

THE SELECTIVE SEPARATION OF ANIONS AND CATIONS IN NUCLEAR WASTE USING COMMERCIALLY AVAILABLE MOLECULAR RECOGNITION TECHNOLOGY (MRT) PRODUCTS

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ABSTRACT

This paper describes the use of some of IBC's SuperLig®, MacroLig®, and AnaLig® molecular recognition technology products to effectively and selectively separate and recover cesium, technetium, strontium, and radium from radioactive waste solutions. Distinct advantages are given over conventional separation techniques. Separations are described and results given for the target ions over chemically similar ions often present at much higher concentrations. The separations are performed in solutions of either high or low pH and usually containing high concentrations of salts. Other separations involving components (Hg^{2+} , Pb^{2+} , UO_2^{2+} , Pu(IV) , I^- , and Bi(III)) of radioactive and mixed waste are noted.

INTRODUCTION

A formidable technical and financial challenge faces the U.S. Department of Energy. The cost of remediation of the 4×10^8 liters of high-level and low-level radioactive waste stored at its Hanford, Savannah River, Oak Ridge, Idaho, and Fernald sites (1) has been estimated to be 100 billion U.S. dollars (1,2). In addition, radioactive waste is accumulating worldwide at a significant rate from the generation of electric power using nuclear reactors. The magnitude of the task is indicated as follows in a recent C & EN article (3): "In the past ten years or so, the government has spent some \$60 billion on cleanups, which have mostly resulted in waste containment. At least another \$200 billion and 70 years are thought to be needed to address environmental damage to more than 100 sites that participated in the nation's nuclear weapons program".

A major goal of the radioactive nuclear waste treatment program is the selective removal of ^{137}Cs and ^{90}Sr (4). Nuclear plant operation produces large volumes of these nuclides which are highly radioactive (^{137}Cs is a β^- emitter (5) and ^{90}Sr is a β^- emitter (6)) and have half-lives of 30.2 years (^{137}Cs) and 29 years (^{90}Sr). Removing these radioactive nuclides from nuclear wastes would result in a significant radioactivity and volume reduction. The latter would result in markedly reduced storage costs. Much effort has been put into developing, testing, and using various methods to achieve effective separations of ^{137}Cs and ^{90}Sr from radioactive waste (7). These methods have included organic ion exchangers (8, 9), electrically switched ion exchange (10), ion chromatography (9), precipitation (8), solvent extraction (11, 12), solid-liquid extraction (13), inorganic ion exchangers (14), and adsorption (5, 15). Recently, predesigned macrocyclic compounds have been used with considerable success in the selective removal of these ions (4, 13, 16-23).

The technical challenge of radiocesium removal from high-level tank wastes has been described (16). In addition to the technical challenges, Cs^+/Na^+ and Cs^+/K^+ selectivities must be adequate. Accomplishment of required selectivities requires the use of specially designed macrocyclic molecules of the crown ether and calixarene types (17, 18). We (24, 25) were the first to show the high selectivity of

several calixarenes for Cs^+ over other alkali metal ions using competitive transport in liquid membrane systems. Selectivities of Cs^+/Na^+ of *ca.* $10^4 - 10^5$ and of Cs^+/K^+ of 80-600 have been achieved using calixarene-type macrocycles (17). Wastes under study may contain as much as 1 M K^+ in a typical matrix containing 5-7 M Na^+ , but only 10^{-6} to 10^{-3} M Cs^+ (17). Selectivities for Cs^+ over K^+ have been increased markedly to >4200 by new dideoxygenated calix[4]arene crown-6 ethers (17).

^{99}Tc is produced in nuclear processing plants, nuclear weapons tests, and nuclear power plants (26). The half-life of ^{99}Tc is 2.13×10^5 years. Entrance of this radionuclide into the environment is of great concern (27). In oxygenated and suboxygenated environments, ^{99}Tc is in the form of TcO_4^- , which is chemically stable, highly soluble, and highly mobile in ground water and other aqueous environments (26). A number of studies have been aimed at developing ion exchange resins (16, 26, 28) and a novel macrocycle extraction agent (29) for TcO_4^- removal.

