SEPARATION AND DETERMINATION OF RADIONUCLIDES IN ENVIRONMENTAL SAMPLES: EXTRACTION CHROMATOGRAPHY

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Introduction

Determination of radionuclides (e.g. Am, Pu, U and Th) in soil and sediment samples is required for monitoring of environmental radioactivity. This type of research is useful not only to monitor any possible accidental release of the elements from installed nuclear facilities but also to carry out studies on migration mechanisms of the elements in the biosphere. These elements are enriched in humans through numerous food chains and, even in small amounts, can cause health hazards. Accurate, reliable and rapid analytical methods with low detection limits are need to be determined the concentrations of radionuclides in environmental samples. Environmental radiochemical analyses have several steps such as sample pre-treatment, sample pre-concentration, separation of anaytes and determination. Many separation methods, using solvent extraction and ion exchange chromatography are applied to the preconcentration and separation of radionuclides. These methods are time-consuming, use large amounts of strong acids and produce organic wastes.

Recently, separation methods based on the extraction chromatography have became increasingly popular in radiochemical analyses. In this presentation, we briefly summarize the published literature on priciples and various applications of extraction chromatography method that have been commonly used in radionuclide separations.

Principles of the Extraction Chromatography

The complexity of most environmental matrices and the poor resolution of the detector systems for alpha and beta particles make the separation step essential. Numerous methods have described this separation step, including ion exchange, liquid-liquid extraction and combinations of both. However, extraction chromatography, which combines the advantages of both these procedures, has developed considerably in the last decade. It couples the selectivity of organic compounds in solvent extraction with the easier use and multistage character of a chromatographic process. Extraction chromatographic resins are prepared by simply coating or impregnating a solid support (e.g. silica or various polymers) with the extractant. This is usually accomplished by contacting the support with a solution of the extractant in a volatile solvent, which is then slowly evaporated off, or (less commonly) by incorporating the extractant directly into the support during its preparation [1]. The performance of an extractant chromatographic material is defined in terms of seven parameters: retention, selectivity, efficiency, capacity, stability (physical, chemical and radiolytic), ease of regeneration or reuse, and reproducibility. Column efficienty is a complex function of a number of system characteristics, including the mobile phase velocity, the diffusion coefficients of the metal ion in the stationary and mobile phases, the diameter of the support particles, the temperature, and the average depth of the stationary phase. ,

Applications of the Extraction Chromatography In Environmental Samples

Table 1 summarizes much of the work that has been recently conducted on extraction chromatographic systems for separations of radionuclide in samples.

Table 1. Applications of extraction chromatography in radionuclide separations of interest in environmental samples

Investigators	Column	Separation
Mathur et al. [2]	CMPO[a]/chromosorb-102 (CAC)	Am, Pu and U in PUREX HAW solution
Horwitz et al. [3]	U/TEVA Resin[b]	U
	TEVA Resin[c]	Th, Pu and Np
	TRU Resin[d]	Am in nuclear waste solutions
Michael et al. [4]	TnOA[e]/chromosorb-102 (TnOAC)	Pu
	CMPO/chromosorb-102 (CAC)	Am from laboratory acidic waste solutions
Rodríguez et al. [5]	TRU Resin	Pu, Am, Cm in samples from nuclear power plants
Goutelard et al. [6]	TRU Resin	Am and Cm from sediment samples and biological samples
Testa et al. [7]	HDEHP[f]/Microthene-710	Pu in sea sediments
	TOPO[g]/Microthene-710	Pu and Am
	HDEHP/Microthene-710	in lichens and mosses
Pilviö and Bickel [8]	TRU Resin	Th, U, Pu, Am
	UTEVA Resin	Th, U
	TRU Resin	Pu, Am in bone ash
Kim et al. [9]	TRU Resin	Am, Pu, Th, U
	TEVA/SCN Resin	Am
	U/TEVA Resin	U in soil and sediment samples
Torres et al. [10]	Sr Resin[h]	Sr in aquatic organisms
Pilviö and Bickel [11]	TEVA Resin	Pu
	TRU Resin	Am from MOX samples
	UTEVA Resin	U from Th
Mellado et al. [12]	TRU Spec	Transuranic elements
	U/TEVA Spec	U and tetravalent actinides
	Sr Spec	^{90}Sr in marine sediment
Lee et al. [13]	TBP[i] and HDEHP	Fission products from spent pressurized water reactor (PWR) fuels
Warwick et al. [14]	TRU Resin	Pu and Am in soils and sediments

