides with separation factors between 60 and 6000.

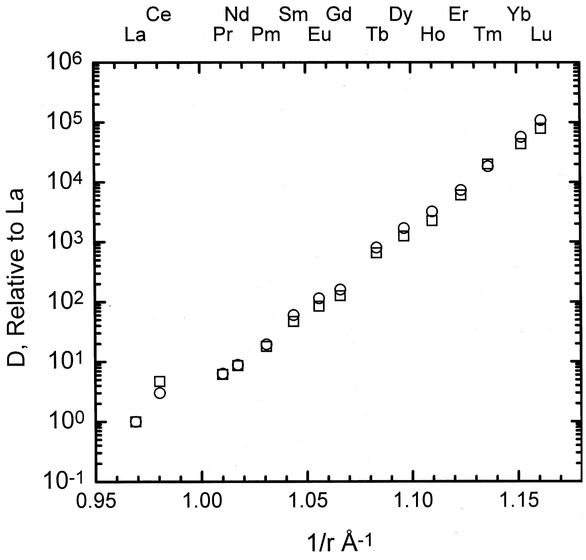

***Figure 1.*** Cumulative separation factors of lanthanides in $HClO_4$ by HDEHP. (❒) Extraction chromatography on a polyvinylchloride/polyvinyl acetate copolymer at 60°C. (◑) Solvent extraction into toluene at 25°C. Data adapted from Pierce et al..(23).

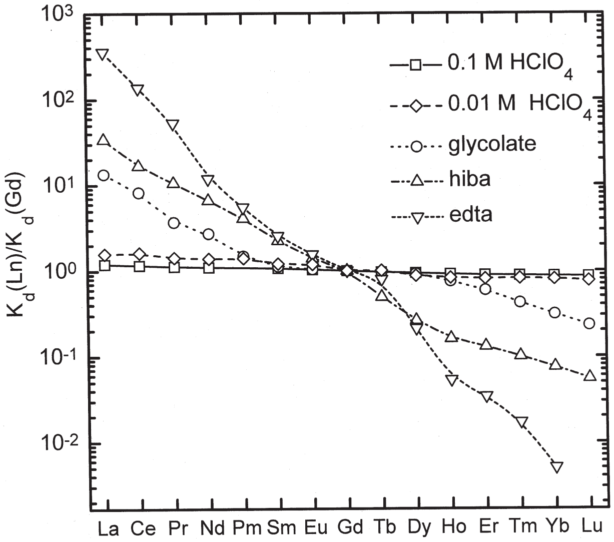

***Figure 2.*** Comparison of the relative distribution of lanthanides onto Dowex 50 cation exchange resin from various aqueous media.

The intrinsic separation of lanthanide ions on sulfonic acid resins is minimal. They typically offer only a few parts-per-thousand separation factors (ratio of distribution ratios or extraction equilibrium coefficients) for adjacent lanthanide ions, as is shown in Fig. 2.(26, 27) The limitations of ion exchange materials for lanthanide separations based on the aquo cations led to the development of separation procedures mediated by aqueous complexants. The first such separations used ammonium citrate as the eluant. The displacement of $Ln^{3+}$ from the resin by $H^+$ and $NH_4{}^+$ is greatly augmented by the formation of lanthanide-citrate complexes, which tend to enhance transfer of the lanthanide ions to the mobile phase. The relative rates of movement of the rare earth cations down the column is thus impacted not only by the affinity of the resin phase for the cations, but also by the relative stability of the aqueous citrate complexes. Thermodynamically, the separation factor between any two metal ions is directly proportional to their relative tendency to undergo phase transfer and inversely proportional to the strength of their aqueous complexes:

$$\begin{aligned} S^{M}_{M'} &= \frac{D_M}{D_{M'}} = \frac{[M]_{org}/[M]_{aq}}{[M']_{org}/[M']_{aq}} \\ &= \frac{[MX_3]_{org}/([M^{3+}] + [ML^{2+}] + [ML_2^+] + \ldots)}{[M'X_3]_{org}/([M'^{3+}] + [M'L^{2+}] + [M'L_2^+] + \ldots)} \end{aligned} \qquad (1)$$

The most efficient separations will be achieved in those systems wherein the lanthanide M is more strongly transported to the counterphase ($MX_3$) and more weakly complexed by the aqueous complexant ($L^-$) (or vice versa).[1] For separations based on the application of solvent extraction/extraction chromatography with acidic extractants (like HDEHP), trends in $K_{ex}$ and $\beta_i$ work in opposition. Aqueous complexants are therefore of limited utility for separation systems in this combination or reagents. For separations based on cation exchange (either using Dowex 50-type resins or dynamic ion exchange resins), the ratio $K_{ex}^{Ln}/K_{ex}^{Ln'}$ increases from Lu-La, i.e. $K_{ex}^{Ln} > K_{ex}^{Ce} > K_{ex}^{Pr}$…., which is opposite the trend in aqueous complex stability. This approach forms the basis of the most useful and successful chromatographic separations of the lanthanides.

