Inorganic Chemistry
Series One

Consultant Editor
H. J. Emeléus, F.R.S.

Volume 7

Lanthanides and Actinides

Edited by **K. W. Bagnall**

Volume 7
Lanthanides and Actinides

Edited by **K. W. Bagnall**
University of Manchester

Contents

1

Separation Chemistry of the Lanthanides and Transplutonium Actinides

E. K. HULET and D. D. BODÉ
Lawrence Radiation Laboratory, Livermore, California

1.1 INTRODUCTION

Some of the most elegant chemistry and techniques yet devised have been introduced during the past 25 years for the mutual separation of the lanthanide and actinide elements in the common tripositive state. The laborious process of fractional crystallisation has disappeared, and the scientist now looks to advanced methods of ion exchange and solvent extraction for fast, effective separations. This chapter deals primarily with these modern methods of separating lanthanides (Ln) and actinides (An).

The chemical principles underlying these processes are reasonably well understood and progress today is mainly in the direction of improving the techniques or introducing newer ones such as extraction chromatography. Successful new techniques have, in turn, created opportunities for investigating the chemistry of the Ln and An further than was possible before their innovation. Because advances in techniques are contributing so abundantly

	2+	3+	4+		2+	3+	4+	5+	6+
La		X		Ac		X			
Ce		X	X	Th			X		
Pr		X		Pa			X	X	
Nd		X		U		●	X	●	X
Pm		X		Np		X	X	X	X
Sm	●	X		Pu		X	X	X	X
Eu	X	X		Am		X	●	X	X
Gd		X		Cm		X			
Tb		X		Bk		X	X		
Dy		X		Cf		X			
Ho		X		Es		X			
Er		X		Fm		X			
Tm		X		Md	X	X			
Yb	●	X		No	X	X			
Lu		X		Lr		X			

Figure 1.1 Oxidation states of the actinides and lanthanides in solution. Very unstable species are denoted by shaded circles

to these investigations, this review will not be confined to purely chemical information, but will include progress in the technology of performing Ln and An separations.

Separation methods for 24 elements, comprising nearly one-quarter of those in the Periodic Table, are presented here. The chemical behaviour of the lighter An elements (Th to Pu) is complex, and it seemed appropriate that their separation chemistry should be discussed apart from the heavier group at some later time. However, the chemistry of a majority of the An and Ln is remarkably similar and there is no reason not to treat these family members as a single class when describing separation methods. Accordingly, this review is organised into three sections for discussing advances, primarily within the last 5 years, in separating all Ln and the transplutonium elements (Am to Lr).

Although a large portion of this chapter (Section 1.2) is devoted to reviewing the separation of the lanthanide and the transplutonium groups as tripositive ions, it is significant that one-third of these elements can be oxidised

or reduced from the $3+$ state (see Figure 1.1), resulting in greatly simplified and specific separations. A discussion of separations that are based on oxidation or reduction can be found in Section 1.3 for the following: Eu, Sm, Yb, Md, and No as dipositive ions or amalgams, Ce^{4+} and Bk^{4+}, and Am in the penta- or hexapositive oxidation state.

The separation chemistry of any element is usually examined for some ultimate application to a practical problem. Investigations of the Ln and An are no exception, so when the eventual application is a large-scale separation process, we normally find that the research and testing have been more thorough than usual. It is instructive to review a selection of the large-scale processes since they represent the state-of-the-art in the field of chemical separations. Therefore, major processes are described and illustrated in Section 1.4 in the form of flow-diagrams. It was necessary to abbreviate the description of each process and, regrettably, not all large-scale methods could be included.

In recent years there has been a vast increase in the production of rare earths and transplutonium elements and, as part of this growth, the literature dealing with their chemical separation has proliferated tremendously. Earlier books and reviews[1-23] have consolidated a part of this information, but many new reports appear every month. It is not possible in a review of this size to examine all of these references; therefore, we will generally emphasise the more effective chemistry and techniques along with newer developments that in our opinion may be of eventual service. Not all separation methods that have been studied extensively have found significant use, either because they are less effective than other methods or because they leave the product in a medium where recovery becomes an added burden. Among those methods which are not covered in this review are thin-layer and paper chromatography, electrophoresis, and the ring-oven technique.

