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Chelating Scintillation Fibers for Measurements of ^{137}Cs

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Solid scintillating fibers, coated with a dual-mechanism bifunctional polymer shown to bind Cs(I) in alkaline solutions, were developed for measurement of ^{137}Cs. The effect of the epoxy−polymer coating thickness on attenuation of the signal from ^{137}Cs was evaluated. After optimal coating conditions were determined, both scintillation fiber and resin functions were retained, producing stable field-ready fibers. Temporal studies were performed to examine the kinetics of ^{137}Cs uptake into the resin. Calibration curves of the fiber response were generated by β-emission from solutions of ^{137}Cs dissolved in 1 M sodium hydroxide. The plots exhibited a linear response over a range of 4−3200 nCi/mL (3.4×10^{-10}−2.7×10^{-7} M ^{137}Cs), with a limit of detection of 3.65 nCi/mL (~42 parts per trillion ^{137}Cs). The distribution coefficient of Cs was determined to be 490 ± 50 mL/g from these measurements. Selectivity studies of the resin were performed in the presence of 100 fold excess of Sr(II), Al(III), and nonradioactive Cs(I). Linear calibration plots were obtained in the presence of these potential interferences, but at a reduced sensitivity. The fibers were also used to evaluate the ^{137}Cs content of a mock tank waste sample to show the potential of the fibers in complicated matrixes.

A major project of the DOE is the safe remediation of high-level radioactive waste that has been stored in underground tanks throughout the United States. There are 271 waste tanks of varying designs, containing more than 93 million gallons of radioactive waste at four sites across the United States.[1] The Hanford Reservation in Washington state contains nearly two-thirds of the high-level waste stored in the United States.[2] Many of these tanks are reaching their expected lifetimes and some are known, or are presumed, to have leaked waste into the surrounding environment.[3,4] The bulk of the radiation from these waste tanks comes from ^{137}Cs and ^{90}Sr. Respectively, they represent 40% and 25% of the total curie content of these tanks.[5] The tanks were filled with waste from numerous chemical processes, and the resultant waste is a complex mixture of various forms (supernatant, salt cake, sludge).[3] To properly process this stored waste into stable forms and to remediate the storage sites, it is necessary to characterize the contents of the waste within these tanks.

Scintillation counting techniques are among the most useful methods for the detection of a wide assortment of radiation types.[6] The most commonly used scintillating materials are inorganic alkali halide crystals and organic liquids and plastics. Inorganic scintillators produce better light yields but exhibit slower response times than organic scintillators. Organic scintillators are generally used for α- and β-particle detection because of their fast response times.[6] The ease with which plastic organic scintillators can be fabricated and shaped makes them extremely useful for scintillation techniques. In β-particle scintillation counters, the kinetic energy from the radiating particle is absorbed by scintillator molecules, which then relax via fluorescence emission of radiation. The resultant photons can be measured by a photomultiplier tube or other phototranducer. Plastic scintillation fibers consist of a core that is primarily polystyrene, doped with an aromatic scintillator that exhibits a good fluorescence quantum yield. The scintillating core is then covered with a coating (e.g., poly(methyl methacrylate), PMMA) that has a lower refractive index than the core to induce total internal reflections and reduce light losses at fiber surface interfaces.[7] Thus, a scintillating fiber combines scintillation properties with the light transmission characteristics of a fiber optic.

Dual-mechanism bifunctional polymers (DMBPs) consist of two distinct functional groups on a given supporting network, each of which functions by a different complexing mechanism. One mechanism is typically aspecific and serves to rapidly bring the species of interest into the polymer matrix, making it easily accessible to a highly specific recognition mechanism. Ion exchange is typically the access mechanism to bring metal ions into the polymer and into range of the highly specific recognition

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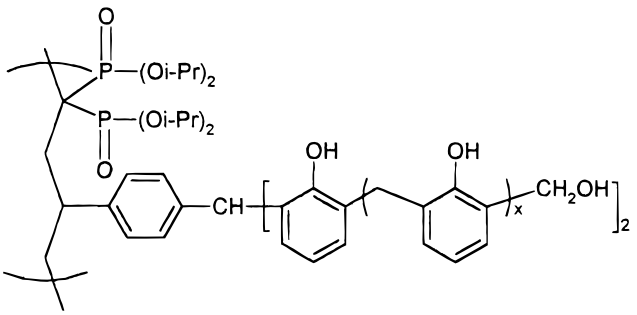

Figure 1. Cs-selective DMBP resin structure.

site.[8,9] The recognition site functions to selectively retain the analyte of interest within the polymer. DMBPs are divided into three classes based upon the recognition mechanism. Class I DMBPs consist of ion exchange/redox resins, Class II consist of ion exchange/coordination resins, and class III are ion exchange/precipitation resins.[9]

This study utilizes commercially available scintillation fibers that have been coated with a class II DMBP for the detection of ^{137}Cs in aqueous samples and in tank waste simulants. Specifically, the DMBP is composed of phenol−formaldehyde oligomers grafted onto a polystyrene-based resin bearing diphosphonate ligands (Figure 1). The DMPB has been shown to be selective for Cs(I) in the presence of Na(I) with distribution coefficients greater than 400 mL/g.[8] Further selectivity studies have been performed in this work to evaluate possible interfering species of the DMBP that are common within sample matrixes that contain ^{137}Cs. These fibers are similar to solid-phase microextraction (SPME) fibers, as they are able to combine sampling, extraction, concentration, and sample introduction techniques into a solitary step. Unlike SPME fibers, which combine two processes, the partitioning of the analyte between the coating and sample and the desorption of the analyte into an analytical instrument, there is no need of a desorption step for these chelating, scintillation fibers.[10] However, the desorption step can be performed to regenerate the fiber. The instrumental and procedural simplicity of this approach should facilitate field measurements.