Early studies of the separation of lanthanides by ion exchange was done using either gravity-feed or low pressure elution techniques and chelating agents like lactic acid, citric acid, or edta as eluents. Typically, these separations were done at pH 3–5 in buffered solutions of the ammonium salts of the complexant. Though each chelating agent achieved some success in separating lanthanide ions, these reagents also suffered limitations that reduced their utility. The carboxylic acids often performed well for the light members of the series, but failed to separate the heavy lanthanides adequately. The aminopolycarboxylates gave good separations of individual lanthanides across the series, but were plagued by excessively slow kinetics.

In 1956, the chelating agent α-hydroxyisobutyric acid (hiba) was reported as a superior reagent for separation of individual members of the lanthanide series from a mixture using column chromatography on Dowex 50 cation exchange resin.(28, 29) This complexant was actually identified as a unique separations reagent as a part of the development of procedures for discovery of the transplutonium elements that were being synthesized principally at the Lawrence Berkeley Laboratory.(30) Though many chelating agents have been tested and used in lanthanide chromatographic analyses, hiba remains the most effective reagent. The fundamental chemistry that accounts for this pre-eminent role will be discussed below.

In modern analysis for lanthanide quantitation, the most common and useful chromatographic methods are those techniques generally classified as High Performance Liquid Chromatography (HPLC). These techniques were developed

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beginning in the 1960's and were first applied for lanthanide analysis by Sisson.(31) In essence, these methods consist of operation of solid separations media, either as thin plates or (more often) cylindrical columns, in a chromatographic mode. Conduct of column chromatography under pressure leads to substantially improved resolution and efficiency of the separation process. A variety of different interactions between solvents, solutes, and reactive solid phases contribute to such separation systems. With computer controlled instrumentation, the chemical and physical properties of the solution can be manipulated over a wide range to optimize the separation.

The common characteristic of the various HPLC techniques is the reliance on small differences in the strength of interactions between species in the mobile (liquid) phase and the solid material that accomplishes phase transfer. Except for extraction chromatography, few solid-liquid separation procedures for lanthanides derive their selectivity from the properties of the solid phase material. For most HPLC separations of the lanthanides, water-soluble chelating agents that form complexes of steadily varying strength across the series are used to accomplish separation of the individual lanthanide ions. These reagents are often applied using a technique called gradient elution, in which the composition of the eluting solution is changed over the course of the analysis. In some applications, abrupt changes in the reagents or pH are made. Often, a linear ramping of the concentration of one or two complexants is used to accomplish the target separations.

Despite the success of analytical methods based on non-selective solid sorbents and differentiating aqueous solvents, the preparation of ion selective chelating resins is a continuing goal for those who design chromatographic materials. For example, Inoue et al.(32) have reported rare earth separations using a stationary phase consisting of nitrilotriacetic acid chelating groups on a glycidyl methacrylate gel, a macroporous hydrophilic resin. Using a nitric acid gradient elution technique, they report a moderately successful separation of the lanthanides (without Y). The resin fails to separate Eu/Gd and Sm partially overlaps with the Eu/Gd peak. Dy and Ho also are poorly resolved. The inadequate resolution of Gd/Eu and Dy/Ho pairs in the nta resin is identical to that of Kuroda et al (33) who used aqueous nta as an eluant for an ion-pair chromatographic separation of the lanthanides (using a gradient elution procedure) and is consistent with the relative stability constants for the metal ions. This resin appears to outperform an earlier polystyrene-based bis(carboxymethyl)amino resin (dtpa functionality bound at the center nitrogen).(34) Nitrilotriacetic acid also has been applied as a mobile reagent in ion-pair chromatography.

Paper chromatography and thin-layer chromatography have been applied, but quantitation is somewhat problematic. These methods are also poorly suited to the demands of automated instrumentation. Computer aided experiment design and analysis of plates provide some enhancement in the utility of thin layer techniques.(35) Gas chromatography (GC) requires that the analyte have a substantial volatility at a temperature below its decomposition point in order to conduct the analysis. Though certain classes of chelating agents (e.g., β-diketones) have been reported to form potentially volatile complexes with lanthanide ions, these complexes tend, as is true of most lanthanide complexes, to be moderately labile and hence not generally compatible with the demands of gas-solid chromatographic techniques. The inherent lability of lanthanide complexes is exacerbated by the elevated temperatures generally needed for gas chromatographic analysis. Dissociation of the lanthanide complex leads to deposition of the non-volatile lanthanide cation and fouling of columns. Supercritical fluid chromatography (SFC) relies on the unique solvating properties of supercritical $CO_2$ (predominantly), $CO_2$/solute mixtures, or other solvents of suitable properties, like freons. SFC was applied for lanthanide analysis very early in the development of the technique.[11] Though a number of fluorinated β-diketone ligands have been investigated as carrier ligands for lanthanide analysis by SFC, continuing research has yet to provide any truly successful examples of lanthanide analysis by this technique. It has been established that, as is true of gas chromatography, non-labile complexes are highly desirable for a successful SFC separation. Overcoming the inherent lability of lanthanide complexes may ultimately prove to be an insurmountable obstacle to the successful application of this technique for lanthanide analysis.