This paper describes case studies of the use of commercial products developed by IBC and currently in industrial use for the separation of radionuclides from different waste types. Uses of the following materials will be described: SuperLig® 644 for Cs removal and SuperLig® 639 for Tc removal; SuperLig® 620 and SuperLig® 640 prepared at IBC and used in Rad Disks manufactured by 3M for the selective separation and analysis of Sr and Ra, respectively; and MacroLig® 209 (BOB Calix C6) used in the cesium solvent extraction (CSSX) Process at Savannah River, South Carolina. Separations of several other anions and cations of interest to the nuclear industry will be noted.

MOLECULAR RECOGNITION TECHNOLOGY

Separations involving nuclear waste components present severe challenges to existing separation procedures. These challenges include removal from highly acidic or highly basic matrices and from high concentrations of often-competing anions and cations. The difficulties are usually compounded by the target species being present in very small concentration in the presence of high concentrations of chemically similar species. A review of common traditional as well as recently developed novel separation procedures together with the basis, advantages, and disadvantages of each procedure has been given (30). In general, traditional procedures rely on inexpensive reagents and are not designed to achieve the highly effective and selective separations usually required to effectively and selectively separate target ions in the nuclear waste field.

A significant and successful effort has been made by IBC Advanced Technologies, Inc. (IBC) to develop and commercialize solid phase extraction (SPE) technology for nuclear waste separations using an approach based on the designed specificity of host-guest recognition. The basis of this approach is the design and synthesis of host molecules with pre-determined selective affinities for specific target cation or anion species. This molecular recognition technology (MRT) approach takes into consideration at the design level the speciation at the pH of the solution in which the separation must occur, the nature of the matrix from which the target species must be removed, the relative affinities of the target and matrix guest species for the host, and the means for selectively eluting the target species from the solid phase employed. It is evident that considerable knowledge and skill are required to develop satisfactory SPE procedures. The desirable features of an effective separation system are summarized in Table I (30).

It is apparent that the requirements listed in Table I impose severe challenges for the development of effective separations procedures for given target species. Traditional technologies fail or perform poorly on many of the points in Table I (30). However, the MRT approach developed at IBC has produced several effective products that are now used commercially in the analysis and separations of components of nuclear waste. The SPE particles are called SuperLig® and are identified by number. In these particles, the host ligand and solid phase support are connected by a spacer (30). This spacer is attached by stable covalent bonds to the ligand and the solid phase support. The spacer is important in that it allows the ligand to be immersed in the aqueous phase. The solid phase must be compatible with the solution from which the separation is made and must not dissolve in or react with the medium used. A variety of supports have been used allowing effective separation to be made in highly acidic, highly basic, and HF-containing solutions (23).

Table I. Requirements for an Effective Separation System (30)

1. Have sufficient specificity for the target species even if present at ppm/ppb level in the presence of high concentrations of other similar species.
2. Have sufficient specificity for a given oxidation state of an element when the element has multiple oxidation states.
3. Have sufficient selectivity for the target species when it is in a difficult matrix, such as a strong acid, strong base, F ⁻ /HF, redox agents, other complexing agents, high solute concentrations.
4. Be capable of operation without adding potential contaminants, such as solvents, replacement ions, precipitants.
5. Be capable of removing target species to sufficiently low target levels.
6. Be capable of handling large solution volumes at rapid flow rates.
7. Have rapid separation kinetics for diffusion, host-guest interaction, and host-guest dissociation.
8. Have adequate longevity due to resistance/stability to matrix chemical effects, including, if applicable, intense nuclear radiation, acid/base, redox, and other chemical reactants.
9. Be capable of automation in a continuous mode.
10. Be capable of concentrating desired species by large factors leading to rapid and efficient recovery of highly purified product.