EXPERIMENTAL SECTION

Instrumentation. Experiments were performed using an EG&G ORTEC (Oak Ridge, TN) photon-counting system. The system consisted of a series bin and power supply (series 401/2), a high-voltage power supply (model 456) with an output range of 10−3000 V, a photon counter (model 9315), and an amplifier discriminator (model 9302) with a gain setting of 20 or 200 for the amplifier and a 0.050−1 V threshold range for the discriminator. An RCA IP28 or a Hamamatsu R928 (Iwata-Gun, Japan) photomultiplier tube was used to collect impeding photons in a Pacific PMT housing (model 3377D) cooled with dry ice. Counting times for all experiments was 100 s and data presented are typically the average of 10 count cycles.

Scintillating fibers were positioned by the use of a machined Delcron piece that was threaded to fit into the PMT housing. A hole was drilled through the center of the Delcron piece that extended back to contact the window in front of the photocathode. This allowed the fiber to be positioned as close to the photocathode as possible and assured that the same area of the photocathode was impeded with photons from each scintillation fiber used in these studies. In this arrangement, no optics external to the fiber are needed to efficiently couple scintillation photons onto the PMT photocathode.

Cs-Selective DMBP. The phenol−formaldehyde grafted polystyrene-based resin was prepared by a suspension polymerization of tetraisopropyl 1,1-vinylidenediphosphonate, vinylbenzyl chloride, and acrylonitrile in a 1:1.35:2.25 mole ratio.[8] The resin contained 5% divinylbenzene as a cross-linking agent. The benzyl chloride moiety on the resin was then converted to a benzaldehyde moiety by a reaction with excess dimethyl sulfoxide and sodium bicarbonate at reflux for 8 h. The aldehyde site serves as the attachment point for the phenol−formaldehyde chains, which were grafted onto the resins.[8] The resin beads had diameters in the range of 75−150 μm.

To reduce attenuation of β-emission by the beads and to produce a stable resin bed, the beads were ground to a smaller size using a ball mill filled with ceramic beads. A large volume of the resin beads in water was placed in the ball mill and ground for 24 h. The diameters of the collected resin particles were then measured using a technique known as fineness of grind. This technique uses two calibrated plates to measure the particle diameter. One plate is spotted with the particles and the other is pulled across it smearing the sample across the first plate. The plates are designed so that as they are pulled across each other the gap between them decreases. At the point where the particle size and the gap are equal, the particles are dragged across the surface leaving streaked lines on the plate. The size of the particles can then be read from the calibrated plate. Using this technique, the particles were determined to have diameters of 3−5 μm. The particles were then dried in an oven.

Materials and Chemicals. The scintillating fibers BCF-12 were obtained from Bicron. The dimensions of the scintillating fibers were 1 mm diameter × 1.5 m as received from the supplier. They were cut to desired working lengths by hand. Radioactive ^{137}Cs was donated by Professor Larry Miller of the UTK Nuclear Engineering Department and had an activity of 80 μCi in 20 mL of solution. Chemicals used in preparing the double-shell slurry feed (DSSF) Hanford simulant were KOH, NaOH, and NaCl from Mallinckrodt (St. Louis, MO); Na_2SO_4, Na_2CO_3, $NaNO_2$, and $Ca(NO_3)_2{\cdot}4H_2O$ from Fisher (Fairlawn, NJ); $Na_2HPO_4{\cdot}7H_2O$, $Al(NO_3)_3{\cdot}9H_2O$, and NaF from Aldrich (Milwaukee, WI); $Ba(NO_3)_2$ from Allied Chemical & Dye Corp. (New York, NY); and $Sr(NO_3)_2$ from J. T. Baker Chemical Co. (Phillipsburg, NJ). A sulfonic acid functionalized ion-exchange resin, Amberlite IRP-69, was obtained from Aldrich. The ion-exchange resin had a wet mesh size of 100−500 and an exchange capacity of 4.3 mequiv/g. The resin particles were ground down using a ball mill to match the particle size of the Cs-selective DMBP.