## DETECTION METHODS

Application of ICP-AES (inductively coupled plasma-atomic emission spectroscopy) can be used for detection in chromatographic lanthanide analysis, but the eluants used for HPLC separations of individual lanthanides can compromise the analysis. Sawatari et al.(36) describe an integrated lanthanide analysis system that combines HPLC separation and ICP-AES detection. They report conditions under which the hiba eluant does not compromise operation of the detection system. Chemical constituents of the HPLC eluants can also degrade the sensitivity of ICP-MS (ICP-mass spectrometric) detection of lanthanides in the analyte. Kawabata et al.(37) report on the general characteristics of lanthanide analysis using a combination of ion chromatography (IC) and ICP-MS. Ion chromatography is well-suited to mass spectroscopic detection, as the polishing column is designed to remove contaminants and prepare the sample for analysis.

With the availability of a neutron irradiation source, neutron activation analysis accompanied by γ-spectroscopy can be applied for detection of lanthanide ions. Choppin and Rydberg (38) tabulate the following detection limits for lanthanide ions for 1 hour irradiation in a neutron flux of $10^{13}$ n $cm^{-2}$ $s^{-1}$: Dy (1–3x $10^{-6}$ mg), Eu, Ho, Lu (1–3x$10^{-5}$ mg), Sm (4–9x$10^{-5}$ mg), Y (1–3x$10^{-4}$ mg), La, Er (4–9x$10^{-4}$ mg), Nd, Yb (1–3x$10^{-3}$ mg), Pr, Gd (4–9x$10^{-3}$ mg), Ce, Tm (1–3x$10^{-2}$ mg), Tb (1–3x$10^{-1}$ mg). Neutron activation analysis for lanthanides is adversely effected by the presence of U, Th, transuranium elements, Fe, and Ta. The actinides undergo neutron-induced fission to produce some of the same lanthanide nuclides as fission products. The $\gamma$-ray energy for $^{59}$Fe overlaps that for $^{141}$Ce, while the $\gamma$-emission of $^{182}$Ta overlaps $^{170}$Tm. Quantitative separation of lanthanides from these elements is therefore of primary importance for application of neutron activation analysis. For the analysis of inherently radioactive samples (e.g., those containing $^{147}$Pm), standard radiometric analytical techniques ($\gamma$-spectroscopy, liquid scintillation) are applicable.

Detection methods based on optical properties of the target analyte are the most commonly employed methods for quantitation of most species in chromatographic analysis. As the lanthanide cations are only weakly colored, direct detection using standard UV-visible spectrophotometric methods are of minimal applicability. Selected lanthanide cations exhibit an intrinsic fluorescence which can be used for direct detection of the ions leaving the column. Fluorimetric detection of their complexes in an organic phase at $10^{-9}$ M is possible.(39–40) Tran and Zhang (41) applied thermal lensing to the detection of lanthanides at sub-millimolar concentrations in organic phases, taking advantage of the superior thermo-optical properties of certain organic solvents.

The most widely applied detection method for chromatographic analysis of lanthanides is post-column derivatization with the colorimetric indicator ligands PAR (4-(2-pyridylazo)resorcinol) or Arsenazo III (2,2′-(1,8-dihydroxy-3,6-disulfonapthalene-2,7-bisazo)bis(benzene arsonic acid)). These ligands form strongly colored complexes with the lanthanides in dilute acid media. They are typically added to the column effluent after the separation is complete but before the sample passes a single wavelength, photo-sensitive detector. The principal requirement of the post-column derivatization reagent is that it form complexes with the lanthanide ions that are stronger than those formed by the reagents that accomplish the chromatographic separation (e.g., hiba). A limitation cited by many authors in the application of PAR is its affinity for d-transition metal ions. Interference by transition metals is less significant if a group separation step is applied prior to the lanthanide analysis. Arsenazo III is more selective for the lanthanides over divalent transition metal ions, and so to some degree may reduce the need for the pre-separation step. PAR has been reported to be susceptible to biodegradation, which requires that the reagent be prepared more frequently.

Walker (42) has described an HPLC method for lanthanide analysis based on phenol red as the stationary phase complexant and colorimetric indicator in the mobile phase. Lanthanide separation is based on the hiba complexes. The presence of the indicator in the mobile phase eliminates the need for post-column derivatization. Overall, the technique is not as effective as the more conventional post-column derivatization methods, but it offers rapid analysis and moderately good separation of the heavy lanthanides. The example chromatograms suggest quantitation may be somewhat problematic.

## BASIC CHEMICAL PRINCIPLES OF LANTHANIDE SEPARATIONS

Because their interactions with the media are governed principally by electrostatic factors, the separation of individual lanthanides is ultimately based on the chemical effects caused by the decrease in ionic radius  with increasing atomic number.(43) Trivalent lanthanide cation radii decline across the series because the valence f electrons compensate relatively poorly for the steadily increasing nuclear charge. The decreasing ionic radii result in increased strength of cation-anion, ion-dipole and ion-induced dipole interactions. Decreasing cation radii therefore lead to stronger bonds between lanthanide ions and ligand donor groups, and simultaneously to stronger interactions with polar solvent molecules like water (via ion-dipole interactions). Because these are competing effects, the overall effect of shrinking cation radii is not always straightforward in lanthanide separations chemistry.

## SOLVATION EFFECTS

Partial substitution of non-aqueous solvents for water results in a net decrease in the hydration of the cation, thereby reducing the energetic requirements for desolvation and promoting phase transfer. Occasionally, mixed aqueous/organic media have been used to try to improve separation performance. For example, Vera-Avila and Camacho (44) have applied acetonitrile-water-lactate solutions for lanthanide analysis.