Another configuration in which the SuperLig® materials are used involves Empore membranes (23). These thin membranes (0.5 mm) manufactured by 3M are composed of SuperLig®-containing materials, which are enmeshed in an inert, fibrous matrix without using binders or adhesives. The particles can compose up to 95% of the membrane's weight and are very small compared to particles used in typical SPE columns. The small particles are closely packed and flow rates are 10 to 2000 times faster than those in columns. Equal extraction efficiencies are achieved. Channeling or wall effects typical of columns are absent.

For the past decade, IBC and 3M have combined selective separation particles with Empore technology to produce a novel and effective separation procedure. The resulting Empore disk may be considered to be a short column that is much more compact than a normal column. The enclosed SuperLig® material has a mesh size of less than 10 µm (compared to 100 µm in the column mode) allowing for a very large concentration of active sites. Much more rapid separations are possible than with a fixed bed column or with ion exchange (23, 30, 31). Flow rates in the Empore system can be up to 2,000 times faster than those in column and ion exchange systems. An important feature of Empore systems is that the selectivity and separation ability of the SPE ligands are maintained at these flow rates making it possible to effectively and rapidly separate trace amounts of target species from large volumes of solution. Examples will now be described of the use of SuperLig® products in separating and recovering species of interest to the nuclear waste program. In each case, the product is in commercial use.

NUCLEAR WASTE SEPARATIONS

In this section, the use is described of SuperLig® 644 and SuperLig® 639 to remove ¹³⁷Cs and ⁹⁹Tc, respectively, from three Hanford nuclear waste solutions and the use of a new calixarene derivative to remove ¹³⁷Cs from Savannah River nuclear waste solutions. The constituents of the three Hanford waste solutions (Envelopes A, B, and C) are given in Table II together with their concentrations.

Cesium

Hanford, Washington

The separation of Cs from actual Hanford alkaline nuclear waste illustrates well the use of MRT. The requirements for the separation are four fold (30). First, the SuperLig® material used must be capable of high selectivity of Cs^+ over Na^+ and K^+ . This requirement results because the nuclear waste solution (see Table II) contains large amounts of these ions, which are chemically similar to Cs^+ . Feed solution ratios of Na: Cs and K: Cs are around 100,000 and 2,000, respectively. Second, the affinity of the SuperLig® material for Cs^+ must be large enough to be able to reduce the total (radioactive and non radioactive) Cs^+ concentration to the low ppb/ppt range. Third, the Cs should be eluted in a relatively small volume of dilute HNO_3 (5-15 bed volumes). Fourth, integrity of the SuperLig® material must be retained in the presence of a highly basic solution. Finally, the SuperLig® material must resist degradation from the radioactive solution for a sufficient period of time or volume of liquid ($10^8 - 10^9$ rads).

Samples of Envelopes A (19,22), B (20), and C (21) Hanford High Level Waste Supernate were tested at the Savannah River Technology Center with SuperLig® 644 containing columns for cesium removal. The results demonstrate the ability of the SuperLig® 644 to effectively remove ^{137}Cs from the test solutions. The percent removal of ^{137}Cs during polishing of the Cs was 99.988 ± 0.001 (Envelope B), 99.985 ± 0.005 (Envelope C), and > 99.99 for Envelope A (22).

