

CONF-951057--3

Ninth Symposium on Separation Science and Technology for Energy Applications

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JAN 11 1995

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Separations Chemistry for f Elements: Recent Developments and Historical Perspective

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### ABSTRACT

With the end of the cold war, the principal mission in actinide separations has changed from production of plutonium to cleanup of the immense volume of moderately radioactive mixed wastes which resulted from fifty years of processing activities. In order to approach the cleanup task from a proper perspective, it is necessary to understand the nature of the problem and how the wastes were generated. In this report, the history of actinide separations, both the basic science and production aspects, is examined. Many of the separations techniques in use today were developed in the 40's and 50's for the identification and production of actinide elements. To respond to the modern world of actinide separations, new techniques are being developed for separations ranging from analytical methods to detect ultra-trace concentrations (for bioassay and environmental monitoring) to large-scale waste treatment procedures. Some of these new methods are "improvements" or adaptations of the historical techniques. Total actinide recovery, lanthanide/actinide separations, and selective partitioning of actinides from inert constituents are of primary concern. In this report, we offer a historical perspective, review the current status of f element separation processes, and suggest areas for continued research in both actinide separations and waste cleanup/environment remediation.

Work performed under the auspices of the Office of Basic Energy Sciences, Division of Chemical Sciences, United States Department of Energy, under contract numbers W-31-109-ENG-38 at Argonne National Laboratory and at Florida State University.

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## INTRODUCTION

The transuranium (5f) elements are not naturally occurring. They were produced in the last 50 years as a result of the research of nuclear scientists who predicted how they could be synthesized and developed the methods to do so as well as to isolate and purify the few atoms made in the discovery experiments. Since their discovery, these elements have been made in amounts which range from tons (Pu) to micrograms (Es) as a part of nuclear power and weapons operations. Some small amounts have been introduced into the environment. Highly specific, rapid separations as well as remote automated procedures continue to be developed to meet the needs in 5f element science and technology.

In this review, we will present a historical background for the development of actinide separation science, summarize the current drivers for continued development of actinide separation processes, and suggest potential new frontiers for continued research in this field. We will not discuss lanthanide separations except as they impact the science and technology of actinide separations.

### Basic Actinide Solution Chemistry

To discuss the separation of actinides, a little consideration of basic actinide solution chemistry is needed. For the elements beyond plutonium, except for nobelium, the trivalent oxidation state is the most stable although Am(V) and Bk(IV) can be utilized in separations in basic systems. As a result, the solution chemistry of the transplutonium elements strongly resembles that of the trivalent lanthanides. For thorium, only the tetravalent oxidation state is important. For U, Np, and Pu, the redox chemistry is varied and different oxidation states are of use in separation schemes. The lower oxidation states (III and IV) exist as hydrated cations in aqueous solutions while the upper oxidation states (V and VI) are linear dioxocations having formal +1 and +2 charges. In general, acidic solutions favor lower oxidation states while basic media promote the stability of the higher states. In actinide processing the most important species are  $U^{4+}$ ,  $UO_2^{2+}$ ,  $Np^{4+}$ ,  $NpO_2^+$ ,  $NpO_2^{2+}$ ,  $Pu^{3+}$ ,  $Pu^{4+}$ , and  $PuO_2^{2+}$ , though the hexavalent oxidation states of Pu and Np are moderately strong oxidants. The middle oxidation states (IV and V) are prone to disproportionation at moderate concentrations in acidic solutions. The multiplicity of readily available oxidation states for these elements is of major significance in their process chemistry.

These ions form weak complexes with halides (except  $F^-$ ) and moderate to strong complexes with oxygen donor ligands like aminopolycarboxylates and polycarboxylic acids. The relative order of complex stability is typically  $An^{4+} > AnO_2^{2+} > An^{3+} > AnO_2^+$ . The relative strength of trivalent and hexavalent complexes is occasionally reversed for complexes of appropriate coordination geometry. The coordination numbers for these ions in solution are high: 9-12 for  $An^{4+}$ , 7-9 for  $An^{3+}$ , and 4-6 for

$\text{AnO}_2^{+ / 2+}$  (axial coordination only). They are strongly hydrated in aqueous solutions and readily hydrolyzed (hydroxides precipitate at pH 1 for  $\text{An}^{4+}$ , pH 5 for  $\text{AnO}_2^{2+}$ , pH 7 for  $\text{An}^{3+}$ , pH 9 for  $\text{AnO}_2^{+}$ ). The actinides exhibit a slightly greater tendency to interact with soft donor atoms (sulfur, chloride, nitrogen) than analogous lanthanides. These chemical characteristics are important in the separation chemistry of these elements.

### The Beginnings of Actinide Separations

Actinide separations had its beginning with the discovery of radioactivity. Crookes and Becquerel found that addition of carbonate to a solution containing uranium caused the formation of a precipitate which contained the  $\beta$ ,  $\gamma$  radioactivity while the uranium remained in the solution phase. Rutherford and Soddy made a similar observation for thorium. Marie and Pierre Curie began a program to separate the components of pitchblende. In 1898 they announced the discovery of the new element polonium, 400 times more radioactive than uranium. The separation method used by these pioneers involved precipitation, which remained the predominant separation technique until the Manhattan Project of World War II.

Between 1934 and 1939, about 50 research papers described the discovery and study of transuranium elements with  $Z=93, 94, 95, 96$ . In 1939, Hahn and Strassman conducted very careful separations on irradiated uranium samples and proved that these "transuranium elements" were, in fact, products of nuclear fission with atomic numbers below 60. This led to new experiments in 1940 in which neptunium ( $Z=93$ ) and plutonium ( $Z=94$ ) were synthesized and isolated. These new elements were isolated using an oxidation-reduction cycle (with  $\text{BrO}_3^-$  as the oxidizing agent) followed by precipitation of the reduced metal ions with crystalline  $\text{LaF}_3$ .

Within the context of world politics in the 1930's and 1940's, it was perhaps inevitable that the discovery of fission would be first valued for its potential military applications. Two approaches to the assembly of a critical mass were immediately recognized, isotope enrichment to increase the atom percent of the fissionable uranium isotope  $^{235}\text{U}$ , and transmutation of  $^{238}\text{U}$  by neutron capture and  $\beta$  decay to produce  $^{239}\text{Pu}$ . The former option required a many theoretical plate separation process where the stage-wise efficiency is limited by the small difference in mass of the two principal isotopes. Plutonium production relies on neutron capture (without fission) as the rate limiting step with the different chemistries of uranium and plutonium favoring more efficient separation processes. Both methods were pursued on a large scale as a part of the Manhattan Project.

Plutonium production was accomplished at the Hanford site on the Columbia River near Richland, Washington (1). Plutonium production began with B reactor in September, 1944 and continued through the lifetimes of eight single-pass reactors, N reactor (the only dual-use Hanford reactor which produced both usable steam and Pu), and the Fast Flux Test Facility ending in the early

1980's. The isolation of plutonium from uranium and fission products was initially accomplished by precipitation with  $\text{BiPO}_4$ . The process, pioneered by S. G. Thompson, involves coprecipitation of  $\text{Pu(IV)}$  by  $\text{BiPO}_4$  followed by oxidation to  $\text{Pu(VI)}$ , which doesn't carry on  $\text{BiPO}_4$ . This batch process is inherently inefficient and has the additional disadvantage of losing uranium to the precipitate. It was soon replaced by solvent extraction processes based on the use of methyl(isobutyl)ketone (REDOX Process) and later tributyl phosphate (PUREX Process). PUREX remains the principal method for processing spent reactor fuel today.

