HP199

Extraction Chromatography of Actinides and Selected Fission Products: Principles and Achievement of Selectivity

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Abstract

Extraction chromatography is a technique that combines the selectivity of solvent extraction with the ease of operation of column chromatography. Extraction chromatography is ideally suited to laboratory-scale analysis of a wide range of metal ions present in environmental and bioassay samples. Eichrom Industries, Inc. manufactures and markets a number of resins specifically focused on facilitating the determination of the actinide elements and selective fission products. The selectivity of the Eichrom resins is based on exploiting the differences in the extraction of metal ion-nitrato complexes, on differences in charge density and steric effects, and on ionic recognition.

Introduction

The growing concerns for public health and safety over the use of nuclear technology, both in the production of nuclear materials for weapons and in the use of nuclear power, have made reliable methods for the determination of various actinides and selected fission products in environmental and bioassay samples increasingly important. The separation and preconcentration of radionuclides from environmental and bioassay samples for subsequent determination is frequently complicated by the presence of complex matrices that may contain large quantities of silica and various metal ions (e.g., Al, Ti, and Fe) as well as various anions, particularly phosphate and sulfate.

Horwitz, D.P., "Extraction Chromatography of Actinides and Selected Fission Products: Principles and Achievement of Selectivity", presented at International Workshop on the Application of Extraction Chromatography in Radionuclide Measurement, IRMM, Geel 9-10, Belgium November 1998. (HP199)

Extraction chromatography (EXC) is a technique that is ideally suited to the separation of radionuclides from a wide range of sample types. This technique combines the selectivity of liquid-liquid extraction with the ease of operation of column chromatography. Updated reviews of extraction chromatography have appeared within the last few years [1,2]. This report will focus on extraction chromatographic resins that are manufactured and marketed by Eichrom Industries. Table 1 lists these resins together with their selectivities for various elements or groups of elements.

Table 1. Chromatographic Resins from Eichrom Industries

Material	Selectivity
TRU Resin	Actinides(III, IV, VI), Ln(III)
UTEVA Resin	U(VI)
TEVA Resin	Th(IV), Np(IV), Pu(IV), Tc(VII)
Sr Resin/Pb Resin	Sr, Pb
Ln Resin	Ln(III)
Actinide Resin	Actinides

Principles

Figure 1 is a simplified depiction of a portion of an extraction chromatographic resin bead showing the three major components of an EXC system: the inert support, the stationary phase, and the mobile phase. The inert support usually consists of porous silica or an organic polymer ranging in size from 50 to 150μm in diameter. Much smaller or larger particles have been studied for special applications. Liquid extractants, either single compounds or mixtures, are used as the stationary phase. Diluents can also be used to help solubilize the extractant and to increase the hydrophobicity of the stationary phase. The mobile phase is usually an acid solution, e.g., nitric or hydrochloric acid, although complexants, such as oxalic or hydrofluoric acids, are frequently used to enhance selectivities or the stripping of strongly retained metal ions from columns.

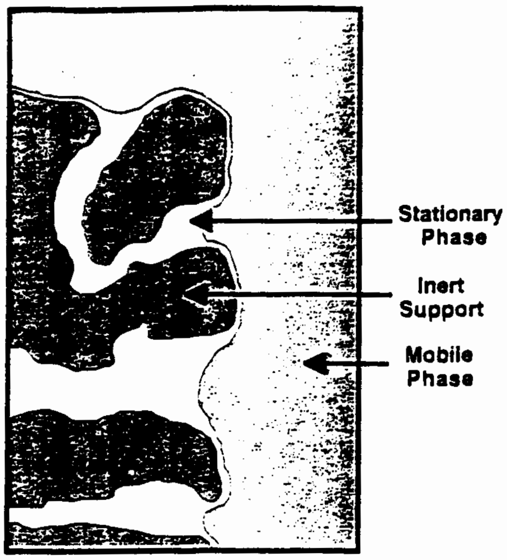

Figure 1. Depiction of Extraction Chromatography (EXC) Surface of Porous Bead

The relationship between the distribution ratio (D) as measured in a solvent extraction (SX) system and the number of free column volumes to peak maximum, k', for the corresponding EXC system is shown below:

$$k' = D \bullet \frac{v_s}{v_m} \tag{1}$$

where v_s and v_m are the volumes of stationary and mobile phases, respectively. It is important to note the concentration of extractant is usually much higher in EXC systems where diluents may be absent altogether than in conventional SX systems. Therefore, D and k' are not usually measured directly for EXC systems, but calculated from the weight distribution ratio, D_w, which is easily measured. The weight distribution ratio, D_w, is obtained by measuring the amount of a given metal ion taken up by a measured weight of resin from a given volume of aqueous solution. In the studies described in this report, radioactive isotopes were used to measure the uptake of metal ions. The weight distribution ratio is then calculated using the following equation:

$$D_w = \frac{A_o - A_s}{A_s} \bullet \frac{mL}{g} \tag{2}$$

where $A_o - A_s$ = activity sorbed on a known weight of resin, g, and A_s = the activity in a known volume, mL, of solution. The volume distribution ratio D is calculated from the volume of stationary phase per gram divided into D_w[3]. The volume of stationary phase is obtained from its weight percent sorbed on the inert support and its density. (The density of the stationary phase is obtained from an independent measurement.) The number of free column volumes to peak maximum, k', is then calculated from equation (1). The quantities, v_s and v_m, are measured from the weight of resin required to fill a column to a known volume and the density of the EXC resin. Details for the calculation of D and k' and the independent measurement of v_s and v_m can be found in [3-5]. Table 2 gives the ratio of v_s/v_m and the factors to convert from D_w to k' for six Eichrom EXC resins.

Table 2. Converting D_w to k'

Resin	v_s / v_m	To convert Dw to k' divide by
TEVA	0.23	1.9
UTEVA	0.25	1.7
TRU	0.22	1.8
Actinide	0.20	1.9
Sr	0.22	2.0

Achievement of Separation

To achieve separation in EXC, band spreading must be sufficiently small to avoid early breakthrough and to avoid excessive cross-contamination of the constituents that one is trying to separate. Even if the extractants comprising the stationary phase exhibit very high selectivity for one of the ions, poor column efficiency, as manifested in excessive band spreading, can result in essentially no practical separation. Column efficiency is generally expressed in terms of the height equivalent to a theoretical plate. Plate height is a complex function of a number of physical and chemical factors. In EXC systems column efficiency is determined primarily by flow phenomena, diffusion in the stationary phase and extraction kinetics [6]. The relative importance of each of these three factors to column efficiency depends on the specific chemical system, the particle size and porosity of the support, the extractant loading and mobile phase velocity, and the operating temperature. For a detailed discussion of each of these phenomena, [6,7] should be consulted.

Achievement of Selectivity

The EXC resins listed in Table 1 cover a wide range of selectivities and enable one to perform a number of novel highly efficient separations of selected fission products and individual actinides or groups of actinides. Figures 2-6 show the acid dependencies for the uptake, as measured by k', of selected actinides and non-actinides. Table 3 summarizes the important properties of these resins.

Table 3. Properties of Eichrom EXC Resins

Particle Size (μm)	100-150, 50-100
Bed Density (mg/mL)	0.33 to 0.39
Free Column Volumn (% of Bed Volume)	65 to 69
	Working Capacity* (mg/mL of Bed)
TEVA	15 (Pu)
U/TEVA	32 (U)
TRU	4.5 (Am)
Sr	6.5 (Sr), 12 (Pb)
Ln	11 (Nd)
Actinide	14 (Am), 8.6 (Nd)

*50% of maximum loading capacity

TEVA resin contains a trialkylmethylammonium nitrate as the stationary phase [4]. TEVA resin enables one to selectively sorb all tetravalent actinide ions (as their nitrato complexes) over a wide range of nitric acid concentrations. Note that the uptake of actinide (IV) ions is at a maximum around 3$\underline{M}$ HNO_3, unlike a strong-based anion exchange resin which requires 8$\underline{M}$ HNO_3 to achieve the maximum uptake. U/TEVA resin contains diamyl amylphosphonate (DA[AP]) as the stationary phase [4, 8]. DA[AP] extracts U(VI) as a neutral nitrato complex and is highly selective for U(VI) over all commonly occurring constituents such as Al, Fe, alkali and alkaline earth ions. The stationary phase in TRU resin consists of a mixture of carbamoylmethylphosphine oxide derivative

(CMPO) and tri-n-butyl phosphate (TBP). The CMPO-TBP combination increases significantly the uptake of trivalent actinides, e.g. Am(III), as well as tetra-and hexavalent actinides [4,9]. As was the case with TEVA and U/TEVA, TRU resin extracts the actinides as their nitrato complexes. One of the novel features of TEVA, U/TEVA, and TRU resin is that they can be used in tandem [4]. The same load solution is passed through all three columns coupled together in the above order. After rinsing, the columns are separated and different actinides are sequentially eluted from each column. This technique has been applied successfully to the analysis of high-level nuclear waste solutions [4].