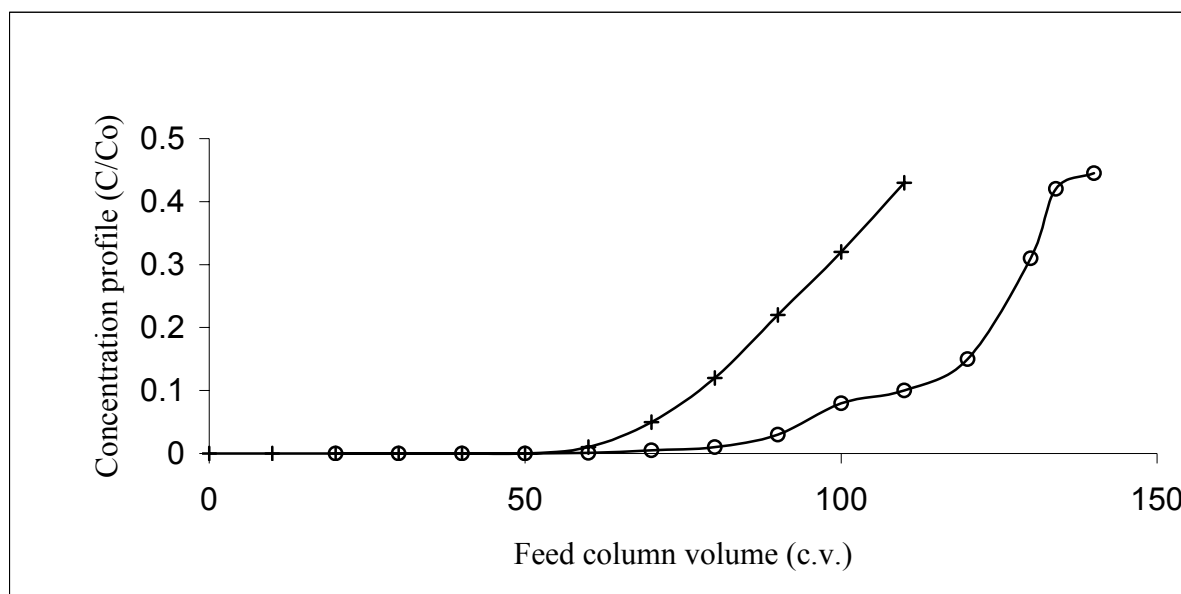


Figure 1. Breakthrough profiles for ^{137}Cs from Envelope B (+) and Envelope C (B) salt solution using SuperLig® 644. (20, 21)

In Figure 1, breakthrough profiles for ^{137}Cs are given for Envelopes B and C salt solutions with SuperLig® 644. The results in Fig. 1 show two important points. First, polishing level ^{137}Cs removal is found up to a feed of approximately 55 column volumes in both cases indicating strong and selective binding of ^{137}Cs to SuperLig® 644. Second, 50% breakthrough ($C/C_0 = 0.5$) is reached at approximately 120 to 140 feed column volumes. These results exceed the design criteria for these separations, which are usually $C/C_0 = 0.5$ at 100 column volumes.

A typical elution profile for ^{137}Cs from Envelope B salt solution with SuperLig® 644 is given in Figure 2. The elution is accomplished with 0.5 M HNO_3 at one column volume per hour in well under the 15-column volume requirement.

Savannah River, South Carolina

The separation of Cs from nuclear waste solutions at Savannah River is being accomplished by a solvent extraction process (11) using a calixarene crown extractant and process developed at Oak Ridge National

Laboratory (ORNL), and tested at Argonne National Laboratory. The calixarene crown extractant is manufactured by IBC. The experimental procedure has been described in detail (11).

Table II. Concentrations (M unless otherwise indicated) of Constituents in Hanford Waste, Envelopes A, (19) B, (20), and C (21).