1.2 SEPARATION OF THE TRIVALENT LANTHANIDES AND ACTINIDES

Separating individual Ln and An is no longer viewed as a difficult procedure in the light of the high discrimination afforded by modern extraction and ion-exchange methods. Exploiting very small chemical differences between adjacent elements, these methods easily resolve complex mixtures of the tripositive ions. Such separations are founded upon variations in the strength of complexes formed between the metal cations and diverse anionic ligands. Among the factors involved in the formation of these complexes are steric hindrance, rearrangement of water molecules in the hydration spheres of the cation and the ligand, and electrostatic attraction between the metal ions and ligand. In the vast majority of cases, the latter two are decisive factors regulating the relative complex strengths among members of the Ln and An series.

It would be difficult indeed to devise ways for separating these elements from one another were it not for a contraction of the size of the aqueous ion with increasing nuclear charge. This results in slight incremental increases in charge density of the metal ions as the atomic number increases through

either series of elements. Due to greater electrostatic attraction, the smaller ion will form the stronger ionic complex. This small but significant effect furnishes the grounds for most of the Ln=An separation chemistry known today. Of course, hydration or dehydration of the metal ion, ligand, or chelate can greatly modify and, in many cases, invert the ordering of complex stability within a series. An inversion in ionic size occurs in outer-sphere complexes because water molecules attracted to the smaller uncoordinated metal ion produce the larger hydrated ion.

Much of the ion-exchange and extraction chemistry discussed here is based on these simple principles, although a detailed knowledge of these systems is still very imperfect.

1.2.1 Ion-exchange chromatography

With the mounting variety of separation techniques based on an ion-exchange mechanism (liquid extraction, extraction chromatography, etc.), one of the original definitions of the term, ion exchange, is becoming slightly blurred. We would hope that it continues to describe a separation method performed on column beds of organic and inorganic exchange materials, as well as to define a reaction mechanism.

The tripositive Ln–An are most often separated from one another by elution from columns filled with cation-exchange resin using complexing agents as eluants. These separations depend more on differences in the complexing powers of the eluants toward the metal ions than on any selectivity by the resin. The heavier metals with the smaller ionic radii form the stronger complexes and, as would be expected, they are eluted first. The metal cation is attracted by both the exchange sites in the cation resin and the competing ligands in the eluant.

Cation exchange is by now a rather old and familiar method of separating individual Ln or An. Significant advances in recent years are restricted mainly to enhancing the performance of exchange columns by bettering the kinetic processes. Completely new developments, which are described later, concern inventions dealing with ion-exchange separations of Ln on standing columns of foam or by electrochromatography in cation-exchange resin beds. Otherwise, progress is represented by improvements in the theories governing the displacement mode of operation in column chromatography[24]. The displacement method is associated with processing multi-gramme amounts of Ln and An, in contrast to the familiar elution technique used for separating lesser quantities in the laboratory.

Complexing agents that most effectively resolve mixtures of either the Ln or An (but not members of both series simultaneously) using cation exchange are α-hydroxyisobutyric acid (HIBUT) and ethylenediaminetetra-acetic acid (EDTA). At high pH values, chelates formed with EDTA are exceedingly stable, leaving insignificant concentrations of uncomplexed metal ions in the aqueous eluate. Unfortunately, the solubility of the free acid, $H_4(EDTA)$, is low and it tends to precipitate in the resin bed ahead of the Ln during elution. This can be circumvented in displacement chromatography by saturating the cation-resin bed with retaining ions such as Cu^{2+} or even lanthanides.

Kinetics for the overall ion-exchange process are exceptionally slow with EDTA and other amino-polycarboxylic acids, apparently due to the great stability of the chelates.