The strontium/lead selective resin is based on the principle of ionic recognition [3,11]. The stationary phase consists of a dicyclohexano-18 crown-6 derivative dissolved in an aliphatic alcohol. The data in Figure 4 show that the uptake of Sr is greater than the uptake of other alkali and alkaline earth ions. The selectivity for Sr over Ca is particularly noteworthy because Ca is a major constituent in many samples.

The Ln and Actinide resins contain a dialkyl phosphoric acid and a tetraalkyl methanediphosphonic acid, respectively, as the stationary phase. These resins achieve selectivity through a combination of electrostatic and steric effects [5,10]. Extraordinarily high uptake of actinides is achieved with the actinide resin [5]. The actinide resin has been used for the preconcentration of actinides from soils and large volumes of water [12]. Recovery of actinides is achieved by eluting the stationary phase with iso-propyl alcohol and then destroying the stationary phase through oxidation. The resultant residue arising from the destruction of the stationary phase is processed further using the tandem column system described in [4].

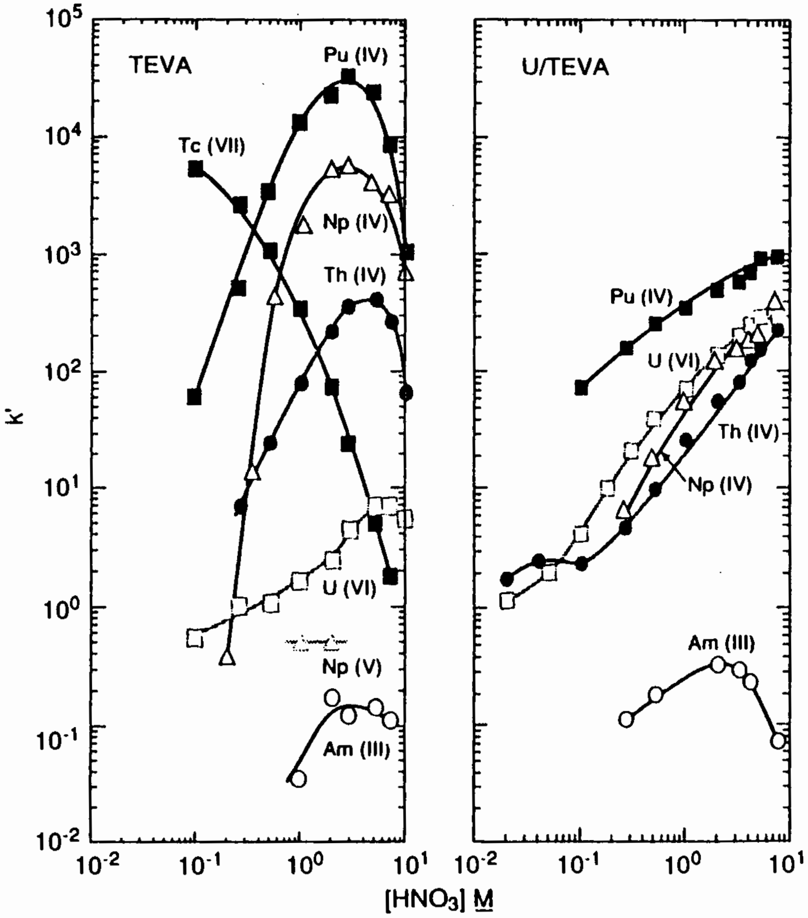

Figure 2. Comparison of Acid Dependencies for the Uptake of Several Actinides by TEVA and U/TEVA Resins. Temperature ≈ 23-25° C [4,8]