### Isotope Separation

The natural abundances of these isotopes are 0.7%  $^{235}\text{U}$ /99.3%  $^{238}\text{U}$ . The heavy isotope,  $^{238}\text{U}$ , is a fertile material suitable for breeding fissile isotopes like  $^{239}\text{Pu}$  but does not fission with thermal neutrons. On the other hand,  $^{235}\text{U}$  is a fissile material. The concentration of  $^{235}\text{U}$  in natural uranium is too low to sustain a nuclear chain reaction. Separation of the isotopes is required to convert natural uranium to either low-enriched (about 3%  $^{235}\text{U}$ , suitable for a sustained chain reaction in a reactor) or high-enriched (>80%  $^{235}\text{U}$ , suitable either for energy generation or nuclear explosives) by several techniques generally centered around uranium hexafluoride.  $\text{UF}_6$  is a volatile compound of  $\text{U(VI)}$ , which sublimates at  $64^\circ\text{C}$ . It is highly corrosive and reacts with water to produce insoluble  $\text{UO}_2\text{F}_2$  (and four equivalents of  $\text{HF}$ ). Several methods for isotope separation enrichment of uranium are known:

**Gaseous Diffusion:** Gaseous  $\text{UF}_6$  flows through cells divided into two parts by a membrane (10-100 nm pore size) at elevated temperature. The theoretical separation factor for separation of the isotopes is 1.0043 ( $(\text{mass}_{238\text{UF}_6}/\text{mass}_{235\text{UF}_6})^{1/2}$ ). At this enrichment factor, 3000 stages are required for enrichment to 80%  $^{235}\text{U}$  (from natural abundance). This method is a very energy-consuming process requiring about 3 MWh/kg. As a result of the large number of stages required, gaseous diffusion plants are enormous (2).

**Electromagnetic Separation:** During the Manhattan Project, electromagnetic separation was used to obtain pure  $^{235}\text{U}$ . Operationally equivalent to a mass spectrometer,  $\text{UF}_6$  is isotopically separated in giant electromagnetic separators called *calutrons*. These clautrons have been used since the was for the preparation of pure isotope of essentially all elements.

**Gas Centrifuge:**  $\text{UF}_6$  is separated in large centrifuges with a per-stage separation factor of 1.4-2.0 requiring 10 stages for enrichment from 0.7 to 3.0 mole %  $^{235}\text{U}$  (with a 0.2 % tail). This process is less energy intensive than gaseous diffusion, but many centrifuges are needed for large-scale production hence eliminating most of the cost advantage of this method.

**Photoionization Processes:**  $\text{UF}_6$  is irradiated by a laser beam producing selective vibrational excitation in the  $^{235}\text{UF}_6$  molecule. By irradiation with ultraviolet light, the photoexcited  $^{235}\text{UF}_6$  (but

not  $^{238}\text{UF}_6$ ) is dissociated forming  $^{235}\text{UF}_{6-x}^{x-}$  which is collected by electromagnetic fields.

### The PUREX Process

From the late 40's through the early 80's, plutonium production for nuclear weapons was the principal driver for technology development in actinide separations. The (Plutonium/Uranium Extraction) PUREX process became the standard method for plutonium production and remains the predominant method in use today. The PUREX process solvent is typically 1.0-1.4 M tributylphosphate in a kerosine diluent. The process is typically run from nitric acid media. The PUREX Process solvent extracts plutonium as the complex  $\text{Pu}(\text{NO}_3)_4(\text{TBP})_2$  and uranyl as  $\text{UO}_2(\text{NO}_3)_2(\text{TBP})_2$  but does not extract trivalent (Am, Cm) or pentavalent (Np) actinides. Likewise, most fission products or non-radioactive components are not extracted by this solvent. Plutonium is removed from the extractant phase by contact with a reducing nitric acid solution ( $\text{Fe}^{2+}$  or  $\text{U}^{4+}$ ) as  $\text{Pu}^{3+}$ .  $\text{UO}_2^{2+}$  is subsequently stripped with dilute  $\text{HNO}_3$ . The relative extractability of actinide ions is shown in Figure 1.

### The Transplutonium Elements

Prior to 1940, the transuranium elements were unknown. Following the discovery of neptunium and plutonium in 1940, a major research effort was launched to synthesize and determine the properties of the transplutonium elements. It was not clear at this time whether these new elements represented the 6d-transition series or 5f series, analogous to the lanthanides. Seaborg proposed that these elements represented the 5f series and headed a team that synthesized and characterized the remaining 9 members of the series (which begins with actinium, hence the name actinide) over the period of 1944 - 1961 (Table 1).

The irradiation methods used to produce the new elements are always accompanied by some fission. Most important among fission products from a separations perspective are lanthanides, whose solution chemistry closely resemble that of transplutonium actinides. Identification of the new transplutonium elements therefore required efficient separations methods not only for actinides from actinides but also for actinides from lanthanides. Fortunately, there are two characteristics of the trivalent lanthanides and actinides which can be exploited to affect the necessary separations: 5f actinides interact more strongly with soft-donor ligands like  $\text{Cl}^-$  and  $\text{SCN}^-$ , and cation radii contract across the series. The former characteristic can be used to separate actinides from lanthanides and the latter to separate individual members of the series. Many of the chemical properties of the transplutonium elements were predicted based on those of the corresponding lanthanides.

The development of synthetic ion exchange resins provided the necessary phase-transfer

TABLE 1. Transplutonium elements: year of discovery, investigators, method of production.

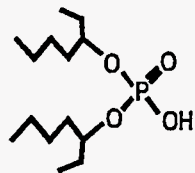
Element	Year	Discoverers	Method
Neptunium	1940	Mc Millan, Abelson (3)	Cyclotron Bombardment of U with neutrons
Plutonium	1940	Seaborg, Wahl, Kennedy (4)	Cyclotron bombardment of U with $^2\text{H}$
Americium	1944	Ghiorso James, Morgan, Seaborg (5)	Neutron capture $^{239}\text{Pu}$ in a reactor
Curium	1944	Seaborg, James, Ghiorso (6)	Cyclotron bombardment of $^{239}\text{Pu}$ with $\alpha$
Californium	1950	Thompson, Street, Ghiorso, Seaborg (7)	Cyclotron bombardment of $^{242}\text{Cm}$ with $\alpha$
Berkelium	1949	Thompson, Ghiorso, Seaborg (8)	Cyclotron bombardment of $^{241}\text{Am}$ with $\alpha$
Einsteinium	1952	Ghiorso et. al. (9)	Thermonuclear explosion bomb debris
Fermium	1952	Ghiorso et. al. (9)	Thermonuclear explosion bomb debris
Mendelevium	1955	Ghiorso, Harvey, Choppin, Thompson, Seaborg (10)	Cyclotron bombardment of $^{253}\text{Es}$ with $\alpha$
Nobelium	1958	Ghiorso, Sikkeland, Walton, Seaborg (11)	HILAC bombardment of $^{244}\text{Cm}$ with $^{12}\text{C}$
Lawrencium	1961	Ghiorso, Sikkeland, Larsh, Latimer (12)	HILAC bombardment of Cf with $^{10}\text{B}$

"platform" for accomplishing these separations. Early work by Diamond et al (13) established that in concentrated HCl solutions (greater than 6 M),  $\text{Am}^{3+}$  and  $\text{Pm}^{3+}$  were effectively partitioned on cation

exchange resin due to the greater interaction strength of Am with the soft-donor chloride ion (Figure 2). Similar separations were reported for anion exchange separations from 10 M LiCl and 2 M NH<sub>4</sub>SCN solutions. The LiCl anion exchange separation method is still in use at the REDC for the production of research quantities of transplutonium elements for research purposes (14).