Actinide separations by cation exchange are usually made with HIBUT, whereas EDTA is employed chiefly for technical-scale separations of the

Table 1.1 Separation factors of lanthanides and transplutonium elements obtained by elution with several complexing agents using Dowex 50 ion-exchange resin

Elements	HIBUT* (at 87 °C) S	HIBUT* (at 25 °C) S	HIMBUT† (at 87 °C) S	EDTA‡ S§
Md	1.4‖			
Fm	1.7			
Es	1.5			
Cf	2.2			
Bk	1.7			(2.0)¶
Cm	1.4			(3.1)
Am				(2.0)
Lu	1.3**	1.4††	2.4‡‡	(1.9)§§
Yb	1.4	1.5	1.4	(1.8)
Tm	1.4	1.6	1.7	2.0‖‖
Er	1.3	1.4	1.3	2.0¶¶
Ho	1.6	2.0	1.8	1.9***
Dy	1.8	1.8	1.8	(2.3)
Tb	1.9	1.9	1.9	(4.2)
Gd	1.4	1.5	1.4	1.4†††
Eu	1.7	1.9	2.0	(1.5)
Sm	1.7	1.7	1.8	1.5‡‡‡
Pm	1.5	1.6	1.5	2.2§§§
Nd	1.5	1.4	1.4	(1.8)
Pr	1.7	1.7	1.6	(2.5)
Ce	2.1	2.1	3.0	(3.7)
La				

* α-hydroxyisobutyric acid (2-hydroxy-2-methylpropanoic acid)
† α-hydroxy-α-methylbutyric acid (2-hydroxy-2-methylbutanoic acid)
‡ ethylenediaminetetra-acetic acid
§ Values in ( ) were derived from static equilibrium measurements or the ratios of the 1:1 stability constants
‖ Avg. S from elution data; Ref. 25, 26, 58
¶ Ref. 27
** Avg. S from elution data; Ref. 25, 28
†† Avg S from elution data; Ref. 29, 30
‡‡ Ref. 31
§§ Ref. 32
‖‖ Avg. S from elution data; Ref. 33–35
¶¶ Ref. 34
*** Avg S from elution data; 33, 34
††† Avg. S from elution data; Ref. 33, 34, 36
‡‡‡ Ref. 37
§§§ Calculated from Ref. 32, 37

Ln. The comparative performance of EDTA, HIBUT and HIMBUT is rated in Table 1.1. HIMBUT, a hydroxycarboxylic acid very similar to HIBUT, might be the slightly more selective of these two, although it has not been examined for An separations[31, 38].

Separation factors (S) listed in Table 1.1 for adjacent pairs of tripositive

elements are defined for two-phase systems, such as ion exchange and extraction, by the ratio of distribution coefficients of the two metals, i.e.,

$$S = K_{d(Z)}/K_{d(Z \pm 1)}$$

Occasionally, separation factors for non-adjacent pairs of elements will be mentioned in this report, and these are indicated by, for example, La/Pr, $S = 3.4$. So long as the concentration units used in expressing the distribution coefficients are consistent, it makes little difference whether values of S are measured by static equilibrations or by column elutions with tracer amounts of Ln and An.

In addition to separation factors, the quality of the separation is measured by peak resolution, which is a parameter governed largely by kinetic processes within the exchanger. For the most part, diffusion of ions inside the resin particle is the rate limiting step. The exchange rates are indeed very small inside the tight network of a highly cross-linked resin, which is the type most often used for Ln–An separations. Improving these rates of diffusion continues to attract the attention of a number of investigators[39-43]. Raising the operating temperature of the exchange column improves the resolution (peak widths) somewhat[40] by increasing the diffusion coefficients. Highly cross-linked resins (12% divinylbenzene) have an adverse effect on the resolution[44] but, by increasing the temperature or column length and by lowering the rate of flow of the eluant, it can be compensated[40]. Without question, the most direct way of improving the resolution is to reduce the resin particle size (to 5–20 μm), since the diffusion period is directly proportional to the square of the particle diameter[40-43]. This has an important practical consequence; well resolved peaks are obtainable from columns packed with a finely divided, homogeneous resin at much higher flow rates than could be tolerated by columns filled with coarser-sized particles[42]. There may be a limit as to how far one can reduce the particle size before processes other than particle diffusion control the exchange rate. In this connection, evidence now exists[39] that diffusion from the eluant to the resin boundary (film diffusion) is becoming an important rate step which should, however, be improved by increasing the temperature and by creating turbulence in the solution phase through higher flow rates.