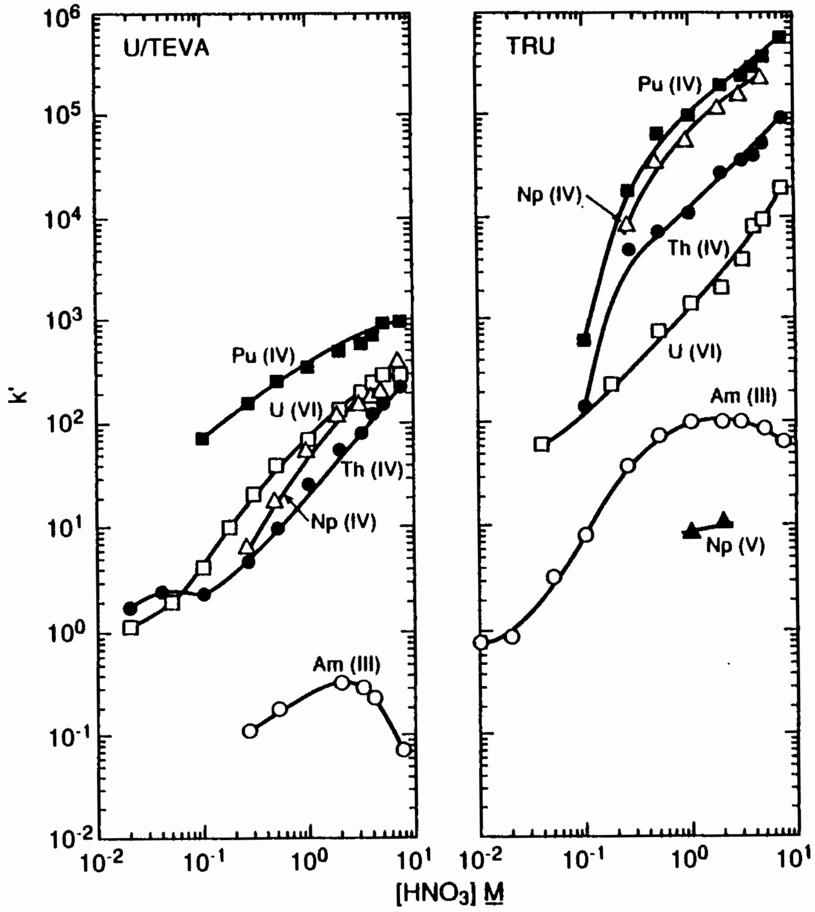

Figure 3. Comparison of Acid Dependencies for the Uptake of Several Actinides by U/TEVA and TRU Resins. Temperature ≈ 23-25°C [4,8,9]

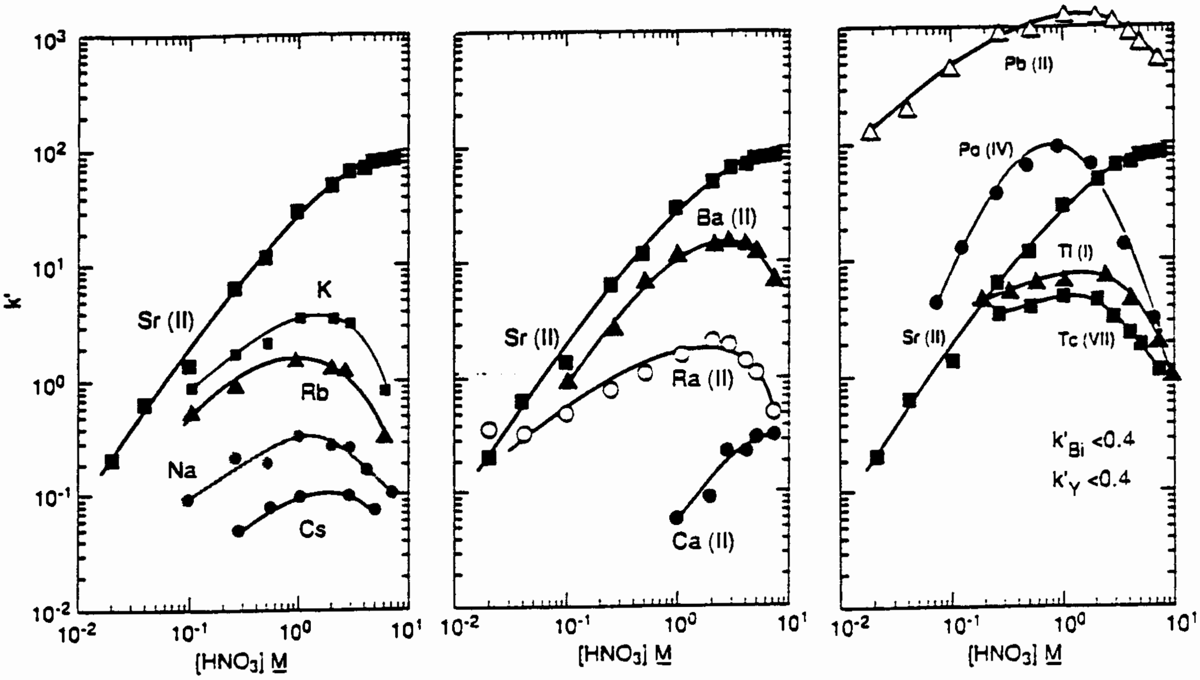

Figure 4. Acid Dependencies for the Uptake of Selected Metal Ions by Sr Resin. Temperature ≈ 23-25°C [3]