[a]octyl(phenyl)-N,N-diisobutylcarbamoylmethylphosphine oxide. [b]UTEVA resin consists of a neutral organophosphorus diamyl amylphosphonate extractant adsorbed onto an inert polyacrylamide support. [C]TEVA resin is prepared by impregnating Amberchrom CG-71ms with undiluted Aliquat 336 (a mixture of the trioctyl and tridecyl methyl ammonium chlorides). [d]TRU resin is a commercial extraction chromatographic resin consisting of an octyl(phenyl)-N,N-diisobutylcarbamoylmethylphosphine oxide-tributyl phosphate mixture coated onto an inert polyacrylamide support. [e]tri-n-octylamine. [f]di(2-ethylhexyl)phosphoric acid. [g]tri-noctylphosphine oxide. [h]Sr resin consists of crown ethers, in particular 18-crown-6 in different derivate compounds, such as dicylohexano-18-crown-6 and dibenzo-18-crown-6, and sorbed on an inert polymeric support. [i]tri-n-butyl phosphate.

In 1997, for example, Goldstein et al. [15] suggested a simplified procedure to the solation of Am and lanthanides from other components of the sample (Fig.1.). Tracer recoveries for the air filter and water samples increased from ~54% for the prior method to ~70% for the new extraction chromatography separations.

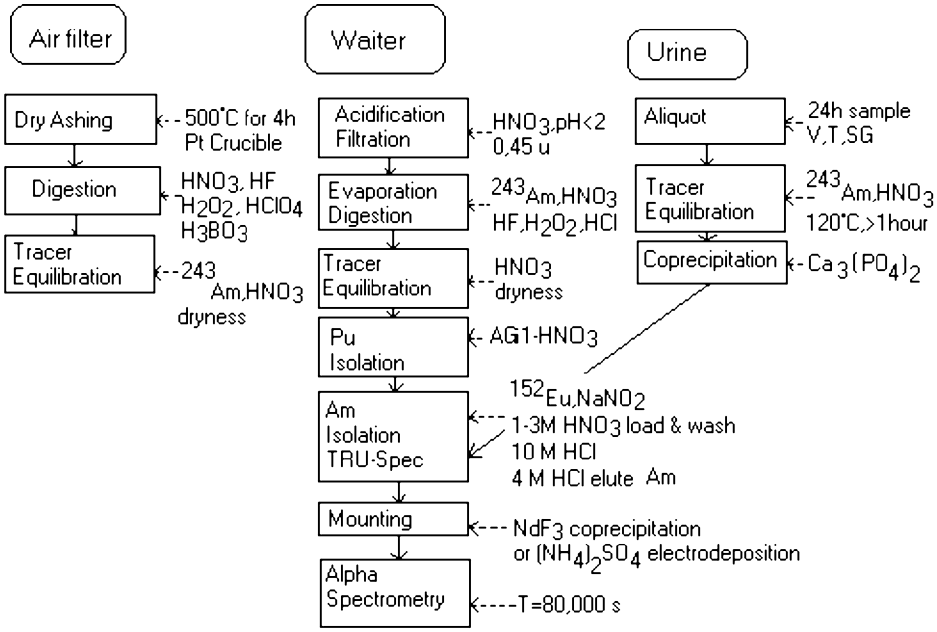

Figure 1. Flow chart illustrates the new analytical procedures for environmental and bioassay samples. These methods require to use a single 2 mL of extraction column volume for the isolation of Am from other components of the sample. The overall duration of the procedure has been shortened from 7 to 4 days [15].