A high-pressure method of cation exchange, based on the kinetic concepts discussed above, is a very important new development in separating Ln and An[45, 46]. Derived from a similar method used in biochemistry for the analysis of body fluids and amino acids, the technique was modified by Campbell and Burton specifically for separating milligramme amounts of transcurium elements. Operating at pressure drops up to 2500 lb in^{-2} across the resin bed, long columns packed with finely-sized (10–20 μm) Dowex 50 × 12 resin readily separate adjacent pairs of Ln or An in substantially less than 1 h. Flow rates of the eluant, HIBUT, can be made amazingly high without affecting the separations undesirably. In one elution, the actual velocity of the eluant down the column was 60 cm/min, which corresponds to a flow rate of 10 ml min^{-1}. Many Ln–An separations were made with flow rates near 24 ml cm^{-2}min^{-1}, which is ~25 times the rate normally found satisfactory in ion exchange.

The elution curves obtained by the high-pressure technique are unsym-

metrical. They show a slow increase in metal ion concentration upon approaching the peak maximum and a very rapid decrease in concentration behind the peak. This shape is just opposite to the commonly encountered steep rise followed by tailing. Lowering the temperature from 80 °C to 25 °C had little effect upon the resolution of Nd and Pr elution peaks, but loading the resin bed to more than 4% of its capacity caused some overlapping of elution bands. Separations of the transplutonium elements are now made routinely by high-pressure cation exchange at the Oak Ridge and Savannah River laboratories[47]. Damage caused by exposure of the resin to intense radiation is reduced by the high flow rates and, because of the high pressures, radiolytic gases are either dissolved or swept out of the column before gas pockets can form in the resin bed.

More in the class of a novelty at the moment, foam fractionation of the Ln is being evaluated for large-scale separations[48]. The separation mechanism is clearly ion exchange, but the process is extraction at surfaces of thin films. In a long glass column, stable foams are created from a cationic surfactant by bubbling nitrogen through the column base into an aqueous solution containing the Ln and a chelating agent, EDTA. Partitioning many times on the surface of the bubbles, the individual Ln separate into distinct bands that move upward with the foam and eventually emerge from the top of the column. Even though this technique is at a very early stage in its development, a respectable separation factor of ~ 2 for Nd/Ce was obtained.

A d.c. voltage applied through annular rings in a bed of Dowex 50 resin produces a transverse migration of Ln ions, which is in addition to their movement in the direction of eluant flow. In this unusual system[49, 50], the Ln are fed to the centre area at the top of the resin bed and an eluant (EDTA) is forced evenly (laminar flow) through the column. Due to the electric-potential field between the rings and a central electrode, uncomplexed Ln ions migrate outward toward the walls, while the complexed ions stay nearer the centre axis of the column. Concentric ports at the column base divide the output stream containing the radially separated Ln. The resulting separation depends on solution- and resin-phase mobilities of the ions and on the selectivity of the complexing ligand. Currently, a unit 22.5 cm in diameter and 120 cm high is operating, but the Ln separation factors are unreported.

Intra-Ln or An separations by anion exchange have never gained wide acceptance, principally because the formation of anionic complexes required high concentrations of inorganic salts. Besides increasing the problem of recovering the metals, high ion concentrations caused poor resolution of the elution bands. At present, investigations of mixed-media eluants consisting of mineral acids diluted with polar solvents are being made in order to overcome these objections[51–57].