Constituent	Envelope A	Envelope B	Envelope C
Na	5.07	5.7	5.71
K	0.448	0.14	0.026
Al	0.468	0.86	0.0021
Ca	0.0002	0.00055	0.0086
Cd	0.000013	-	-
Cr	0.00089	0.024	0.0011
Fe	0.00057	-	0.0069
Mo	0.00031	-	-
Ni	0.000079	-	-
P	0.0058	0.0092	-
Pb	0.00017	-	0.00076
Si	0.00143	0.0082	-
Sn	0.00051	-	-
Zn	0.000088	-	0.000103
Zr	0.000034	-	-
Cl ⁻	0.0769	0.17	0.033
F ⁻	-	-	0.063
OH ⁻	2.33	-	0.394
NO ₃ ⁻	1.39	1.41	2.48
NO ₂ ⁻	0.875	1.43	0.829
PO ₄ ³⁻	-	<0.058	<0.063
SO ₄ ²⁻	<0.010	<0.058	<0.063
Formate ion	-	-	<0.133
Oxalate ion	0.011	-	<0.068
TIC	0.150	-	0.95
TOC	0.279	-	2.68
Sr – 90	0.026 Φ CiAmL	-	70.3 Φ CiAmL
Cs – 137	204 Φ CiAmL	293.8 Φ CiAmL	246 Φ CiAmL
Tc – 99	0.060 Φ CiAmL	0.121 Φ CiAmL	0.051 Φ CiAmL
Eu – 154	-	-	0.42 Φ CiAmL
Am – 241	-	-	<0.29 Φ CiAmL
Pu – 239/240	0.014 Φ CiAmL	-	-
Pu – 238	0.124 Φ CiAmL	-	-
U	-	1.38 mgAL	-

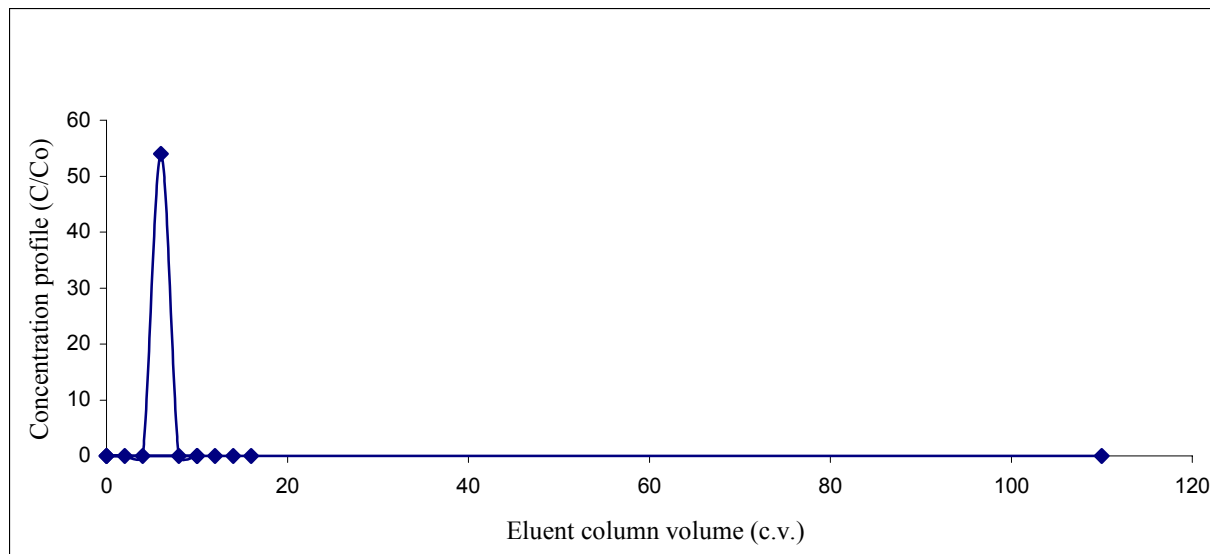


Figure 2. Elution profile for ^{137}Cs removed from Envelope B salt solution with SuperLig® 644 (20).

The results demonstrate that the technique is a very attractive one for the removal and concentration of cesium from the Savannah River alkaline-side tank wastes (11). The compound used is MacroLig® 209, calix[4]arene-*bis*(*tert*-octylbenzo-crown-6), designated as BOBCalixC6. The structure of BOBCalixC6 is shown in Figure 3.