The radioactive isotope ^{90}Sr belongs to the group of very toxic radionuclides effecting human health. For that reason, ^{90}Sr is determined in various kinds of natural samples from which it can enter the human organism. The natural samples containing radioactive strontium are contaminated with a large number of elements that interfere with its quantitative and qualitative determination. In addition, due to its radiochemical properties (a pure beta emitter with a low energy of beta particles), the determination itself is very complex and time-consuming. The extraction chromatography performed with the Sr resins combines the advantages of solvent extraction and ion exchange. It possesses the selectivity of solvent extraction and the ease of use of column chromatography. In almost all cases , the procedures in extraction chromatography are usually simpler than ion exchange chromatography,which is reflected in shorter analysis time, higher recoveries, and more reproducible results. Grahek et al. have reported that chromatographic separation of strontium from other cations (Ba,Ca,K,Cs,Y) was possible by means of nitric and sulphuric acids, while it is not possible with HCl [16]. This procedure was applied water and sediment samples. Isolated ^{90}Sr can be detected by means of Cherenkov counting.

Torres et al. [10] were also developed a method for the determination of ^{90}Sr in plankton and cod matrices using extraction chromatography. ^{90}Sr separation was carried out using Sr resin (EIChrom Inc.) column containing a crown ether sorbed on an inert substrate. Separation yields range from 80 to 100%. Columns have been used up to 10 times without causing any problems during experiments with model solutions.

A method involved the use of TEVA, TRU and UTEVA resin columns, manufactured by Eichrom, was previously presented for the separation of Th,U,Pu,Am and Np. This resin columns was studied by Horwitz et al. [3] in order to investigate their effective parameters.

The sheme for actinide separation from bone ash was shown in Fig 2. UTEVA resin was used to separate Pu, Am and Cm from Th and U [8]. The separation of Pu from Am and Cm was performed using TRU resin. The mean recoveries for the bone ash analyses were 78±2, 86±5, 81±5 and 76±4% for Th, U, Pu and Am, respectively.

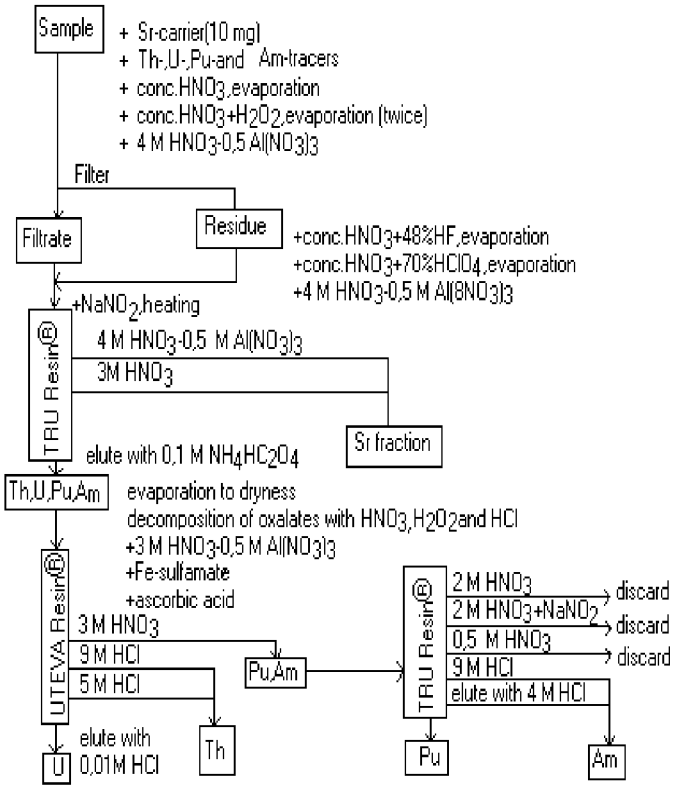

Figure 2. The scheme for separation of Th, U, Pu and Am from a bone ash matrix [8].

The wide use of nuclear power and clear waste disposal plans have made the public increasingly concerned about health hazards of radionuclide pollutants in nature. Actinides are considered to be the most toxic radionuclides in the environment since most of them are α active and have long half-lives. These elements are enriched in humans through numerous food chains and, even in small amounts, can cause health hazards. Accurate, precise, reliable and rapid analytical methods with low detection limits are therefore needed to be determined the concentrations of activides in environmental samples.