1.2.2 Solvent extraction

With the use of the most selective extractants and simple new methods of multiple extraction, solvent extraction has proved a viable alternate to ion exchange for the separation of adjacent An and Ln. Similarly, extraction systems, comparable to ion exchange are successfully used for the group

separation of Ln from the An. The raising of solvent extraction to a position competitive with ion exchange for such separations is mainly due to three important advances that began 11–15 years ago. These may be listed as the studies by Peppard of acidic phosphorus-based extractants[59], the development by Moore of long-chain tertiary and quaternary amines as anion extractants[60, 61], and the development of the new technique of extraction chromatography, first successfully applied by Siekierski and Kotlinska[62]. Because these developments form the foundation for the most effective separations of tripositive An and Ln elements, we shall concentrate upon their features, by passing a discussion of some of the older extractants such as tributyl phosphate (TBP) and thenoyltrifluoroacetone (TTA).

In technical terms, solvent extraction is defined as the distribution of a dissolved metal salt, ion-association complex or chelate between two immiscible liquids that are in contact. Because of the very marked ionic

Table 1.2   Abbreviations for some common extractants and their nomenclature. First group extracts cations and the second extracts anions

HDEHP	bis(2-ethylhexyl)phosphoric acid
HEHφP	2-ethylhexyl hydrogen phenyl phosphonic acid
OPPA	bis(2-ethylhexyl)pyrophosphoric acid*
HDOP	bis(n-octyl)phosphoric acid
HD(DIBM)P	bis(2-6-dimethyl-4-heptyl)phosphoric acid
DDCP	dibutyl-N,N-diethylcarbamyl phosphonate
TLMANO₃	tridodecylmethylammonium nitrate (trilaurylmethylammonium nitrate)
Alamine 336 Adogen-364-HP	trioctyl- and tridecylamines*
Aliquat 336-S-X	trioctyl- and tridecylmethylammonium salt†

* A commercial mixture consisting of ~ 50% OPPA with mono- and dialkyl esters of phosphoric acid
† S and HP denote high purity products; X denotes anion

character of the Ln and An, one of the immiscible liquids is normally an aqueous solution; the other is an organic phase containing the extractant. At equilibrium, the metal salt is found distributed (partitioned) between the two liquids in a manner governed by its solubility in each phase. The equilibrium distribution of the metal is most commonly given as a ratio of the metal concentration in the organic phase to its concentration in the aqueous solution: i.e.

$$K_d = C_{org}/C_{aq} = \text{'distribution coefficient'} \qquad (1.1)$$

Occasionally, a simple mass distribution ratio is used to express the results of an extraction equilibrium. However, results expressed by such a ratio are sometimes confused with 'distribution coefficient', and in addition, the information content is less than that of K_d.

A list of the extractants that are reviewed in this section and referred to in subsequent sections is introduced in Table 1.2. Several of those listed were only recently investigated, whereas most have already proven useful for effective separations. The list in Table 1.2 is also intended to guide the reader unfamiliar with these compounds through the thicket of abbreviations and synonyms spread throughout the literature.

The organic extractants identified in the Table are divided into two categories, depending on whether they behave as extractants for cations or for anions. Inasmuch as the extraction mechanisms are quite different, each group is discussed separately in the following subsections.

1.2.2.1 Cation extraction

A group of acidic compounds that are discussed in this section form the major source of extractants for the intra-series separation of An and Ln. The extraction of metal cations, at least when in low concentrations, follows a simple ion-exchange reaction, and for this reason they are often termed liquid cation-exchangers. The most useful and widely studied extractants in this class are the monoacidic organophosphorus compounds. Similar diacidic compounds are not considered here because their selectivity is inadequate[63, 64], and because they are highly polymerised in the diluent[65]. We include, however, several bidentate phosphorus compounds that have seen recent applications in the bulk separation of the transplutonium and Ln elements from highly acidic solutions.