Synergistic extraction systems have received attention recently for potential applications in lanthanide separations or analysis when size selective solvating reagents like crown ethers (45, 46, 41) or *o*-phenanthroline (47) are employed. Synergistic lanthanide separations incorporating both an acidic chelating agent and amine extractant instead of a solvating extractant also have been investigated.(48) In this case, the chelating reagents form negatively charged species, which are extracted by the amine. As the trends in the separation factors of the chelating and solvating extractants are parallel, synergistic extraction systems should improve intralanthanide separations. However, the effect is not always predictable based on the behavior of individual components. To date, no synergistic extraction system has been identified that will enable intralanthanide separations in a single solvent extraction stage.

## LANTHANIDE COMPLEXES WITH WATER-SOLUBLE CHELATING AGENTS

One might guess that since the lanthanide cationic radii change regularly across the series and their bonding is dominated by electrostatic attraction,  there

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should be a variety of chelating agents that are effective for accomplishing the isolation of individual lanthanide ions. A considerable amount of research effort has been expended on the testing of various chelating agents for lanthanide separations and on the determination of complexation equilibrium constants across the lanthanide series. Examination of the extensive database of critically evaluated stability constants (49) for lanthanide complexes reveals that there are in fact very few aqueous complexant systems that exhibit as consistent a trend across the entire lanthanide series as hiba.

If we simplify equation 1 by eliminating some fractions and substitute the complexation equilibrium constants, including that for the phase transfer equilibrium ($K_{ex}$), it is clear that the separation factor is a relatively simple function of the extraction equilbrium constants for the metal ions ($K_{ex}$), the complex stability constants, and the free ligand concentration:

$$S_{M'}^{M} = \frac{D_M}{D_{M'}} = \frac{K_{ex}^{M} \cdot (1 + \Sigma\, \beta_i^{M'} [L]^i + \Sigma\, \beta_j^{M'} [L']^j + \ldots)}{K_{ex}^{M'} \cdot (1 + \Sigma\, \beta_i^{M} [L]^i + \Sigma\, \beta_j^{M} [L']^j + \ldots)} \tag{2}$$

This expression has been made more generic through the inclusion of a second chelating ligand (L′). It ignores the possible existence of mixed complexes (involving both L and L′), for which there are very few thermodynamic data available. It also assumes that the stoichiometry of the phase transfer equilibrium is the same for both metal ions. A generic expression in this format is most appropriate for analytical separations, as there are a number of standard gradient elution techniques that exploit changes in the concentrations of more than one ligand at a time. The unknown parameters in this expression are the free ligand concentrations [L] and [L′], which can be calculated from the mass balance expressions (written in terms of the appropriate equilibrium constants, ligand charge omitted for clarity):

$$[Ln]_t = [Ln^{3+}](1 + \sum \beta_i^{Ln}[L]^i + \sum \beta_j^{Ln}[L']^j + \ldots) \tag{3}$$

$$[L]_t = [L] + \sum K_h^{L} \cdot [H^+]^{i'} \cdot [L] + [Ln^{3+}](1 + \sum i \cdot \beta_i^{Ln}[L]^i) \tag{4}$$

$$[L']_t = [L'] + \sum K_h^{L'} \cdot [H^+]^{j'} \cdot [L'] + [Ln^{3+}](1 + \sum j \cdot \beta_j^{Ln}[L']^j) \tag{5}$$

As the condition of excess ligand prevails and the pH is controlled, two simplifications to equations 3–5 can be made:

1) the absolute concentration of the metal ion is no longer needed as the speciation of the metal ion can be solved in terms of the mole fraction of each species. If we set $[Ln]_t = 1$, the variables in equation 3 can be separated and we can solve for the mole fraction of free metal as:

$$1/[Ln^{3+}] = 1 + \sum \beta_i^{Ln}[L]^i + \sum \beta_j^{Ln}[L']^j + \ldots \tag{6}$$

and the mole fraction of free metal ion can be calculated from the β's and the free ligand concentration. Substitution of the free metal concentration thus determined into the equilibrium constant expressions enables calculation of fractional speciation of all complexes.

2) As the metal complexes are present at microscopic concentrations, ($[L] + \sum K_h^L \cdot [H^+]^i \cdot [L]) >> [Ln^{3+}](1 + \sum i \cdot \beta_i^{Ln}[L]^i)$ and the free ligand concentration becomes :

$$[L] = [L]_t / (1 + \sum K_h^L \cdot [H^+]^i) \qquad (7)$$

which allows simple calculation of the free ligand concentrations considering only pH, the total ligand concentration and the $pK_a$'s. Metal complex species and separation factor calculations can be made as a function of the analytical concentrations of the ligands and pH. Such calculations are readily accomplished with the aid of a computer.

We can use these same mass balance expressions to calculate a term we have previously called a "stripping" or "holdback" factor. The holdback factor is the ratio of metal ion distribution ratios in the absence and presence of an aqueous complexing agent. Repeating the general formalism of equation 2, the distribution ratio in the absence of an aqueous complexant is $D_o = [M]_{org}/[M^{3+}]_{aq}$. Upon introduction of an aqueous complexing agent, the distribution ratio is reduced due to aqueous complexation, $D = [M]_{org} /([M^{3+}] + \sum [ML_i])$. The denominator of this expression can be written in terms of aqueous stability constants as we have done previously. The holdback factor is $D_o/D = (1+ \sum \beta_i [L^-]^i)$. We can calculate this term to predict the relative effectiveness of a complexant for a metal ion if we know the appropriate stability constants for the complexes formed.

