

THE APPLICATION OF NOVEL EXTRACTION CHROMATOGRAPHIC MATERIALS TO THE CHARACTERIZATION OF RADIOACTIVE WASTE SOLUTIONS*

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A simple method for the separation and preconcentration of radiostrontium from acidic nuclear waste solutions for subsequent determination is described. The method involves passage of the waste solution, acidified to at least 2M with nitric acid, through an extraction chromatographic column consisting of a 1M solution of bis-4,4'(5')[(t-butyl)cyclohexano]-18-crown-6 in 1-octanol sorbed on an inert polymeric substrate, which preferentially retains strontium. The strontium may then be stripped from the column with a small volume of either dilute ($\leq 0.05M$) nitric acid or water. Actinides present are removed quantitatively prior to strontium separation by passage of the sample through an actinide-specific extraction chromatographic column.

Introduction

The chemical treatment of nuclear wastes and the handling of associated effluent streams require detailed knowledge of the composition of the waste. Often, the necessary characterization involves the determination of various radionuclides in a complex and strongly acidic solution matrix. Previous work in this laboratory has led to the development of two new liquid-liquid extraction processes, TRUEX (for Transuranium Extraction) and SREX (for Strontium Extraction), for the selective removal of transuranic elements and radiostrontium, respectively, from acidic, high-level nuclear waste streams.^{1,2} In this report, we describe an extraction chromatographic system based on the SREX process and its application to the separation and preconcentration of strontium from nuclear waste samples for subsequent determination.

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The separation of radiostrontium from various waste solutions (e.g., aged fission product solutions) has been the subject of a number of previous reports.³⁻⁸ DALTON and WELCH³ for example, passed aliquots of a fission product solution through an anion exchange resin saturated with hydroxide ion. Most cations present were precipitated as the hydroxide and adhered to the resin beads. Radiostrontium and radiocesium were unaffected and passed directly through the column. The strontium was then purified by successive precipitation as the carbonate and the oxalate. BRYANT et al.⁴ adsorbed ⁹⁰Sr from a fission product solution on a cation exchange column and, after a suitable time for ingrowth, eluted the daughter ⁹⁰Y. After further purification, this was counted and the ⁹⁰Sr content of the original sample calculated. STOEPLER^{5,6} combined various features of these two methods to determine both ⁸⁹Sr and ⁹⁰Sr in fission product solutions. More recently, SELUCKY et al.⁷ extracted strontium from a fission product mixture using a solution of dicarbonyl and polyethylene glycol in a nitrobenzene/carbon tetrachloride mixture. Finally, LAMB et al.⁸ determined ⁹⁰Sr in nuclear fuel reprocessing solutions using ion chromatography.

Each of these methods of separation/determination, while generally yielding satisfactory results, suffers from various drawbacks. For example, methods involving precipitation are very tedious, requiring one or more steps to achieve a reasonably pure strontium fraction.³⁻⁶ (Adequate separation from barium is particularly difficult to achieve.) Other methods require the use of toxic solvents.⁷ Finally, none of the procedures is suitable for use with waste solutions containing high concentrations of nitric acid. As will be shown, an extraction chromatographic system consisting of a solution of a macrocyclic polyether (a "crown ether") dissolved in 1-octanol and sorbed on an inert substrate provides a simple method for overcoming these drawbacks. With this system, radiostrontium may be quickly and efficiently separated from a waste solution containing a number of other elements and a range of nitric acid concentrations.

Experimental

Reagents

The composition of the synthetic nuclear waste solution, "dissolved sludge waste" (DSW), is summarized in Table I. Note that this solution composition was chosen to match as closely as possible the solution expected from the dissolution of sludge from nuclear waste currently stored at the

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Westinghouse Hanford Site (Richland, WA) in nitric and oxalic acids. Actinide elements have been omitted, however, for ease of handling.