Among the many cation extractants tested, HDEHP and HEHϕP are the more selective for the separation of individual tripositive Ln and An ions. A variety of other dialkyl-[66] and diaryl-esters[67] of phosphoric acid have been evaluated for intra-lanthanide separations, but none offered advantages over HDEHP and HEHϕP. Within the range of 0.1–2.0 M $[H^+]$, extraction of tripositive ions by these monoacidic derivatives of phosphoric and phosphonic acids may be represented by the following equation[65]:

$$M_{aq}^{3+} + 3(HA)_{2,org} \rightleftharpoons M(HA_2)_{3,org} + 3H_{aq}^+ \qquad (1.2)$$
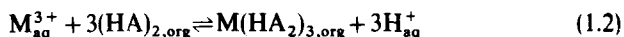
In this reaction, hydrogen is replaced in the weakly acidic extractant by a metal ion, followed by solvation of the metal complex in the organic phase. It should be noted that HDEHP and HEHϕP exist as dimers in most diluents[16]. In principle, the reaction is mainly ionic; thus the strength of the complex consisting of ions of the metal and extractant is dependent mainly on the size and electrostatic charge of the metal ion. This, of course, implies that in a regular series of elements with constant ionic charge, such as the An and Ln, the order of extraction is dependent upon the contraction of the ionic radii with increasing atomic number. The smaller metal ion is bound tighter to the extractant and will be more favourably recovered in the organic phase (Table 1.3).

Separation factors (defined in the ion-exchange section) that were measured for HDEHP and HEHϕP are compared in Table 1.4 with the separation factors found for one of the most selective ion-exchange systems. The separation factors form an interesting grouping described by Peppard et al.[75] as the tetrad effect. A plot of the logarithm of distribution coefficients or separation factors vs. Z displays four smooth curves, with Gd and Cm, the elements possessing half-filled f electron shells, each providing a point common to the second and third tetrad of their respective curves. A quantum mechanical explanation derived from symmetry in interelectron repulsion energies has been proposed by Nugent[77]. A less generalised statement of these regularities

was made earlier by Fidelis and Siekierski[78], which prompted Rowlands[79] to review the effect and find that there was no correlation with many complexing agents. Nevertheless a variety of solvent extraction systems provide examples of this effect[76]; an especially clear case is shown in Figure 1.2 for the HEHϕP–HCl system. This figure further illustrates the selectivity of

Table 1.3 Distribution coefficients of lanthanides and transplutonium elements in HDEHP and HEHϕP

Elements	HDEHP 0.4F in heptane		HÉHϕP		
	(0.4 M HCl) K_d*	(0.4 M HNO$_3$) K_d*	(1.0 M HCl) K_d†	HNO$_3$ (M)	K_d‡
Am	0.10	0.11	0.37		
Cm	0.145	0.144	0.52		
Bk	2.23	1.77	14.0		
Cf	7.1	5.7	45.0		
Es	7.0	5.8	58.0		
Fm	15.0	13.9	146.0		
La				0.21	0.123
Ce					0.543
Pr					0.750
Nd					0.980
Pm					2.39
Sm					8.54
Eu					21.7
Gd					37.7
Tb				1.0	0.919
Dy					3.01
Ho					6.41
Er					17.8
Tm					70.8
Yb				4.5	2.21
Lu					4.36

* Liquid-liquid extraction at 25 °C; derived from Ref. 68 and 69.
† 1.0 F HEHϕP in heptane; room temperature; derived from Ref. 70
‡ 0.038 F HEHϕP in heptane; 25°C; Ref. 71

HEHϕP for separating many individual tripositive ions of the Ln and transplutonium elements, although the separation of certain elemental pairs, Am–Cm, Cf–Es, Ce–Pr, and Pr–Nd, is not outstanding. Taking the Ln series as a whole, the separation factor of Lu/La reaches the remarkably large value of nearly 10^6. The unusual break between Cm and Bk or Cm and Cf has been extensively exploited in practical applications[70].

Under no circumstances can the solvent used in diluting these monoacidic extractants be considered as inert[80]. Gureev and co-workers[66] found that in extracting Am^{3+} with HDEHP the value of K_d fell by a factor of almost 1000 upon changing the diluent from iso-octane to chloroform. The distribution coefficient decreased with the following order of diluents: Iso-octane > Cyclohexane > CCl$_4$ > Toluene > Benzene > CHCl$_3$. Baybarz[70] found a factor of 15 decrease in the distribution of Am^{3+} and Cf^{3+} between 1.0 M HCl and

1.0 M HEHϕP by changing the diluent from heptane to toluene. There appeared to be a direct correlation between the distribution coefficients and the dielectric constant of the diluents. From this, it seems that the more polar diluents suppress the formation of an extractable complex, resulting in less extraction of the metal.