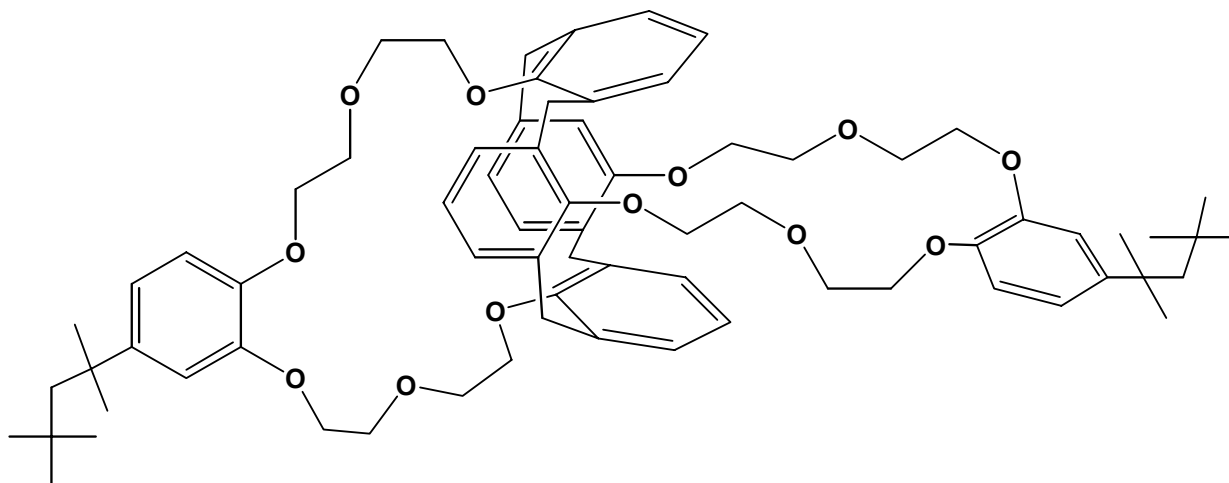


Figure 3. Structure of MacroLig® 209, Calix[4]arene-*bis*(*tert*-octylbenzo-crown-6)
"BOBCalixC6"

Technetium

SuperLig® 639 was tested for its ability to remove $^{99}\text{TcO}_4^-$ from the salt solutions in Envelopes A, B, and C (compositions shown in Table II). It was found to be more effective in Envelopes A and B, than in Envelope C. Removal percentages were 96 or 94 (two different batches) (19), 98.93 ± 0.22 (20), and 20.5 ± 23.6 (21) for Envelopes A, B, and C, respectively. The low value in the case of Envelope C was

attributed to the ^{99}Tc being present in oxidation states other than +7 (TcO_4^-). SuperLig® 639 is not effective in removing Tc when the Tc is present in one of these lower oxidation states. It is of interest that SuperLig® 644 removed the ^{99}Tc present in the lower oxidation states (21). The results for Envelopes A and B demonstrate the effectiveness of SuperLig® 639 in removing $^{99}\text{TcO}_4^-$.

Removal of TcO_4^- can be effectively accomplished from the Hanford solutions. The following criteria are set for technetium removal by SuperLig® 639. First, high TcO_4^- selectivity in $\sim 2\text{ M NO}_3^-$, 1 M NO_2^- , 0.5 M Al(OH)_4^- , $1\text{--}5\text{ M OH}^-$, and other constituents at lower concentrations. Second, high TcO_4^- removal above the ninety percent level for Envelopes A and B. The percentage of Tc removed does depend on the Tc oxidation states present. Third, elution of the TcO_4^- in a relatively small volume of H_2O (5-15 bed volumes). Finally, high chemical and radioactive (10^7 rads) stability of the SuperLig® 639 material.

M^cCabe and co-workers (22) tested SuperLig® 639 for its ability to remove $^{99}\text{TcO}_4^-$ from Hanford Tank 241-AN-103 salt solution. The design criterion for the test was that 50% breakthrough would be reached at 100 column volumes. This design criterion was exceeded using SuperLig® 639 as indicated in Figure 4. The Tc polishing over the first 60 column volumes is also above 90% as needed.