The separation of individual members of the series was initially accomplished by cation exchange using citrate, lactate, or EDTA as the eluant. Individual lanthanides were also produced by this method. In 1954, a new reagent,  $\alpha$ -hydroxyisobutyric acid, was reported as a superior eluting agent for the cation-exchange-based separation of individual trivalent actinide ions (15, Figure 3). Separation factors for adjacent lanthanide or actinide cations average 1.4. This technique remains the optimum method for isolation of individual transplutonium actinides.

Emphasis in f element separation science shifted in the late 1950's and 1960's to the development of separation processes based on solvent extraction. Among these investigations, arguably the most important was the development of acidic organophosphorus extractants. Phosphoric, phosphonic, and phosphinic acid esters containing at least one ionizable proton were extensively investigated as "liquid cation exchangers" for the separation of a variety of metals, but particularly for lanthanides and trivalent actinides. The premier example of these ligands is bis(2-ethylhexyl)phosphoric acid (HDEHP) (16). In Figure 4 is shown the extraction coefficients for



trivalent actinide and lanthanide cations by HDEHP in toluene. The average separation factor for adjacent ions is greater than 2 for both the actinide and lanthanide series. This reagent is perhaps the most important industrial reagent for lanthanide separations, and is extensively used for this purpose.

It is clear from Figure 4 that this extraction system is not useful for the separation of lanthanides from trivalent actinides as the lanthanide and actinide cation radii and their extraction coefficients overlap. However, it does form the phases-transfer basis for a very effective separation of lanthanides from trivalent actinides, the Trivalent Actinide Lanthanide Separation by Phosphorus Extractants and Aqueous Komplexes process (18). In TALSPEAK, the aqueous medium is 1 M lactic acid/0.05 M diethylenetriaminepentaacetic acid (DTPA) at pH 3. The extractant is 0.3 M HDEHP in diisopropyl benzene. The lactic acid serves to promote dehydration of the metal ion, improve kinetics, and act as a coextractant. The DTPA preferentially complexes actinides so that they are retained in the aqueous phase while the lanthanides are extracted. Typical performance of this system is shown in Figure 5. The lanthanide/actinide separation factor is at least 10. If the metal ions are first extracted from dilute nitric acid solution, the actinides can be selectively removed by contact with the

TALSPEAK aqueous medium in a process known as Reverse TALSPEAK.

### Actinide Separations: Next Generation

With the end of the Cold War, the demand for actinide production for weapons has disappeared. Only those nations actively pursuing fuel reprocessing have active research programs investigating new methods for plutonium production. What remains to those nations not engaged in processing are the tasks of preventing actinide proliferation, waste stabilization and cleanup, environmental monitoring and restoration, and a continuing need for efficient bioassay techniques. The current generation of actinide separation processes address these new priorities.

With declining demand for plutonium production, actinide process chemistry has shifted focus to waste minimization. The industry standard PUREX process suffers from the limitation (previously an advantage) that it is not an effective method for extraction of trivalent actinides (Am and Cm). However, PUREX is a comfortable technology. The challenge of the early 80's was to devise a solvent extraction-based process for total actinide recovery which was fully compatible with PUREX technology.

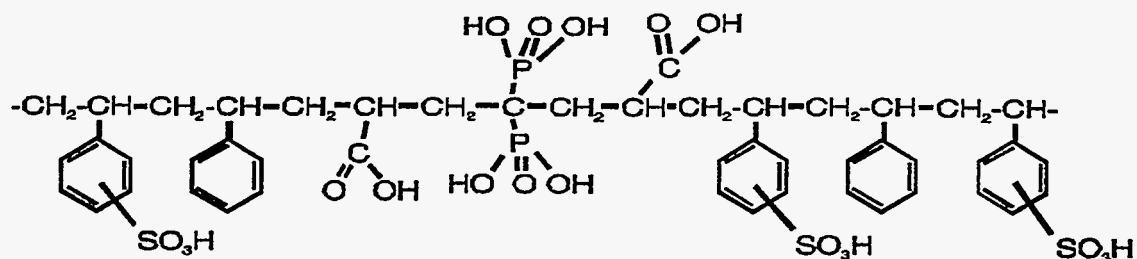
To extract trivalent actinides within a PUREX-style process, Horwitz et al (19) (based on earlier work by Siddall (20, 21)) developed the new extractant octyl(phenyl)-N,N-diisobutyl-carbamoylmethylphosphine oxide (CMPO) and a new process (TRUEX) which uses this extractant. The TRUEX Process Solvent consists of a standard PUREX Process Solvent with CMPO added for trivalent actinide extraction. A typical process solvent formulation would be 0.2 M CMPO, 1.2 M TBP in kerosine diluent. Extraction efficiency for actinides in the tri-, tetra-, and hexavalent oxidation states from nitric acid solutions is shown in Figure 6. All ions are more strongly extracted than they are by PUREX solvent (Figure 1). Extraction of  $\text{Am}^{3+}$  and  $\text{Pu}^{4+}$  is readily reversible by changes in  $[\text{HNO}_3]$  while  $\text{UO}_2^{2+}$  must be stripped from the extractant phase using an aqueous complexant, typically oxalate or carbonate.

For certain applications, ion exchange methods are preferable to solvent extraction. Conventional cation and anion exchange resins have been extensively investigated for actinide sequestration, and many varieties of cationic, anionic and chelating resins are available. The development of pyridine-based anion exchange resins (Reilly Industries, Indianapolis) represents an important addition to the arsenal of ion exchange separations materials (22). Inorganic ion exchangers (zeolites) were used for some of the earliest ion exchange separation of f elements and are getting increasing scrutiny today. Recent work by Clearfield (23) has addressed the use of sodium titanate and pillared zirconium phosphate/phosphonate materials, but interlanthanide separation factors are small for these ion exchangers. Actinide uptake has not been reported for these materials.

A new chelating ion exchange resin which combines good kinetics with the increased power



of diphosphonate chelating groups provides additional options for actinide sequestration by cation exchange. A polystyrene-based chelating cation exchange resin (Diphonix resin) which combines methylenediphosphonate, carboxylate, and sulfonate binding groups displays strong affinity for f-elements in all oxidation states (24), even in the presence of moderate concentrations of complexing anions and in concentrated acid. A representative monomer unit of Diphonix is shown below. This



resin offers the possibility of total actinide removal from acidic, aqueous media. Diphonix has been demonstrated for this purpose in a mixed-waste treatment facility at ANL.

While extractants and solid resins are clearly necessary for effective separations, aqueous complexants are often critical to successful schemes, as illustrated by the LiCl anion exchange separation of Ln/An(III) and TALSPEAK. Besides these specific examples, aqueous complexants are typically used in actinide processing as hold-back or stripping reagents or for the decontamination of process equipment. A series of complexants based on methane diphosphonic acid ( $\text{CH}_2(\text{PO}_3\text{H}_2)_2$ ) have been prepared and characterized as complexants for f elements (at Argonne National laboratory). Numerous applications have been suggested for their use in processing of actinides, including one oxidation state-specific separation based on TRUEX chemistry (25).