Deviations from the rather simple reaction given by equation (1.2) begin when competing complexes form with anions in the aqueous phase[81], when HNO_3 and HCl concentrations are greater[82, 83] than 4 M, and when the metal concentration becomes so large as to saturate the extractant appreciably[84]. In the HDEHP system, the distribution coefficients of the Ln pass through

Table 1.4 **Separation factors of adjacent pairs of lanthanides and trans-plutonium elements obtainable with acidic extractants and by cation-exchange**

Elements	HIBUT (at 87 °C) S	HDEHP (HCl) S	HDEHP (HNO$_3$) S	HEHϕP (HCl) S	HEHϕP (HNO$_3$) S
Am	1.4††	1.26*	1.24*	1.4§	
Cm	1.7	9.4	8.3	30.0	
Bk	2.2	2.67	2.7	3.3	
Cf	1.5	0.993†	1.02†	1.3	
Es	1.7	2.04	2.20	2.5	
Fm	1.4	4.0‡	4.4‡		
Md					
La	2.0	2.8‖	2.7‖	3.3¶	4.31**
Ce	1.7	1.5		1.5	1.41
Pr	1.5	1.3	} 1.55	1.3	1.19
Nd	1.5	2.7	2.1	2.8	2.66
Pm	1.7	3.2	2.7	3.6	3.45
Sm	1.7	2.2	2.1	2.3	2.57
Eu	1.4	1.5	1.7	1.6	1.71
Gd	1.9	5.0	5.5	5.4	6.96
Tb	1.8	2.6	3.0	2.1	3.22
Dy	1.6	2.1	2.2	1.9	2.19
Ho	1.3	2.8	2.7	2.9	2.74
Er	1.3	3.4	3.5	3.8	3.96
Tm	1.4	2.8	3.1	3.2	3.76
Yb	1.3	1.9	1.9	3.0	1.99
Lu					

* Extraction chromatography at 60 °C; Ref. 69
† Same conditions as *; Ref. 68
‡ Same conditions as *; Ref. 72
§ Liquid-liquid extractions at room temperature; Ref. 70
‖ Extraction chromatography at room temperature; Ref. 73
¶ Same conditions as ‖; Ref. 74
** Liquid-liquid extractions at 25 °C; Ref. 71
†† Reference sources listed in Table 1.1

a minimum at HNO_3 concentrations of 4–6 M and then strongly increase up to 16 M HNO_3. A similar sharp minimum is found at an HCl concentration of 6 M. The separation factors also decrease somewhat in either acid system at these higher aqueous acidities[83]. Since the extraction mechanism is apparently changing with the kind of mineral acids tested, it is not surprising that

the separation factors also vary with the acid ligand in the aqueous phase. Recent studies suggest that separation factors of Ln, in high concentrations, are somewhat greater in aqueous HCl than in HNO_3 and $HClO_4$.[84].