The crown ether, di-t-butylcyclohexano-18-crown-6 (DtBuCH18C6), was obtained from Parish Chemical Co. (Orem, UT) and used as received. Nitric

Table I. Composition of Synthetic Dissolved Sludge Waste

<u>Acids</u>	<u>Concentration</u> (mol/L)	<u>Inert</u> <u>Constituents</u>	<u>Concentration</u> (mol/L)
HNO ₃	1.0	Na	0.15
H ₂ C ₂ O ₄	0.05	Mg	0.0017
		Al	0.046
		Ca	0.0014
		Cr	0.0013
		Mn	0.0044
		Fe	0.15
		Ni	0.008
		Cu	0.0017
<u>Anions</u>			
F ⁻	0.008		
SO ₄ ²⁻	0.012		
NO ₂ ⁻	0.005		
<u>Fission Products</u>		<u>Fission Product Rare Earths</u>	
Sr	1.3x10 ⁻³	La	8.0x10 ⁻⁴
Y	6.0x10 ⁻⁴	Ce	2.3x10 ⁻³
Zr	3.2x10 ⁻³	Pr	7.1x10 ⁻⁴
Mo	1.8x10 ⁻⁴	Nd	2.3x10 ⁻³
Ru	2.1x10 ⁻³	Sm	2.8x10 ⁻⁴
Rh	5.5x10 ⁻⁴		
Pd	5.4x10 ⁻⁴	Eu	4.5x10 ⁻⁵
Ag*	3.0x10 ⁻⁵		
Cd	4.4x10 ⁻⁵		
Ba	6.6x10 ⁻⁵		

*Concentration shown is based on the quantity added, not on ICP/AES analysis.

acid solutions were prepared from the Ultrex reagent (J. T. Baker Chemical Co., Phillipsburg, NJ). Deionized water was obtained from a Milli-Q2 water purification system. All other reagents were A.C.S. grade and were used as received. Except for the actinides, which were obtained from Argonne stocks, all radiotracer solutions were obtained from Amersham (Arlington Heights, IL). Where necessary, aliquots were repeatedly evaporated to dryness and taken up in nitric acid to convert the tracer to the nitrate form.

Procedures

Preparation of Crown Ether Loaded Resins. Crude Amberlite XAD-7 (100-125 μm; Rohm and Haas, Philadelphia, PA) or Amberchrom CG-71 ms (50-100 μm; Supelco, Bellefonte, PA) was treated as previously described⁹ to remove traces

of preservatives and unreacted monomer. (Note that the Amberlite XAD-7 and Amberchrom CG-71 ms differ only in particle size.) Once purified, the resin (10 g) was slurried in methanol, along with 6.26 g of a 1 M solution of DtBuCH18C6 in 1-octanol. The resulting mixture was gently stirred for several minutes. The methanol was then removed under vacuum to yield ~ 16 g of the crown-loaded resin. This material, referred to hereafter as Sr*Spec resin, is now available from EIChroM Industries, Inc. (Darien, IL).

Column preparation and characterization. In experiments to determine appropriate conditions for strontium sorption and elution, a small quantity of Sr*Spec resin was slurried in 3 M HNO₃, and aliquots of the slurry were transferred under pressure to a 10 cm long glass Bio-Rad column (2.8 mm i.d.) equipped with polypropylene "Cheminert" fittings (Chromatronix Inc., Berkeley, CA). When the desired bed height had been reached, corresponding to a bed volume of ~ 0.6 cm³, the resin was resettled by backwashing. The resin was then rinsed with several bed volumes of 3 M nitric acid. Prior to use, the column was preconditioned with ~ 10 free column volumes of an appropriate nitric acid solution. Gravity flow rates (1-2 mL/min/cm²) were employed throughout. Relevant column parameters were determined as described by MARKL and SMIDT.¹⁰

For experiments involving synthetic waste samples, experiments were run in glass Bio-Rad Econo-columns (5.0 mm i.d.), this time using a 1 cm³ bed volume.

Measurement of weight distribution ratios

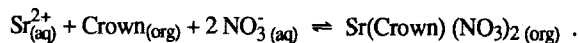
A weighed amount of resin (50-100 μm Sr*Spec) was placed in a culture tube and a measured volume of ⁸⁵Sr-spiked nitric acid solution of the appropriate concentration was added. A magnetic stirring bar was inserted and the mixture stirred until equilibrium was reached (as indicated by no further change in the activity of the aqueous phase). After centrifugation, a portion of the aqueous phase was drawn off and filtered to remove any suspended resin. An aliquot was then taken for gamma counting. From the measured activity and that of the initial solution, the weight distribution ratio of Sr²⁺ between the resin and the aqueous phase, D_w , can be calculated. From this, the capacity factor, k' , of the resin at the acidity used may be calculated by first converting D_w into a volume distribution ratio (D) (the density of the adsorbed extractant solution is 0.912 g/L.), then using the relation $k' = D \times \frac{V_s}{V_m}$, where V_s and V_m are the stationary phase and mobile phase volumes, respectively.