Allowing no credit for the intrinsic ability of the solid material to contribute to lanthanide separation, we can calculate the Gd number for lanthanide separations if we divide the Gd holdback term by that for the other lanthanides. Calculated Gd numbers as a function of [hiba] are shown in Fig. 3a. This plot demonstrates that hiba is an effective separation reagent for lanthanides over its entire range of concentrations. A similar calculation of Gd number for diglycolic acid illustrates the limitations of this reagent for separation of the heavy lanthanides in Fig. 3b.

## THERMODYNAMICS AND THE ROLE OF THE α-HYDROXIDE GROUP

Literature reports indicate that among the carboxylic acid eluants, a hydroxide group on the α-carbon atom is necessary but not sufficient for consistent performance across the series. For example, neither oxalic acid ($HO_2C\text{-}CO_2H$), glyoxylic acid ($HOC\text{-}CO_2H$), nor malonic acid ($HO_2C\text{-}CH_2\text{-}CO_2H$) exhibits as consistent a trend in the stability of their lanthanide complexes as hiba. The polydentate α-hydroxy complexant citric acid does not exhibit as consistent a trend

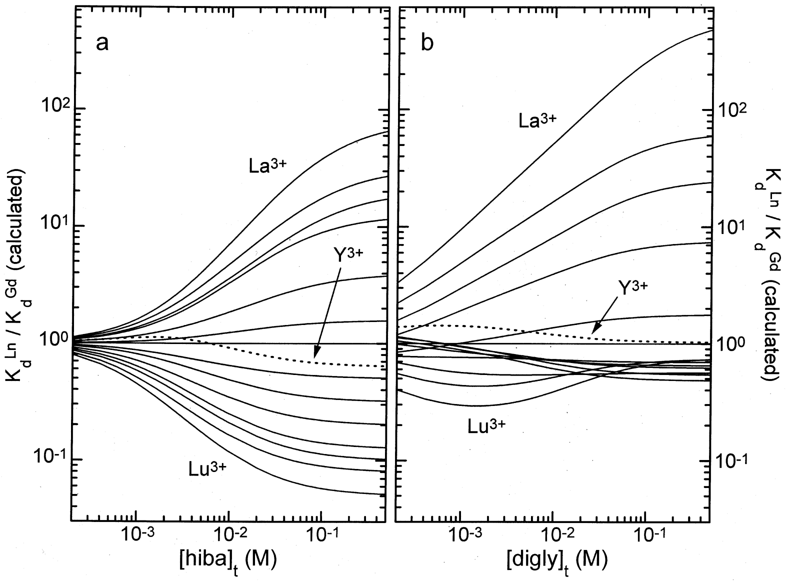

*Figure 3.* Calculated holdback factor, normalized to Gd = 1.0, for a) lanthanide (——) and Y (---) complexes with hiba at pH 4.5 and b) lanthanide (——) and Y (---) complexes with diglycolic acid at pH 3.5.

across the series as hiba or lactate. An ether oxygen in the α-position (bridging a second carboxylate group - diglycolic acid) is likewise a poorer reagent for a complete analysis of lanthanides than hiba.

The stability constants used to predict relative performance across the lanthanide series offer little insight into the nature of these interactions. It is more instructive to compare the ΔH and ΔS values for lanthanide complexes with organic complexants of similar geometries. A plot of the ΔG, ΔH, and ΔS for the consecutive addition of 1 and 2 hiba ligands to the lanthanide cations are shown in Fig. 4a. For the 1:1 hiba complexes, the steady variation in complex stability across the lanthanide series is primarily related to the increasing contribution of a favorable entropy superimposed on a nearly constant exothermic enthalpy. For the 1:2 complexes, the steady change in ΔG correlates most strongly with the trend for ΔH. The comparative thermodynamic parameters for the non-OH-functionalized analog complexant isobutyric acid are shown in Fig. 4b. The free energy of complexation of the 1:1 complexes increases regularly from La to Sm, then reverses for the heavier lanthanides. Interestingly, the regular increase extends from La to Tb for the 1:2 complexes. It seems likely that both of these trends are related to subtle differences in the solvation of the 1:1 and 1:2 complexes, quite possibly re-