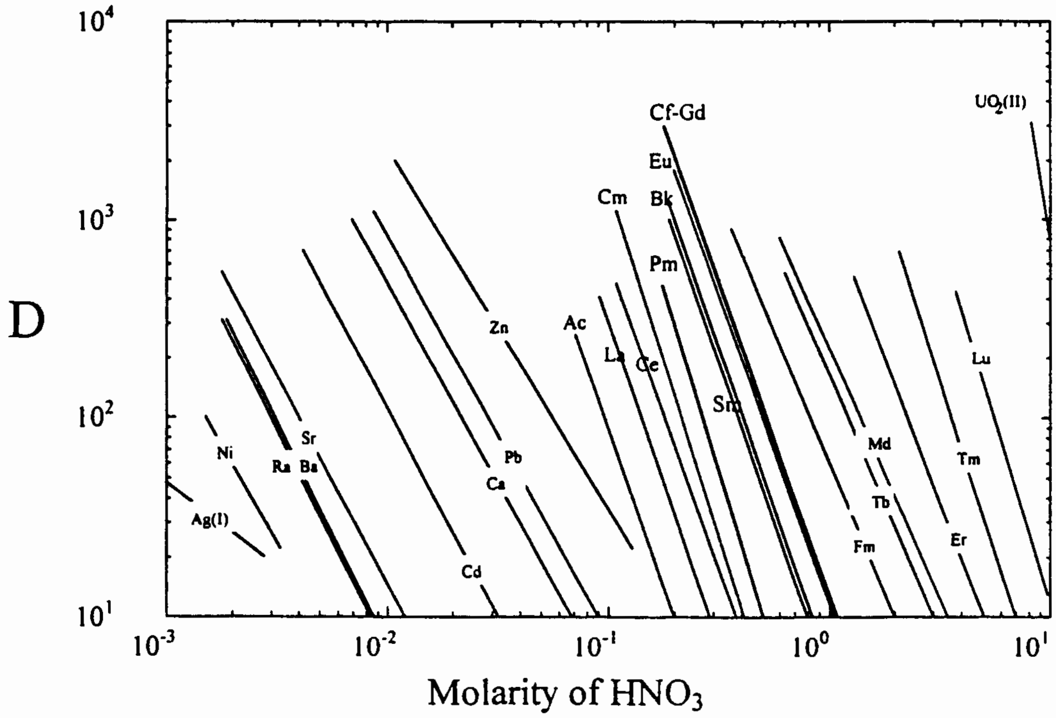

Figure 5. D vs HNO₃ Concentration for Various Metal Ions Using Undiluted HDEHP as the Stationary Phase (To Convert D to k' divide D by 4.3) [10]