Apparatus

γ -counting was carried out on a Beckman Biogamma or a Packard Autogamma counter. Determination of non-radioactive elements was performed using inductively coupled plasma atomic emission spectroscopy (ICP-AES) as described previously.¹¹

Results and Discussion

Previous work in this laboratory has established that strontium may be efficiently extracted from aqueous nitric acid (≥ 1 M) using a solution of DtBuCH18C6 in 1-octanol and that extracted strontium may be recovered simply by contacting the organic phase with either water or dilute (e.g., 0.05 M) nitric acid.² This behavior is consistent with the following extraction equilibrium:



Since there is a direct relationship between the volume of solution required to elute a sorbed ion from an extraction chromatographic column and the ion's distribution ratio (here, $D = [\text{Sr}(\text{Crown})(\text{NO}_3)_2]_{\text{org}} / [\text{Sr}^{2+}]_{\text{aq}}$) in the corresponding liquid-liquid system, it follows that increasing retention of strontium on the Sr*Spec column should be observed as the nitric acid concentration of the sample solution rises. As shown in Figure 1, which depicts the capacity factor for the resin (i.e., the number of free column volumes, FCV., of eluent required to reach the peak maximum) as a function of nitric acid concentration, this is indeed the case. It is important to note here that solutions of DtBuCH18C6 in 1-octanol have also been shown to extract measurable quantities of nitric acid.² This extracted acid could increase the volume of dilute nitric acid or water required to strip the strontium from the column, lowering the concentration factor. As a result, high nitric acid concentrations are not optimal for sample loading; rather, a nitric acid concentration of ~ 2-3 M is preferred. Such a concentration yields acceptable sorption of strontium without making excessive volumes of strip solution necessary.

Figure 2 depicts the elution behavior of strontium on two different particle size Sr*Spec resins using 3 M nitric acid as the eluent. As can be seen, for the finer particle material, more than 50 FCV. of acid may be passed

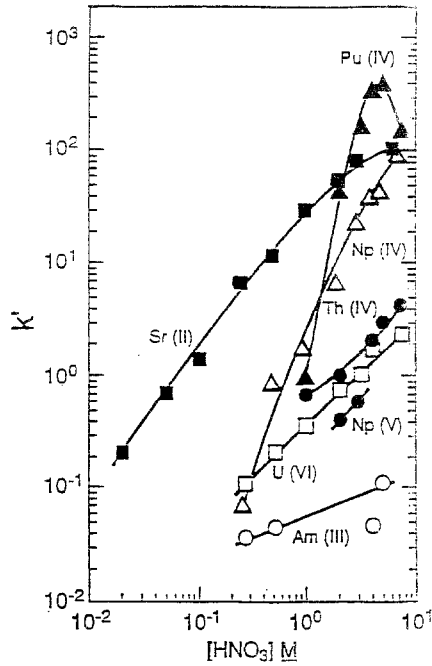


Fig. 1. Acid dependency of k' for selected ions ($T = 23^\circ C$).

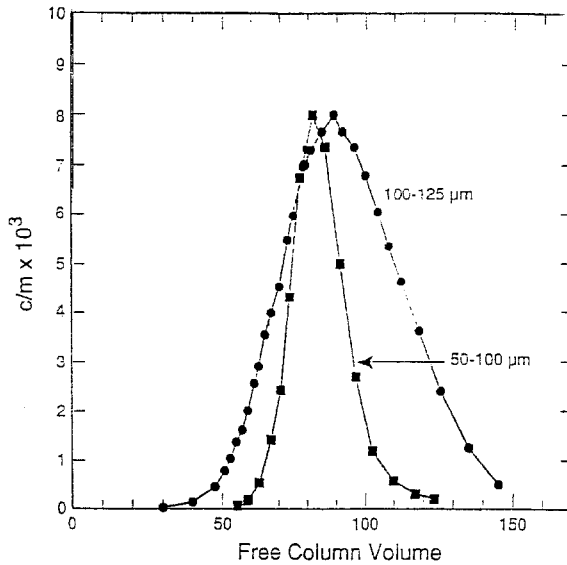


Fig. 2. Elution curves for Sr^{2+} on Sr-Spec resin (Elutrient: $3.2 M HNO_3$; $T = 23^\circ C$).

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through the column before measurable breakthrough of strontium occurs. This is significant because it indicates that the column can be thoroughly rinsed after sample loading to remove other ions without appreciable loss of strontium. Note that the position of the peak corresponds closely to the value of k' shown for this acidity in Figure 1.