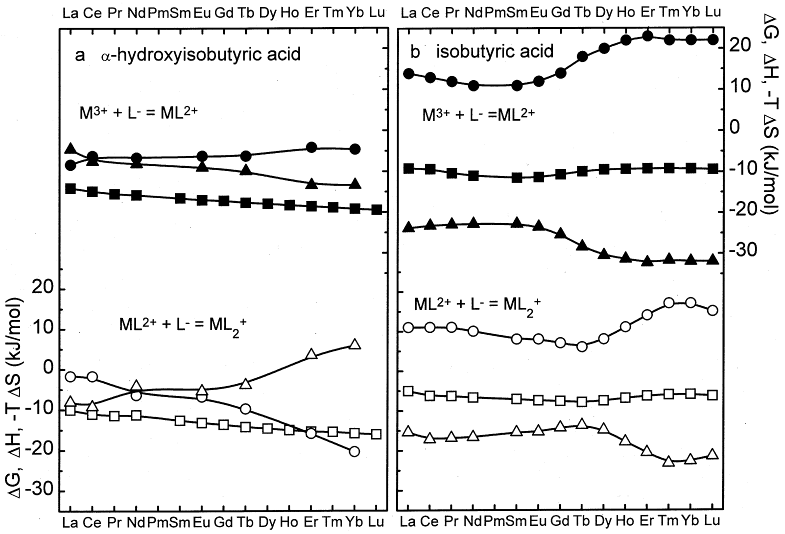

***Figure 4.*** Thermodynamic parameters for 1:1 and 1:2 complexes of lanthanides with hiba and isobutyric acid, ■ ❐ ΔG, ●○ — ΔH, S ▲Δ — ΔS. Closed symbols are 1:1 complexes, open symbols for step—wise addition of a second ligand.

lated primarily to second-sphere hydration effects. The enthalpies of complexation of lanthanides by isobutyric acid show a common pattern of relatively constant endothermic enthalpies for the complexes from La-Eu, a different, more endothermic ΔH for the heavy lanthanides. The shift has been attributed to the change in hydration/coordination numbers that occurs around Gd. Lanthanide-isobutyrate complex stability is derived from a favorable entropy, the magnitude of which exceeds that of the unfavorable enthalpy contribution. Near complete enthalpy-entropy compensation is a common feature of lanthanide complexation reactions.(50) Similar trends are seen for lactate-propionate, glycolate-acetate, and other structural analogs.

## ITINERANT BEHAVIOR OF YTTRIUM IN LANTHANIDE ANALYSIS

Most rare earth minerals also contain yttrium, some in relatively high abundance. Yttrium is also a product, along with several of the lanthanides, of nuclear fission and so is present in irradiated nuclear fuel. Though yttrium is not a member of the lanthanide series, its chemistry closely mimics that of the lanthanides. The best estimate of the eight-coordinate cationic radius of Y is 1.019 Å, very near

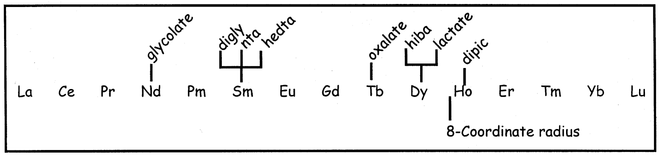

***Figure 5.*** Elution position of yttrium relative to the lanthanides for various eluting agents.

to that of Ho (1.015 Å).(43) Because the interactions of the lanthanides and Y with solvent and solute molecules are predominantly electrostatic in nature, one might expect a close correlation between Ho and Y in analysis. However, the similarity in the radii of the metal ions does not translate into a fully predictable and consistent behavior of Y in analytical separations of rare earth samples. Yttrium has been reported in different separation systems to elute from a column in close proximity to any lanthanide between Ce and Tm, as is shown in Figure 5.

In most cases, the transient elution position of Y is explained by the relative stability of the aqueous complexes rather than inconsistent behavior in the phase transfer equilibria. For example, the 1:2 and 1:3 R:lactate complexes of $Y^{3+}$ and $Tb^{3+}$ most responsible for lactate-based separations essentially overlap. The mono-, bis-, and tris- complexes of $Y^{3+}$ with hiba are most similar to those of $Dy^{3+}$. The lanthanide glycolate complexes show a correlation with the ionic radii of the light and heavy lanthanides but this ligand exhibits little selectivity for the middle of the series ($Eu^{3+}$ to $Er^{3+}$). The stability constants for yttrium-glycolates are most similar to the mid-range values, though Y elutes just after Nd and is separated from the Eu-Er group. Stability constants for $Y^{3+}$ and $Tb^{3+}$ oxalates are nearly identical, as is their elution position. The 1:2 complexes Y(nta) and Sm(nta) are nearly identical, but the Y(hedta) ($\log \beta = 14.75$, $I = 0.1$ M) is more comparable to Pr(hedta) ($\log \beta = 14.71$, $I = 0.1$M) than to Sm(hedta) ($\log \beta = 15.38$, $I = 0.1$ M).

## PERIODICITY IN THE LANTHANIDE SERIES

The rare earth elements can be treated as a group because their chemical properties change little despite the variation in the number of 4f-electrons across the series. As discussed above, the stability constants of complexes formed between trivalent rare earth cations and simple hard ligands should generally increase across the lanthanide series as the ionic radii decrease. Often there are substantial deviations from this ideal behavior because of the changes in hydration number across the series, the impact of the hydration energies, or the steric requirements of more complicated ligands, etc. However, even when these effects are considered, small, periodic variations in the stability constants across the lanthanide series remain. These periodic variations across the lanthanide series, called the tetrad or double-double effect because they appear in four sets of four lanthanides, have been repeatedly observed in lanthanide separations and geochemistry. They were first observed when researchers were trying to separate individual lanthanide elements. A number of possible reasons for the tetrad effect have been suggested, including small variations in nephelauxetic parameters or differences in the orbital angular momentum as summarized by Sinha (51) and Mioduski.(52)