A continuing interest in the use of alkyl phosphates for purifying the transplutonium elements and for separating the lanthanides is demonstrated by reports from throughout the world[85–89]. Extraction chromatography,
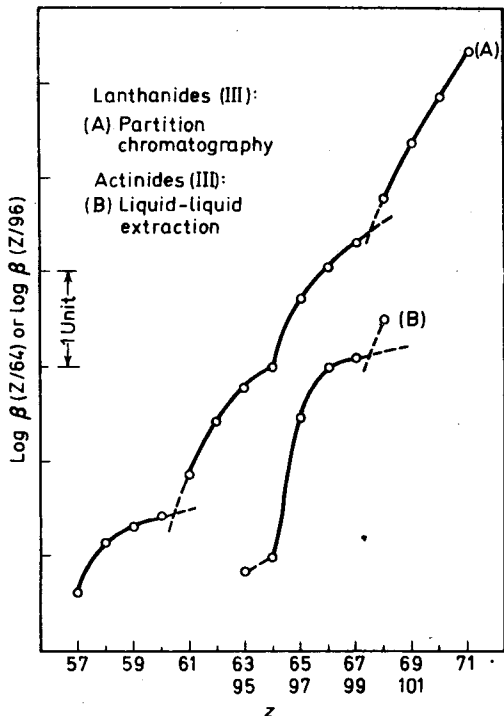
Figure 1.2 Variation with Z of separation factors for Ln^{III} and An^{III} in HEHɸP *vs.* aqueous HCl systems; Ln^{III}: (A) extraction chromatography (Ref. 74); An^{III}: (B) liquid-liquid extraction (diethyl benzene diluent) (Ref. 70). (Reprinted with permission from Peppard *et al.* (Ref. 75) and Pergamon Press)

which is described in a later section, has been widely used for investigating many specific separations, temperature dependencies, and the effect of strongly complexing ligands in the aqueous phase.

Organo-carboxylic[90–94] and -sulphonic[95] acids are among the newer extractants being considered for the extraction and separation of the Ln. These weak acids are effective extractants only at very low $[H^+]$, and so far they have given poorer Ln separations than the alkyl phosphoric acids. Similarly, separations with the β-diketone 2,2,6,6-tetramethyl-3,5-hepta-nedione (Hthd) are unattractive[96, 97].

In addition to the need for separating individual elements, there is a desire to find extractants for the recovery and concentration of transplutonium

elements that have been mixed with vast quantities of other material. These bulk separations are useful mainly in the assay of biological and environmental samples and for recovery of the valuable heavy elements produced in underground nuclear explosions. Concentrations of the actinides in many instances range downward from 10^{-13} g/g of soil.

Essential features required of a suitable extractant are: (1) exceptionally high extractive powers when the aqueous phase is strongly acidic and (2) high discrimination against extraction of the common elements, particularly Ca, Al, Mg, and Fe. An ideal extractant has not yet been found but two
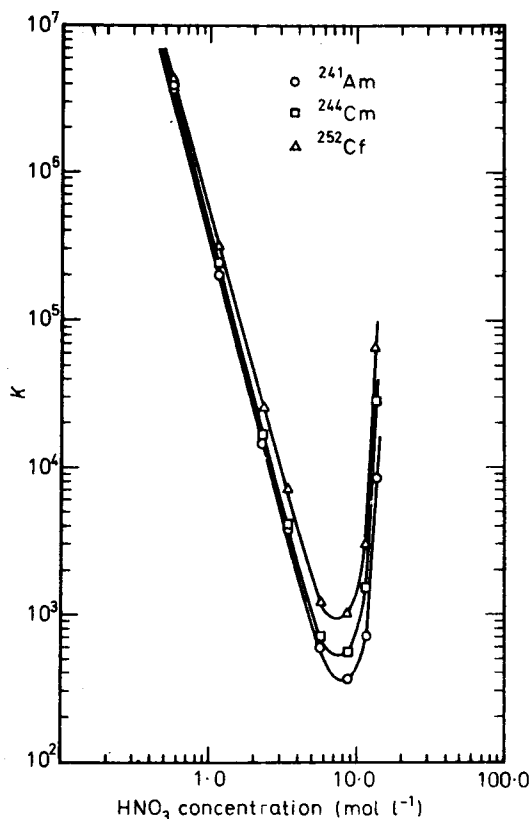
Figure 1.3 Distribution coefficients of representative An^{III} in 8 wt % bis(2-ethylhexyl) pyrophosphoric acid (OPPA) diluted with kerosene. (Ref. 100)

bidentate organophosphorus compounds have been recently developed to a point of practical application.

Butler and Hall[98] described the separation of nine actinides from biological samples using DDCP (formula in Table 1.2) as the primary extractant. This extractant is one of several evaluated earlier by Siddall[99]. Over 90%