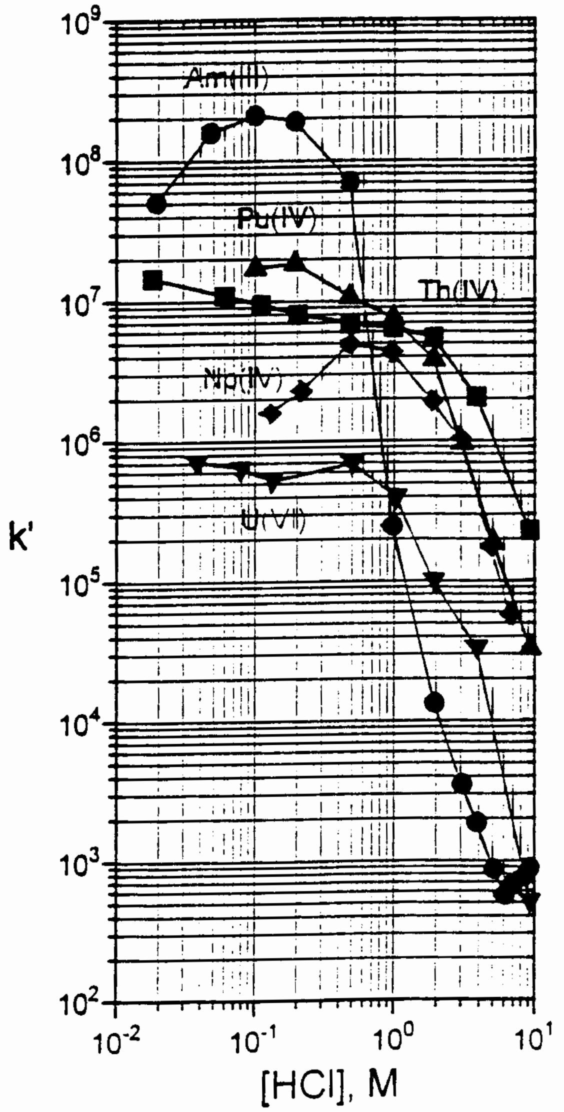

Figure 6. Acid Dependencies of the Uptake of Several Actinides by the Actinide Resin [5]

References

[1] J. L. Cortina and A. Warshawsky, “Developments in Solid-Liquid Extraction by Solvent Impregnated Resins”, In Ion Exchange and Solvent Extraction; Marinsky, J.A., Marcus, Y., Eds.; Marcel Dekker: New York, 1997; Vol. 13, p.195.

[2] M. L. Dietz, E. P. Horwitz, and A. H. Bond, “Extraction Chromatography: Progress and Opportunities,” Metal in Separation and Preconcentration: Progress and Opportunities, Bond, A. H., Dietz, M. L., Rogers, R.D., Eds.; ACS Symposium Series 716, American Chemical Society, Washington, DC, 1999, pp. 234-250.

[3] E. P. Horwitz, R. Chiarizia, and M. L. Dietz, “A Novel Strontium Selective Extraction Chromatographic Resin,” Solvent Extr. Ion Extr. 1992, Vol. 10, pp. 313-336.

[4] E. P. Horwitz, M. L. Dietz, R. Chiarizia, H. Diamond, S. L. Maxwell, III, and M. R. Nelson, “Separation and Preconcentration of Actinides by Extraction Chromatography Using a Supported Liquid Anion Exchanger: Application to the Characterization of High-Level Nuclear Waste Solutions,” Anal. Chim. Acta 1995, Vol. 310, pp. 63-78.

[5] E. P. Horwitz, R. Chiarizia, and M. L. Dietz, “Dipex: A New Extraction Chromatographic Material for the Separation and Preconcentration of Actinides from Aqueous Solution,” Reactive and Functional Polym. 1997, Vol. 33, pp. 25-36.

[6] E. P. Horwitz and C. A. A. Bloomquist, “The Preparation, Performance and Factors Affecting Band Spreading of High Efficiency Extraction Chromatographic Columns for Actinide Separations,” J. Inorg. Nucl. Chem. 1972, Vol. 34, pp. 3851-3871.

[7] E. P. Horwitz and C. A. A. Bloomquist, "High Speed-High Efficiency Separation of the Transplutonium Elements by Extraction Chromatography," J. Inorg. Nucl. Chem. 1973, Vol. 35, pp. 271-284.

[8] E. P. Horwitz, M. L. Dietz, R. Chiarizia, and R. C. Gatrone and A. M. Essling, R. W. Bane, and D. Graczyk, "Separation and Preconcentration of Uranium from Acidic Media by Extraction Chromatography," Anal. Chim. Acta 1992, Vol. 266, pp. 25-37.

[9] E. P. Horwitz, R. Chiarizia, M. L. Dietz, H. Diamond, and D. M. Nelson, "Separation and Preconcentration of Actinides from Acidic Media by Extraction Chromatography," Anal. Chim. Acta 1993, Vol. 281, 361-372.

[10] E. P. Horwitz and C. A. A. Bloomquist, "Chemical Separation for Super-Heavy Element Searches in Irradiated Uranium Targets," J. Inorg. Nucl. Chem. 1975, Vol. 37, pp. 425-434.

[11] E. P. Horwitz, M. L. Dietz, S. Rhoads, C. Felinto, N. H. Gale and J. Houghton, "A Lead-Selective Extraction Chromatographic Resin and its Application to the Isolation of Lead from Geological Samples," Anal. Chim. Acta 1994, Vol. 292, pp. 263-273.

[12] W. C. Burnett, D. R. Corbett, M. Schultz, E. P. Horwitz, R. Chiarizia, M. Dietz, A. Thakkar, and M. Fern, "Preconcentration of Actinide Elements from Soils and Large Volume Water Samples Using Extraction Chromatography," J. Radioanal. Nucl. Chem. 1997, Vol. 226, p. 121.