Table II summarizes the elution behavior of each of the constituents of the dissolved sludge waste solution on the 50-100 μm resin. With few exceptions, each of the test elements can be completely eluted with 10 FCV. or less of 3 M nitric acid. One notable exception is barium. For it, breakthrough does not occur until ~ 11 FCV. and elution continues until ~ 30 FCV. Nonetheless, its elution is complete before strontium breakthrough. Obviously, many actual waste samples will also contain actinide elements (i.e., U, Th, Pu, Np, and Am). Of these, however, only tetravalent Pu and Np are retained by the Sr*Spec column (Figure 1). In an actual analysis, these would be removed quantitatively by passing the sample through an actinide-specific extraction chromatographic column (based upon the TRUEX process⁹) prior to its introduction to the Sr*Spec column.

Table II. Elution Behavior of DSW Constituents on a Sr*Spec Column*

Element	Percent of Element Found in Fraction						0.05 M
	FCV.	3 M HNO ₃				HNO ₃	
	1-5	6-10	11-15	16-20	21-25	26-30	31-40
Na	100	--	--	--	--	--	--
Mg	100	--	--	--	--	--	--
Al	100	--	--	--	--	--	--
Ca	100	--	--	--	--	--	--
Cr	100	--	--	--	--	--	--
Mn	100	--	--	--	--	--	--
Fe	99	0.6	0.2	0.4	--	--	--
Ni	100	--	--	--	--	--	--
Cu	100	--	--	--	--	--	--
Sr	--	--	--	--	--	--	99
Y	100	0.1	--	--	--	--	--
Zr	91	0.4	0.2	--	--	--	--
Mo	-----84-----		-----16-----		--	--	--
Ru	100	--	--	--	--	--	--
Rh	100	--	--	--	--	--	--
Pd	100	--	--	--	--	--	--
Ag	15	88	2	--	--	--	--
Cd	100	0.1	--	--	--	--	--
Ba	--	--	53	42	6	0.7	--
La	100	--	--	--	--	--	--
Ce	100	--	--	--	--	--	--
Pr	100	--	--	--	--	--	--
Nd	100	--	--	--	--	--	--
Sm	100	--	--	--	--	--	--
Eu	100	--	--	--	--	--	--

* Because of uncertainties inherent in the ICP-AES method used for quantitation, the percentages shown for a given element may not total to 100%.

Note that for this particular experiment, strontium was eluted from the column with a single 10 FCV. aliquot of dilute (0.05 M) nitric acid. In certain situations, where it may be desirable to concentrate the radiostrontium present as much as possible, the strontium (99%) can be recovered in a smaller volume (3-4 FCV.) of deionized water. Assuming a 40 FCV. sample (which would permit a 10 FCV. column rinse before Sr breakthrough), this would correspond to an ~ 10-fold concentration of the strontium present.

Decontamination factors (i.e., the ratio of the concentration of the test element in the feed solution, here DSW, to the concentration of the same element in the strontium fraction) obtained with the Sr*Spec column range from ~ 10^2 (for Al) to over 10^5 (for Ca). Large values of this factor, such as are observed here, indicate a satisfactory separation of strontium from the test element, that is, an effective decontamination of the strontium fraction.

Conclusions

The results presented here demonstrate that a solution of DtBuCH18C6 in 1-octanol, supported on an inert substrate, provides a simple and effective method for the isolation of radiostrontium from waste solutions for subsequent determination. Because of its excellent selectivity for strontium, problems associated with interferents (e.g., ^{140}Ba , ^{140}La , ^{103}Ru , ^{95}Zr)⁴ are greatly reduced. Although certain elements (e.g., K, Pb) do adversely affect strontium retention by the resin¹², these materials are not encountered in appreciable quantities in typical nuclear waste streams. For samples containing sufficient nitric acid, no pretreatment is necessary prior to introduction of the sample to the column. The lack of need for reagents other than nitric acid means little additional waste generation during the separation/determination process.

Although information concerning the long-term stability of the material is not yet available, no deterioration in column performance has been noted even after passage of hundreds of free column volumes of water or nitric acid. Thus, the columns can be reused several times.

An obvious extension of the use of Sr*Spec resin to isolate radiostrontium for analysis is the process-scale treatment of waste solutions for volume reduction. The suitability of the resin for such an application will depend upon its stability to both contact with large volumes of nitric acid and prolonged irradiation. Work to address these issues is now underway in our laboratory.

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