The polycarboxylic acid ligand tetrahydrofuran-2,3,4,5-tetracarboxylic acid (THFTCA) has been demonstrated as a highly specific stripping agent for trivalent and tetravalent actinides when used in a TRUEX-like process (26). Uranyl ion is selectively extracted by CMPO from this aqueous medium while  $\text{Am}^{3+}$  and  $\text{Pu}^{4+}$  preferentially distribute to the aqueous phase (Figure 7). This behavior is partially explained by the uncharacteristically weak interaction of uranyl with THFTCA in the aqueous phase (complexes are 100 times weaker than the corresponding europium complexes). NMR spectroscopic data also suggests a strong interaction between uranyl and THFTCA in the TRUEX phase, and the formation of extensively organized polymeric complexes in the extractant phase. The segregation of U from TRU's has important implications for the reduction of the volume of wastes in a high-level repository.

Development and validation of thermodynamic models for actinide behavior in nature require accurate information on oxidation state distribution of the actinides in natural samples. A major difficulty in the determination of (for example) plutonium oxidation states in groundwater samples is the relative ease of conversion between oxidation states. Because of the typically very

low concentrations involved (often less than  $10^{-8}$  M), conventional spectrophotometric techniques are not generally applicable. Separations chemistry and radiometric analysis are the most appropriate techniques. The key objective is to determine the oxidation state without alteration during the measurement. Several complementary separations methods can (and should) be applied to insure accuracy. Some examples of actinide oxidation state speciation methods based on sorption or solvent extraction are:

LaF<sub>3</sub> coprecipitation in which a lanthanide fluoride carries An(III) and An(IV) without An(V) or An(VI). Care must be used in application of this technique as excess fluoride can promote reduction during the precipitation process (27).

Silica gel (SiO<sub>2</sub>) selectively sorbs An(IV) and An(VI) from basic media leaving An(V) in solution (28).

CaCO<sub>3</sub> selectively sorbs An(V) and An(IV) leaving An(VI) in solution as the tris carbonate complex (29).

Thenoyltrifluoroacetone (TTA, 0.5 M in xylene) selectively extracts An(IV) from 0.25 M acid. The same extractant can then be used to extract An(VI) from acetate buffer at pH 4 (30).

Dibenzoylmethane (DBM, 0.2 M in xylene) selectively extracts An(IV) at pH < 2.5, An(VI) at pH 5, An(III) at pH 7. An(V) is not extracted (31).

Quantitative analysis of actinide concentrations in environmental or bioassay samples by standard methods require extensive treatment to promote the release of the radionuclides from the complex matrix. Analyses of such samples have required up to 24 hours processing time. Standard ion exchange and solvent extraction analytical methods have been used for these analyses. The recent development of more selective extraction chromatographic materials and the development of procedures for their use have greatly shortened the time required for these analyses (32). These extraction chromatographic materials are based on well-known solvent extraction methods, as follows:

TRU-Specific Resin for selective sorption of An(III), An(IV), An(VI), Ln(III). The extractant is 0.75 CMPO in TBP

TEVA Specific Resin for sorption of An(IV). The extractant is (C<sub>10</sub>H<sub>21</sub>)<sub>2</sub>(C<sub>8</sub>H<sub>17</sub>)(CH<sub>3</sub>)N<sup>+</sup> (Aliquat 336, neat).

U/Teva Specific Resin for sorption of U(VI), An(IV). The extractant is (C<sub>5</sub>H<sub>11</sub>O)<sub>2</sub>(C<sub>5</sub>H<sub>11</sub>)P=O (DP[PP], neat).

An example of an element-specific separation scheme of actinides using TRU-Specific resin is as follows:

load sample from 2 M HNO<sub>3</sub>, rinse off non-TRU's with 1.0 M HNO<sub>3</sub> then 9 M HCl,  
elute Am<sup>3+</sup> with 4 M HCl,  
elute Pu<sup>4+</sup> with 4 M HCl/0.1 M Hydroquinone,

elute  $\text{Th}^{4+}$  with 2 M HCl,  
elute  $\text{Np}^{4+}$  with 1 M HCl/0.03 M oxalate,  
elute  $\text{UO}_2^{2+}$  with 0.1 M  $\text{NH}_4\text{HC}_2\text{O}_4$ ,  
analyze fractions radiometrically.

### Future Directions in Actinide Separations

Actinide separations for plutonium processing (in connection with either weapons production or as a part of a breeder reactor program) involves primarily solvent extraction processes operating on acidic aqueous solutions. As a consequence of 50 years of both research and process experience, this technology must be considered mature, and has proven to be reliable (though its application has generated complex wastes). Partly as a result of this maturity, but also due to changes in world politics, acid processing to recover actinides is no longer the principal driving force for development in actinide separations. The challenges attendant to the present status of actinide separations are determined by the current emphasis on waste cleanup and environment restoration. The current issues in actinide separations are defined by the physical and chemical state of actinides in the terrestrial environment:

#### 1) Alkaline wastes in underground storage tanks;

The legacy of 50 years of plutonium production is a large volume of mixed wastes (containing TRU's, long-lived fission products, and non-radioactive but chemically hazardous materials). These wastes take the form of sludges, solids, alkaline or acidic solutions, and slurry phases in which actinides coexist with long-lived fission products and non-radioactive constituents. In the face of this complexity, how can the volume of waste going to a repository be minimized? Three potentially important areas for development are: develop sludge washing which selectively remove actinides from the solids or sludges (solid-liquid separation), develop separation procedures suitable for plant-scale development which can operate in alkaline media, develop new methods for selective sorption of actinides from complex matrices.

#### 2) Actinide burnup strategies;

A "permanent" remedy to the long-term hazard of actinides is to "incinerate" them in advanced reactors or accelerators and thus transform them into short-lived fission products. An added advantage of this approach is the potential for recovery of the heat value of the actinides. Because lanthanides have high cross sections for neutron capture and thus interfere with the neutron physics of actinide burnup, robust Ln/An separation methods are demanded, in particular, processes resistant to radiolysis effects. Two areas of actinide separations research relevant to this problem are the continued development of the Integral Fast Reactor concept which includes a pyro-electrochemical separation process, and the development of new soft-donor extractants and aqueous complexants for

actinide/lanthanide separations.

### 3) Actinides in the environment:

Minor concentrations of actinides are present in the terrestrial environment as a result of atmospheric weapons testing, the Chernobyl accident, and actinide production activities (including intentional and accidental releases). Accurate speciation techniques, environment decontamination methods, and in-situ immobilization techniques are needed. Three generic areas for research, all of which involve some form of separation science, are pertinent to this subject: the development of reliable speciation techniques and thermodynamic models, solid-solution separation methods for removal of actinides from soils, contaminated process equipment, etc., solution-mineral conversion techniques to fix residual actinides in-situ and prohibit their entry into the food chain.

Outside of those countries pursuing a closed-loop fuel cycle (based on plutonium recycle), the current drivers for continued development of actinide separations are the need to secure those supplies of plutonium susceptible to diversion, and environment cleanup/restoration/waste disposal. Many opportunities exist for improvements in existing procedures or the development of new methods for actinide isolation. The major change in emphasis does not mean the end of the need for actinide separations, it indicates a shift toward new horizons.