In hindsight, much of the tetrad effect observed in the equilibrium constants of lanthanide reactions can arise from a tetrad effect in the ionic radii in the lanthanide series. An early solvent extraction example using *n*-octyl(*n*-octyl)phosphonic acid in benzene as the extractant. Peppard and coworkers (53) at Argonne National Laboratory first noticed the effect in graphs of distribution ratios (and thus $K_{ex}$) against atomic number, Z. To a first approximation, the distribution ratios of a rare earth cation are expected to follow simple electrostatics with a logarithmic dependence on the reciprocal of the ionic radius. However, when modern values of the ionic radii tabulated by Shannon (43) are used, the tetrad effect largely disappears. This is because much of the tetrad effect observed in lanthanide separations seems to arise from tetradic variations in the radii of the lanthanides, which could in turn be explained by nephelauxetic parameters or total angular momenta, or some other cause. The smoothly varying ionic radii available in the 1960s masked the immediate origin of the observed chemical behavior-electrostatics.

The tetrad effect, however, should not be ignored. There is a difference between explaining chemistry by resorting to tetrads and exploiting the observed tetrad effect to efficiently separate adjacent lanthanides. Purely electrostatic bonding models form an adequate foundation for describing the solution chemistry of rare earth cations, but intra-lanthanide separations are performed as a function of atomic number, not ionic radius. The variations in the intra-lanthanide separation factors that create the breaks between tetrads are real and can be exploited in separations even if the immediate cause is electrostatic.

## APPLICATIONS OF SEPARATION TECHNIQUES FOR LANTHANIDES

Analysis to determine the rare earth content of materials can have many different objectives. Successful separations require a judicious combination of appropriate group separation/ preconcentration, separation of individual members of the series, and the proper detection technique. Recent reviews that are readily available in the chemical literature offer compilations of “cookbook” methods for conducting analyses of samples of different types. In the following sections, we will offer a brief summary of preferred methods for specific types of analyses. The reader is referred to the reviews cited above for a more complete coverage of these analytical methods.

## ANALYSIS FOR MATERIALS SCIENCE

By comparison with natural samples, lanthanide-bearing species from manufactured sources are typically much simpler analytical targets. The samples are often more readily dissolved and, because many of them are rare earth-based materials, preconcentration steps can sometimes be eliminated. Recent reports have applied analytical separation methods to determine lanthanide concentrations in metals (54), alloys (55), and magnets (56), in high purity rare earth oxides (57–62), and in optical materials.(63)

## GEOLOGICAL SAMPLES

There are three general motivations for analysis of natural samples: 1) exploration for rare earth mineral resources, 2) isotopic analysis for elucidation of the geological history of the earth, 3) analysis of living samples to investigate natural distribution of lanthanides in the biosphere. The chemical and nuclear properties of rare earth elements make them excellent tracers of geologic processes. Little differentiation in rare earth concentrations is observed in commonly encountered low temperature processes like mineral weathering. The chemical similarity of the trivalent rare earth cations that makes analytical separations difficult, ensures that rare earths generally follow each other in geochemical cycles, though large anomalies in Ce or Eu concentrations are commonly observed because of the formation of $Ce^{4+}$ and $Eu^{2+}$ under oxidizing or reducing conditions, respectively. By studying the fractionation patterns of the rare earth elements, the origin of the processes that formed a mineral phase can be ascertained with important implications for solar evolution. An application of this methodology can be found in Haskin's (64) review of the rare earth abundances in lunar surface samples.

An example of such an analysis is that reported by Stray and Dahlgren.(65) Their interest is in the isotopic analysis of Nd and Sm in rock samples. They analyzed 40 sedimentary rocks (sand stones, shales and mudstones) using a technique that combines preconcentration by conventional ion exchange with application of ion chromatography for isolation of the lanthanides. An oxalate gradient was used for lanthanide resolution. The detection limits are in the 0.2 mg/g range. Two reports by Pin and coworkers (20, 66) have applied extraction chromatography to the analysis of $^{143}Nd/^{144}Nd$ ratios in silicate rocks.

Analysis in support of mineral exploration typically involves standard techniques for both rock dissolution and chromatographic analysis. For example, Moraes and Shihomatsu (67) report the analysis of U.S. Geological Survey standard rock samples using ion pair chromatography (dynamic ion exchange) with hiba as the eluant. Standard procedures for rock dissolution, preconcentration, and chromatographic analysis are followed. A gradient elution (pH 3.8, [hiba] $= 0.07$ to 0.4 M at 1 ml/min over 20 minutes) was employed with colorimetric detection (using PAR) for post-column derivatization. Each lanthanide was resolved, though there was slight overlap between Y and Dy. The detection limits in the original samples were in the 1–3 ppb range. This technique is a representative recent demonstration of the general technique developed by Cassidy and coworkers in the 1980's for analysis of nuclear materials.(12, 68–71)

## NUCLEAR APPLICATIONS

Among the most common byproducts of nuclear fission are several of the lanthanide metal ions, particularly the light members of the series. Because the fission yields of selected lanthanides are very well known, analysis of dissolved irradiated fuel elements for their lanthanide content can be applied to monitor the status of a nuclear reactor. The application of chromatographic techniques to intensely radioactive samples offers several unique challenges. With the application of radiometric detection techniques, the sensitivity of chromatographic methods can be appreciably extended, at least for short half-life nuclides. The basic analytical procedures for chromatographic analysis of irradiated fuels were developed during the 1980's at the Chalk River laboratory in Canada.