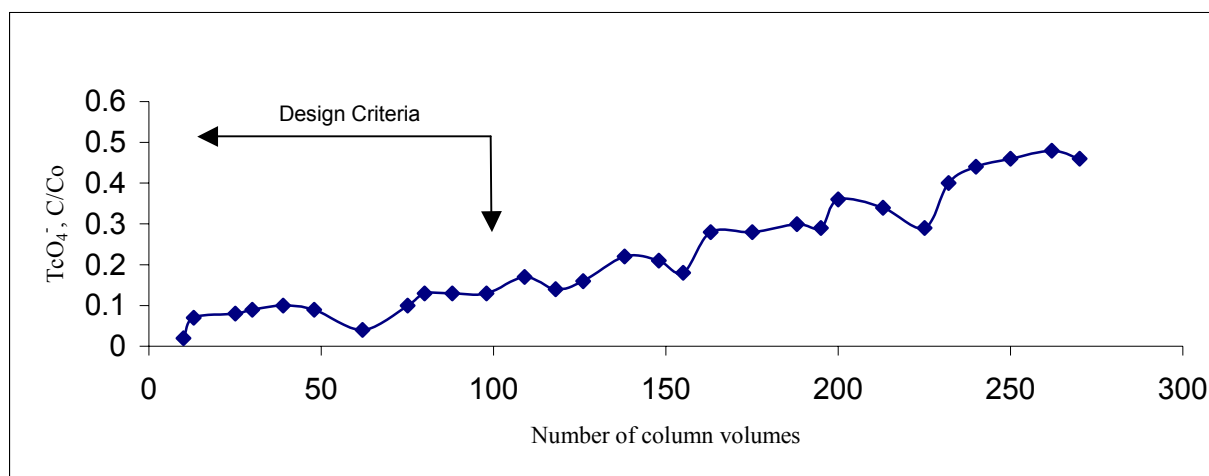


Figure 4. Breakthrough profile for TcO_4^- using SuperLig® 639 small-scale radioactive test with Hanford Tank 241-AN-103 salt solution (22).

The effect of radiation levels on the effectiveness of SuperLig® 639 in the removal of TcO_4^- is given in Table III. As measured by the K_d value, TcO_4^- binding by SuperLig® 639 is not affected up to a dose level of 1×10^7 rads. Above this level, the effectiveness decreases to less than 10% of the base K_d value at 1×10^9 rads.

Table III. Effect of Radiation Levels on SuperLig® 639 Effectiveness

Radiation Dose (Rads)	TcO_4^- K_d (ml/g)
0	285.7
1×10^7	298.6
1×10^8	142.4
3×10^8	124.1
6×10^8	65.38
1×10^9	24.9

STRONTIUM AND RADIUM SEPARATION AND ANALYSIS USING 3M RAD DISKS

In a joint program involving IBC, 3M, and Argonne National Laboratory, a novel and effective separation procedure has been developed. Resulting commercial products combine highly selective IBC SuperLig® materials with 3M Empore® membranes to produce Rapid Analysis Products (RAP). RAP are available for Sr and Ra and are termed Empore Rad Disks (23). IBC, 3M, and Argonne National Laboratory won an R & D 100 award for Empore Rad Disks in 1996 (32). This award was subsequently selected as being in the top one percentile of all awards ever given by R&D Magazine (33). These Rad disks have significant advantages over traditional analysis methods. These advantages and details of the analysis procedure have been given (23). The disks are available commercially from the 2002/2003 Fisher catalog. A summary is given here.

Strontium Rad Disks

The time advantage of the Sr Rad disks is illustrated by comparing the time of separation using them with that using the published EPA Method 905 for Sr (34). The EPA method lists over fifty steps for the separation and analysis of ^{90}Sr whereas the Rad disk method requires only six steps and about thirty minutes to perform (35, 36). The reduction in number of steps and time required for the analysis amount to considerable savings in cost.