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## Figure Captions

Figure 1. Dependence of the extraction of several actinides as a function of nitric acid concentration into 30% (v/v) tributylphosphate in kerosine ( $D=[An]_o/[An]_a$ ) (2).

Figure 2. Lanthanide-actinide separation by cation exchange from HCl solutions (13).

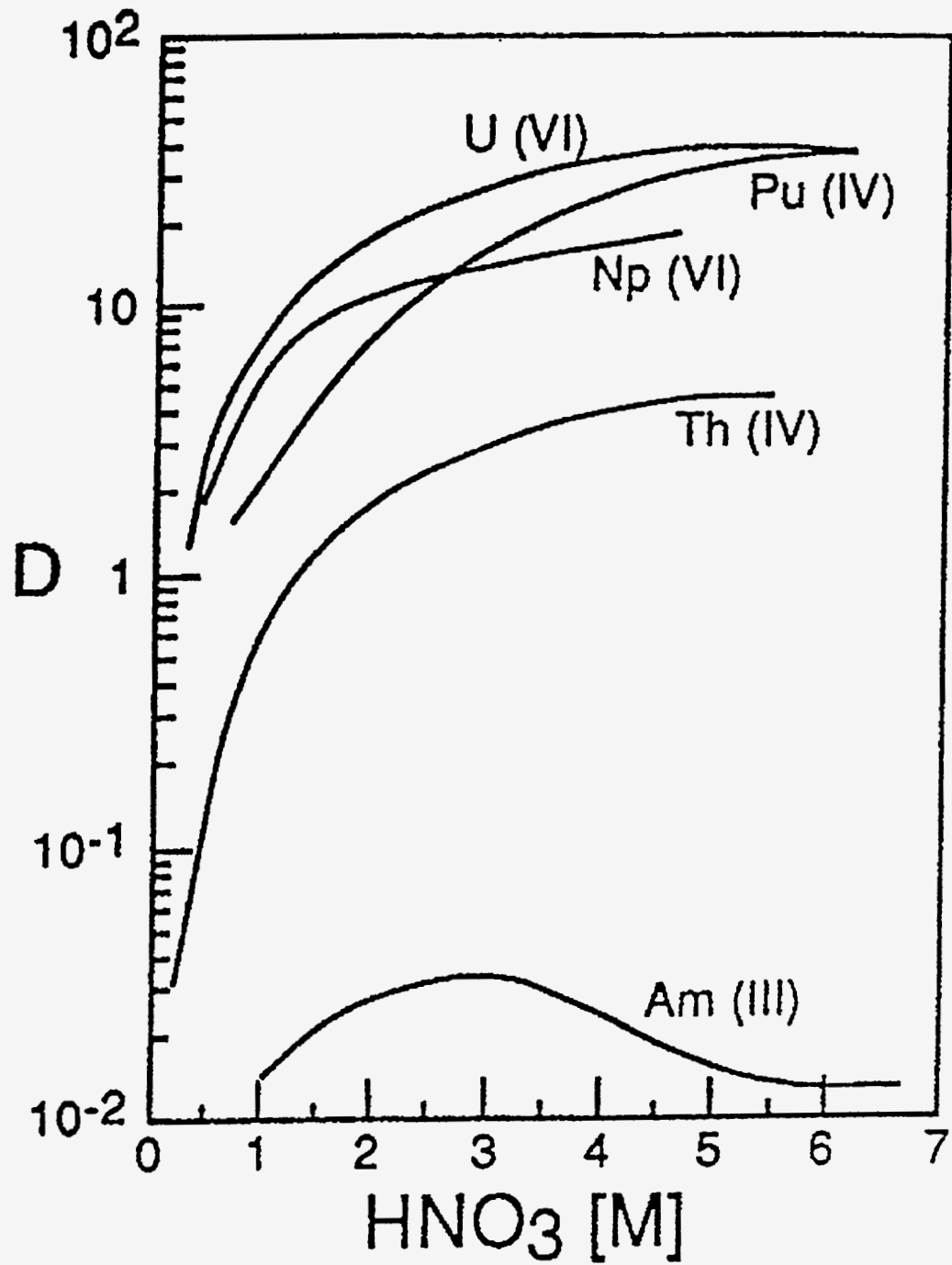
Figure 3. Elution of Ln(III) and An(III) from a column of cation exchange resin by a solution of ammonium  $\alpha$ -hydroxyisobutyrate at pH 4.0 (15).

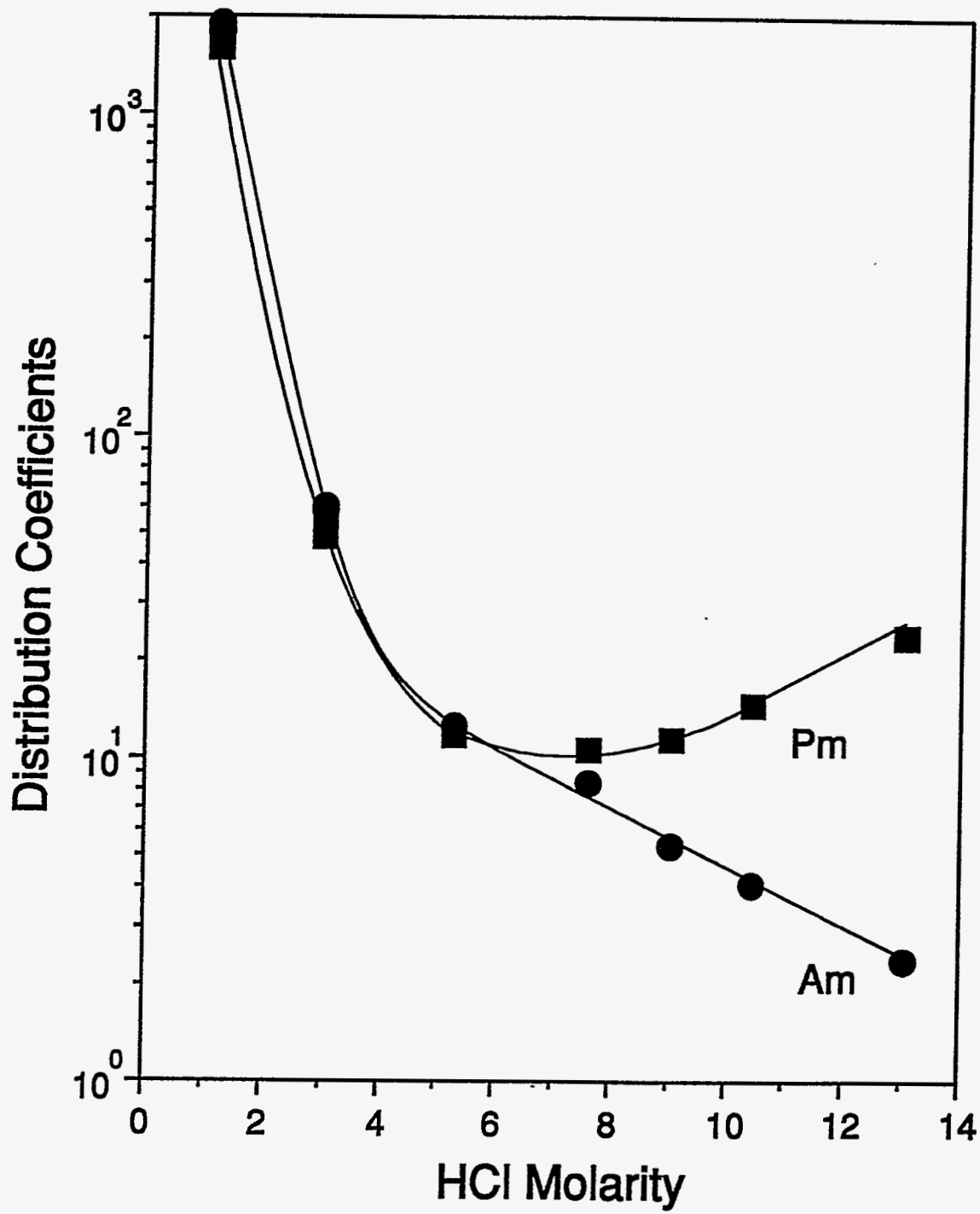
Figure 4. Separation efficiency for trivalent lanthanides and actinides by solvent extraction with bis(2-ethylhexyl)phosphoric acid (shown inset) (17).