Lucy et al.(72) report on a multicolumn method for chromatographic analysis of irradiated nuclear fuels. The first stage is characterized as a semi-preparative reversed phase separation that removes the uranium matrix. A second column concentrates and separates the lanthanides prior to colorimetric detection of the ions using Arsenazo III. Instead of the 0.5–100 g of uranium required for conventional analysis of lanthanide content in such samples, these authors indicate a detection limit of 20 ng/g (uranium) for Sm, Gd, Eu, and Dy from a 20 mg uranium sample.

Good separation of Nd and Sm is observed in most chromatographic separations because the intervening lanthanide ion, Pm, does not occur naturally due to its existence only as short-lived radioactive isotopes, principally $^{147}$Pm ($t_{1/2} =$ 958 days). It is, however, a significant product of uranium fission and so is of concern in the analysis of irradiated nuclear fuels. Elchuk et al.(73) report a chromatographic procedure for the determination of lanthanides, including $^{147}$Pm, in bioassay samples, specifically urine. The authors estimate a decontamination factor for adjacent lanthanides of more than 790 (about 1ppt contamination from either Sm or Nd).

## THE OKLO PHENOMENON AND LANTHANIDE ANALYSIS

The rare earths, isotope geology, and nuclear fission came together at the Oklo uranium mine in Gabon, West Africa, site of the earth's earliest known nuclear reactor, built by natural forces approximately 2 billion years ago.(74–76) Anomalies in the $^{235}$U content of the uranium mined at Oklo were noticed by an analyst in mid-1972. Careful investigation of the isotopic ratios of each of the 10 rare earth elements that have multiple naturally occurring isotopes, showed deviations from the natural occurring isotopic ratios. Nd, in particular, stood out. $^{142}$Nd is the most abundant isotope in natural Nd, accounting for 27.19% of the Nd. However, Oklo Nd contained almost no $^{142}$Nd. Changes in the isotopic composition indicated that a nuclear phenomenon was responsible. Moreover, the low $^{142}$Nd concentrations suggested that the elevated Nd concentrations were due to fission of $^{235}$U because $^{142}$Nd is not produced by fission, unlike all of the other natural Nd isotopes. Research continues into the geochemical and nuclear conditions that prevailed in the reactor zones during the 100–800 million years of intermittent operation, and much of our information comes from studies of the rare earths.(76–80) Studies of the distribution of the rare earths around the Oklo reactor zones have shown that some of the rare earth elements did migrate out of the reactor zones. However, both the lanthanides and actinides produced at Oklo were readily incorporated into phosphate based minerals or sorbed on clays or other minerals, and have moved less than a meter from the reactor zones over the ensuing one billion years.(79–81)

## CONCLUSIONS

Given the increasing technological significance of lanthanides, the need for analysis of samples containing lanthanide ions will continue to increase. The several reviews of lanthanide analysis over the last decade clearly indicate the widespread interest in both analysis and in the development of new and better techniques. It is noteworthy that the most efficient separating reagent for lanthanide analysis is a complexant identified for the purpose 40+ years ago, hiba. It is somewhat ironic that this reagent was actually first examined as a complexant to enable the discovery of the transplutonium actinide elements. This is yet another example of an important technological advance having been developed from purely fundamental research in a related field. In the intervening years and despite a considerable amount of effort around the world, no aqueous complexant has been identified that rivals hiba in its sensitivity to lanthanide cation radius.

As to the need for development of new separations-based techniques for lanthanide analysis, the present array of chromatographic methods has achieved impressive success in both resolution and sensitivity. Many chromatographic techniques can be used for a complete analysis for lanthanide content in less than 30 minutes, not including the time required for sample dissolution and preconcentration/preconditioning. There does not appear to be much demand for a more rapid analytical method, as the aforementioned sample dissolution/preconcentration steps will be rate limiting for analysis of most samples. For a hypothetical system in which on-line monitoring of lanthanide concentrations would be required, separations techniques of any type would ultimately not prove suitable.

The recent application of techniques based on electromigration properties of the analytes (e.g., capillary electrophoresis) offers some promise of improved resolution, and should receive continued attention. Gas and supercritical fluid techniques do not appear to offer any advantages over current liquid chromatographic methods and may suffer the fatal flaw of the inherent kinetic lability of lanthanide complexes. In SFC analysis, the development of chelating agents capable of encapsulating the lanthanide ion (for example, calixarenes or lariat crown ethers) might be worthy of investigation. If substitution-inert complexants were identified, some benefits could be attained in SFC analysis due to the unique solvating properties of supercritical fluids. However, it is debatable whether any such system will exceed the performance presently available in HPLC for lanthanide analysis.

However, we believe that a full understanding of even the hiba system has not been achieved. The impact of inner- and outer-sphere solvation on the thermodynamics of lanthanide complexes with organic chelating agents, and of the effect of the free ligand molecules on the thermodynamics has been somewhat underestimated. Because of the overlapping contributions of solvation and bonding to the overall thermodynamics of lanthanide complexation reactions, it appears that a more direct measure of individual components of the complexation reaction is required. Extra-thermodynamic techniques, particularly NMR spectroscopy and UV-visible spectrophotometry/fluorescence, could provide support for improved interpretations of thermodynamic data.

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