The procedure for analysis with the Sr Rad disk (35, 36), which contains SuperLig® 620, is accomplished by passing a sample in 2 M HNO_3 through a 47 mm disk positioned on a vacuum filter apparatus at a rate of $50 \text{ mL} \cdot \text{min}^{-1}$. The immobilized radioactive Sr can then be quantified using a variety of well-known techniques (23).

Interference studies by various cations for the Sr Rad disk have been reported (23, 36, 37). Strontium recoveries are 95% or greater for the following interfering cation levels: Mg^{2+} , $10,000 \text{ mg} \cdot \text{L}^{-1}$; Ca^{2+} , $500 \text{ mg} \cdot \text{L}^{-1}$; Ba^{2+} , $0.1 \text{ mg} \cdot \text{L}^{-1}$; Ra, $300 \text{ pCi} \cdot \text{L}^{-1}$; Pb^{2+} , $1 \text{ mg} \cdot \text{L}^{-1}$; Na^+ , $1000 \text{ mg} \cdot \text{L}^{-1}$; K^+ , $10 \text{ mg} \cdot \text{L}^{-1}$. It is of particular interest that high separation levels are obtained at high H^+ , Mg^{2+} , Ca^{2+} , and Na^+ levels, since all or some of these cations are usually common in environmental samples.

Radium Rad Disks

Use of Ra Rad disks results in a reduction in the number of steps necessary for Ra analysis (38) similar to that described earlier for Sr analysis. The most significant Ra health hazards result from the isotopes ^{226}Ra and ^{228}Ra , which have their origin in the naturally occurring ^{238}U and ^{232}Th decay chains. These Ra isotopes can be determined simultaneously using the Ra Rad disk. The various procedures that have been used to determine the immobilized Ra have been described and discussed (23). Ion interferences (defined as the levels at which ^{226}Ra recoveries are 95% or greater) for the Ra Rad disk have been determined (37). The interferent ion concentrations are Mg^{2+} , Ca^{2+} , and Na^+ , $10,000 \text{ mg} \cdot \text{L}^{-1}$; K^+ , $1,000 \text{ mg} \cdot \text{L}^{-1}$; Sr^{2+} and NH_4^+ , $100 \text{ mg} \cdot \text{L}^{-1}$; and Pb^{2+} and Ba^{2+} , $10 \text{ mg} \cdot \text{L}^{-1}$. These results demonstrate the ability of the Ra Rad disk to effectively remove ^{226}Ra from solutions containing Mg^{2+} , Ca^{2+} , Na^+ , and K^+ , cations which might be expected to be in an environmental sample. As would be expected, selective removal is most difficult from solutions containing Sr^{2+} , Ba^{2+} , and Pb^{2+} . Scarpitta and Miller (39) note that the presence of these latter ions may not be a problem for ^{226}Ra analysis since their interferents are primarily β or γ emitters.

OTHER RADIONUCLIDE AND MIXED WASTE SEPARATIONS

Several SuperLig®, AnaLig®, and MacroLig® products are commercially available for the separation of the radioactive species and non-radioactive mixed waste components in a variety of matrices. Some examples are given below. Matrices are indicated in parentheses: Pu(IV) (neutral to full acidic range); Bi(III) (neutral pH up to several molar acid range); UO_2^{2+} (neutral and basic range and up to several molar

acid); I⁻ (full pH range); Pb(II) (full pH range); and Hg(II) (full pH range). Full acidic range comprises up to and including 18 M H₂SO₄, 15.7 M HNO₃, or 11.7 M HCl. Full pH range covers from these concentrated acids to > 10 M NaOH. Tests on actual hot or mixed waste have been run on all of these except for UO₂²⁺ and I⁻, where only cold testing has been performed.

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