Figure 5. Trivalent Actinide Lanthanide Separation by Phosphorus Extractants and Aqueous Komplexes (TALSPEAK) process (18).

Figure 6. Dependence of the extraction of  $Am^{3+}$ ,  $Pu^{4+}$ , and  $UO_2^{2+}$  as a function of nitric acid concentration into TRUEX Process Solvent (0.2 M octyl(phenyl)-N,N-diisobutylcarbamoylmethylphosphine oxide (CMPO) and 1.2 M TBP in kerosine diluent) (19).

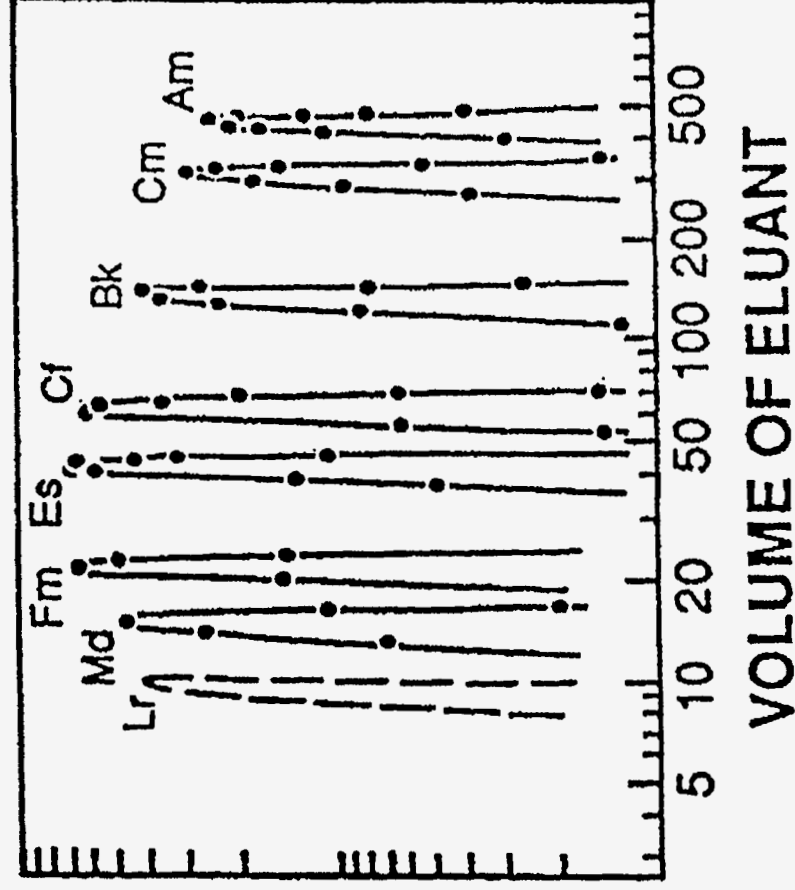
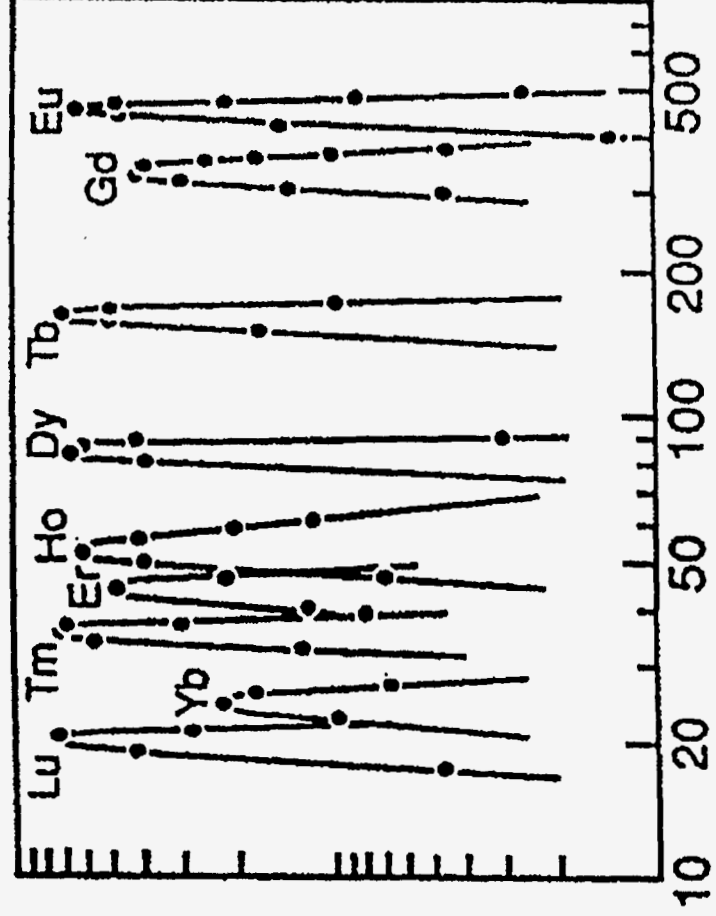
Figure 7. Extraction of  $Am^{3+}$ ,  $Np^{4+}$ , and  $UO_2^{2+}$  as a function of nitric acid concentration from an aqueous solution containing 0.5 M tetrahydrofuran-2,3,4,5-tetracarboxylic acid (THFTCA) into a Combined Process Solvent (0.2 M CMPO, 0.2 M 4,4'(5')di(t-butylcyclohexano)-18-crown-6 (DtBCH18C6), and 1.2 M diamyl(amy)l-phosphonate DA(A)P in Isopar L) (26).