Rodriguez et al. [5] determined Pu, Am and Cm in radioactive waste by extraction chromatography (EC) and ion exchange chromatography (IC). The results obtained by both methods for the ^{238}Pu and $^{239/240}$Pu are in good agreement considering the experimental errors. ^{241}Pu value obtained by EC is higher than that obtained by IC. With respect to ^{241}Am, the value obtained by EC is higher than that obtained by IC. In this work, it had been reported that Fe and ^{238}Pu are interferences in the analysis of ^{241}Pu, ^{236}Pu and ^{241}Am, ^{244}Cm, respectively.

Two separation methods using TEVA and TRU resins had been applied to (1) the determination of Pu and Am in diluted MOX material (mixed oxide fuel pellet) and (2) the analyses of Th from four standart solutions [11]. Pu (IV) was extracted onto the TEVA Resin and Am (III) onto the TRU Resin. The scheme for the separation of Pu and Am was presented in Fig. 3. The activites of the samples were determined by alpha spectrometry. The chemical separation scheme of Th from impurities and other radionuclides was presented in Fig. 4.

Mellado et al. [12] have been used TRV spec, U/TEVA Spec and Sr Spec resins, to isolate Pu, Am, U, Th and Sr in marine sediment samples. The separation procedure for marine sediment samples was given in Fig. 5. It is reported that this method provides sufficiently well recoveries for Pu, U, Sr and Am in sediment samples.

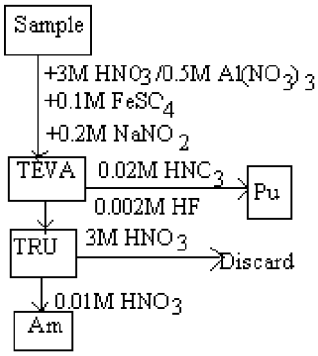

Figure 3. The scheme for the separation of Pu and Am using TEVA and TRU Resin columns [11].

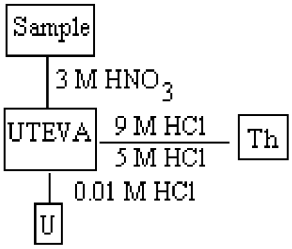

Figure 4. The scheme for the separation of Th and U using a UTEVA resin column [11].

Thorium separation from Ce performed by extraction chromatography method [17]. In our work, thorium that is associated with various impurities in leach solutions from Eskişehir Th ore sample was successfully separated from the other metal ions with a column coated TOPO [18]. Furthermore, a method for the pre-concentration and separation of uranium in low-level radioactive laboratory aqueous waste solution has been developed using extraction chromatography [19].

Conculation

Extraction chromatography provides a simple and convenient method of performing a wide variety of metal ion separations. It has been shown that the application of this technique eliminates most of the problems with regard to chemical isolation that are present in the standart procedure. Due to its mentioned advantages, it is clear that continues studies, focusing on the research and application of new extraction chromatographic materials can beuseful for the determination of the radinuclides.

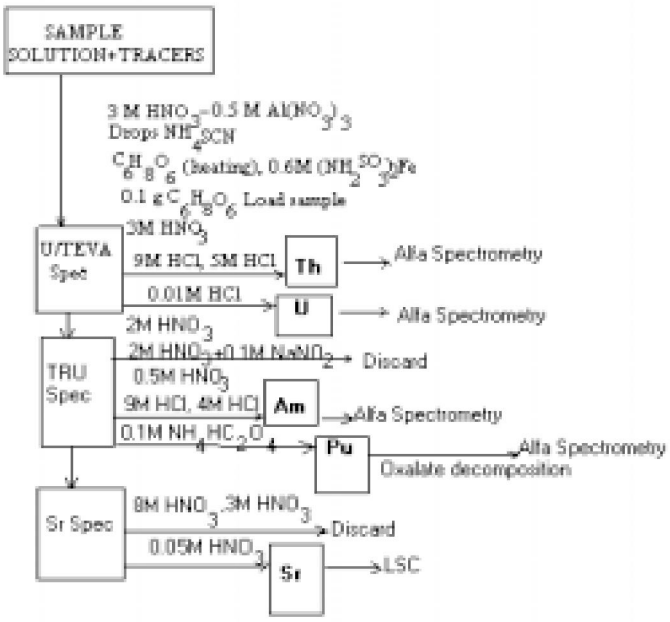

Figure 5. Separation method for the radionuclides analysis in marine sediment samples[12].

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