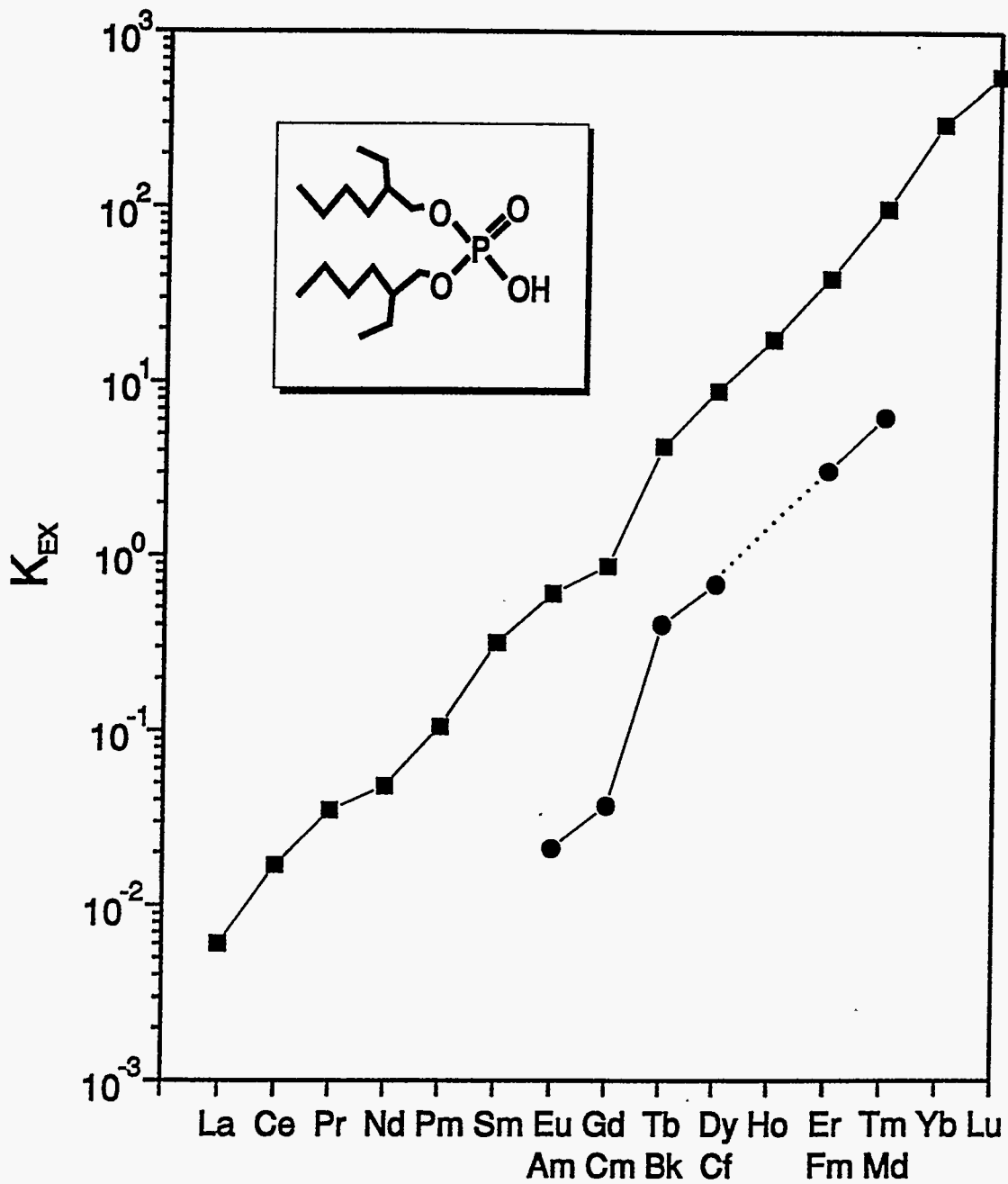


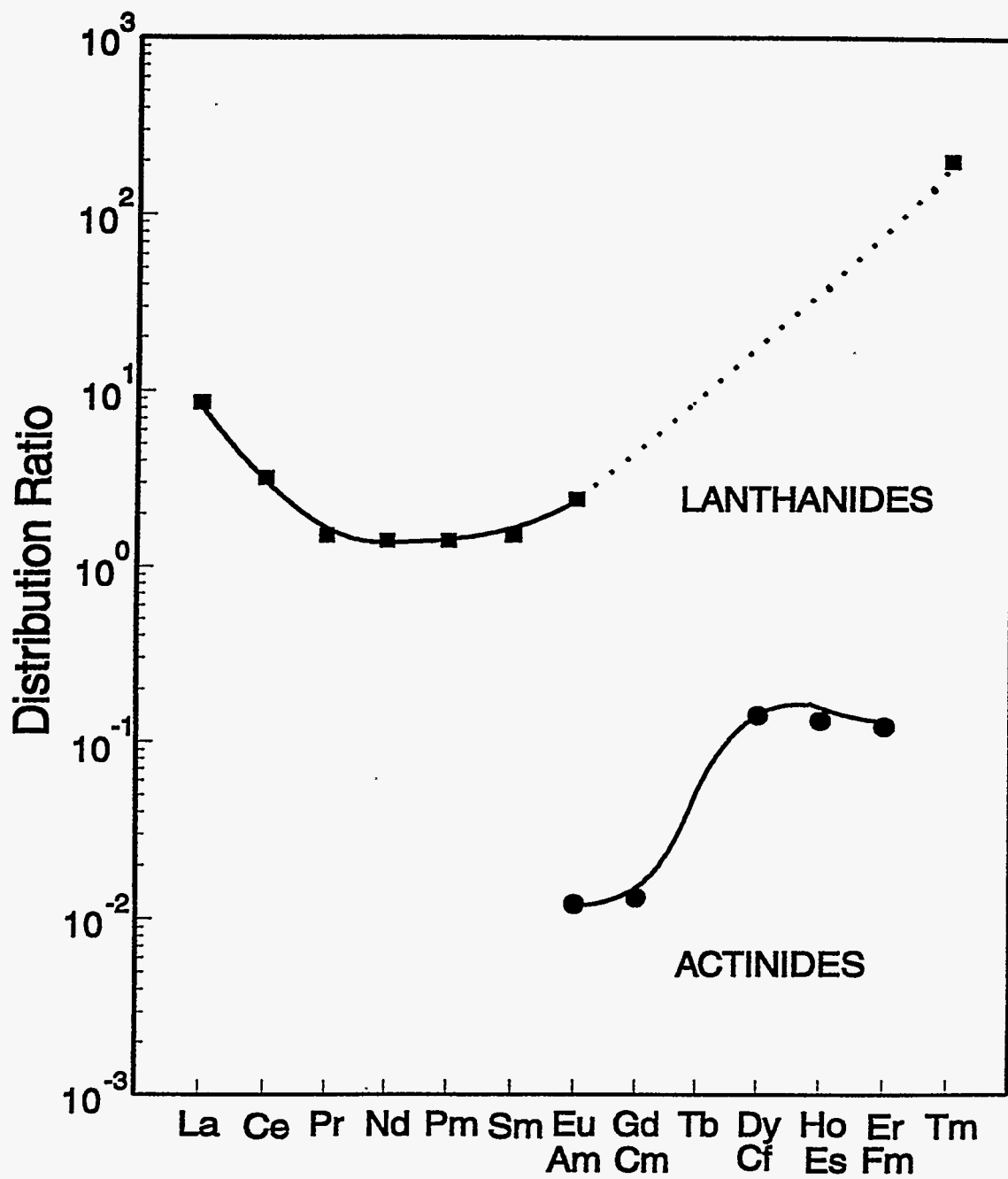




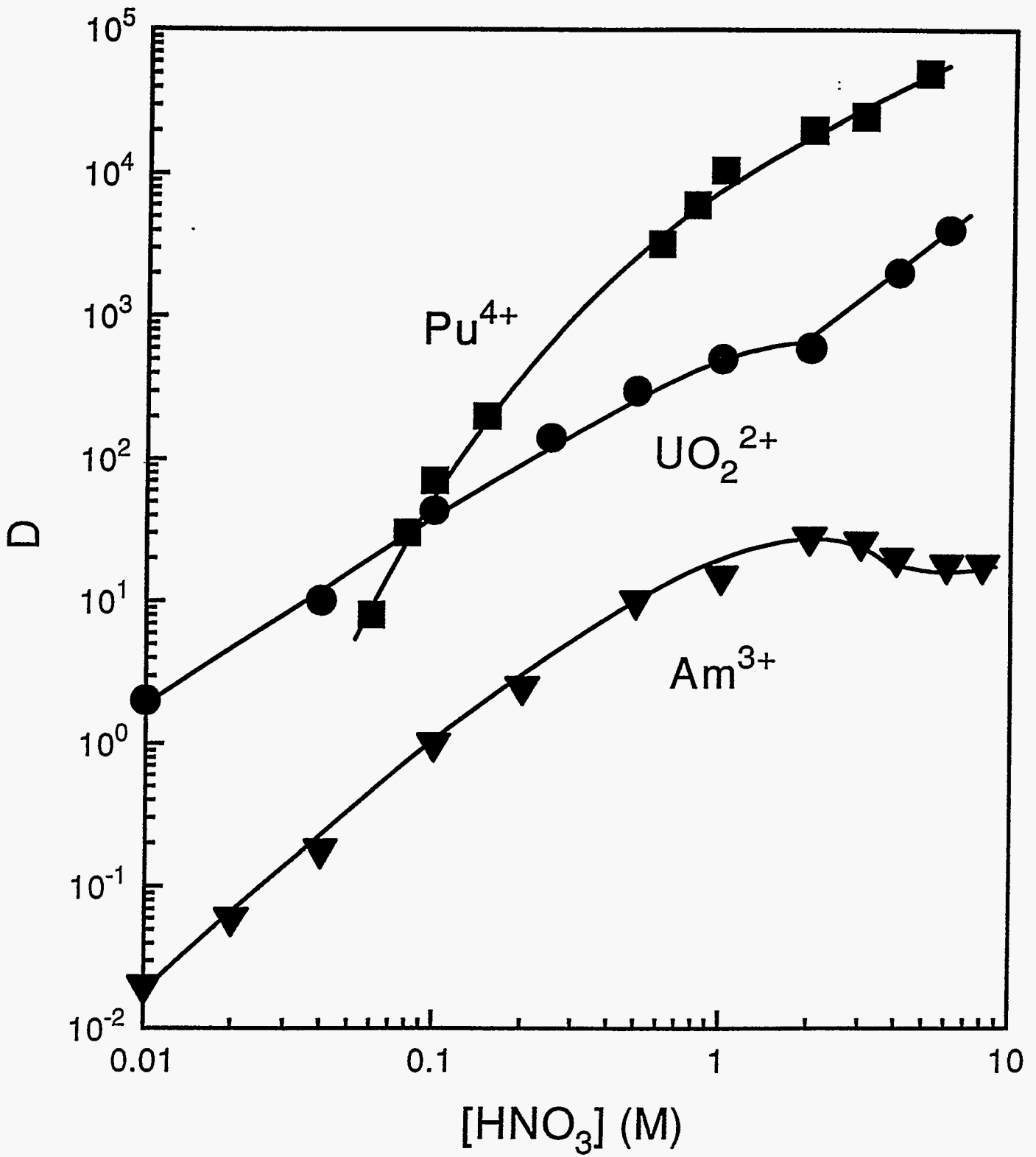
# RELATIVE ACTIVITY

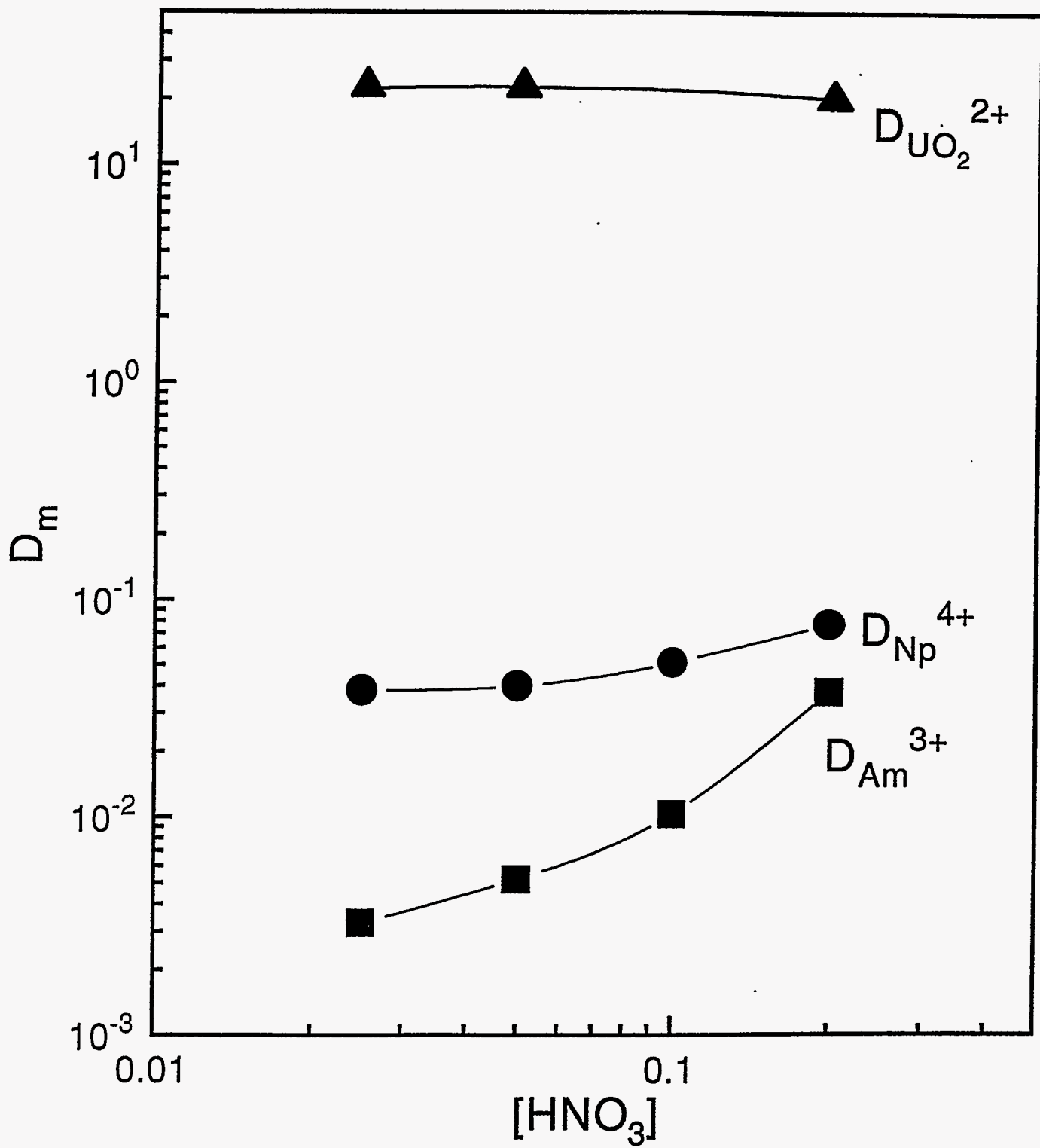






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