Coating of Scintillation Fibers. Plastic scintillation fibers were cut to the desired working length, washed with ethanol to remove any oils and dirt, and then air-dried. Five-minute Epoxy from ITWDevcron (Danvers, MA) was diluted to a desired

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percentage epoxy solution (1−10% w/w) with acetone. The thickness of the epoxy coating was measured using a DekTak 8000 profilometer manufactured by Veeco (Santa Barbara, CA). The clean scintillation fibers were dipped into the epoxy solution and then placed into a bed of particles. After removal from the particle bed, the fibers were shaken to remove any loose particles. The epoxy was then allowed to cure overnight. Upon curing of the epoxy, the fibers were rinsed in deionized water to remove any loose particles and air-dried. Finally, the tips of the fibers were snipped off to eliminate an area of thicker coating that developed as the fibers were pulled from the epoxy solution.

RESULTS AND DISCUSSION

Signal Considerations. The radioactive decay of ^{137}Cs can proceed by the two processes:

$$^{137}\mathrm{Cs} \rightarrow {}^{137\mathrm{m}}\mathrm{Ba} + \beta^- \ (0.512\ \mathrm{MeV}); \quad {}^{137\mathrm{m}}\mathrm{Ba} \rightarrow {}^{137}\mathrm{Ba} + \gamma \tag{1}$$

$$^{137}\mathrm{Cs} \rightarrow {}^{137}\mathrm{Ba} + \beta^- \ (1.17\ \mathrm{MeV}) \tag{2}$$

These processes produce β-particles with maximum energies of 0.512 and 1.17 MeV, respectively.[11] The weighted average energy is 0.171 MeV. Using a relationship provided by Glendenin, the penetration depth for this average energy is 35 mg/cm^2.[12] In a density of 1000 mg/cm^3, this corresponds to a depth of 350 μm.

The signal in counts per second (Sig-cts) depends on the number of β-particles that are launched into the fiber per second that have sufficient residual energy to produce a photon burst that registers above the threshold level set on the amplifier/discriminator. The scintillator material used in these studies is reported to have a photon conversion efficiency of 8 photons/keV.[13] The fraction of β-generated photons that result in photon pulses at the PMT (F_t) is approximated by

$$F_t = f_{ir} f_{opt/pmt} \tag{3}$$

where f_{ir} is the fraction that are internally reflected toward the PMT and $f_{opt/pmt}$ is the product of the fraction transmitted by the optical components in the system (fiber, PMT window) and the quantum efficiency of the PMT; values are estimated to be 0.04 (based on a numerical aperture of 0.58) and 0.05, respectively. This produces a F_t of 0.002. If the discriminator level is set to the equivalent of 2 photons (a value that should adequately reject thermal PMT photocathode pulses), then the residual β-particle energy must be greater than ~125 keV in order to register a count (i.e., energy (keV) = 2 photons/(8 photons/keV × F_t))

The number of β-particles that satisfies these criteria and produces a detectable signal depends on the absolute activity of the source (A_{abs}) in Ci and the fraction emitted in the proper direction; i.e., a direction that will place the β-particle in the fiber core with an energy exceeding 125 keV (see eq 4).

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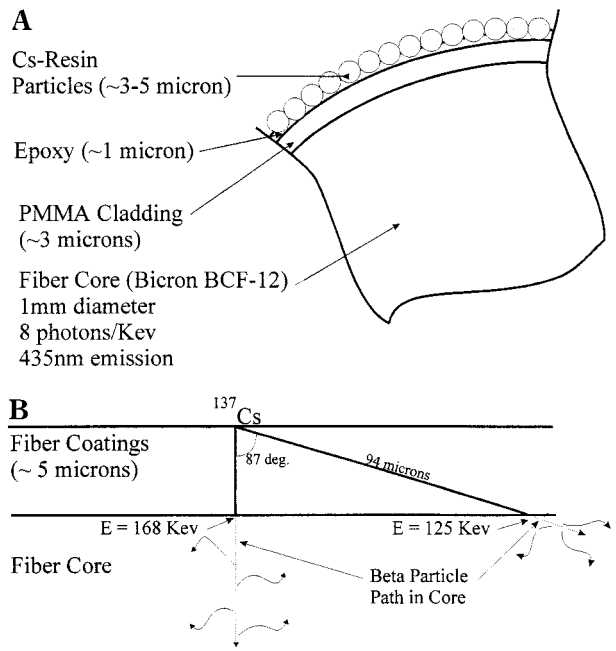

Figure 2. Cross-sectional view of a coated fiber (A) and surface view of a coated fiber showing factors affecting conversion of β-particle energy to photons in the fiber core (B).

$$\text{Sig-cts (counts/s)} = A_{abs} \times 3.7 \times 10^{10}\ (\text{diss/s})/\text{Ci} \times f_{dir} \tag{4}$$

Figure 2A is a geometric depiction of a cross section of the fiber showing the core (1000-μm diameter), optical cladding (~3 μm), epoxy (~1 μm), Cs-specific resin particles (~3−5-μm diameter), and surrounding sample solution. Figure 2B is a two-dimensional graph showing the process of β-emission from a ^{137}Cs located at a distance of 5 μm from the fiber core. β-Particles that are emitted with the weighted average energy (171 keV) and at an angle as depicted that is less than 87° should reach the core with sufficient energy (125 keV) to be counted. This assumes a linear loss in energy as the emitted β-particle travels through cladding, epoxy, or resin all having a density assumed to be close to 1000 mg/cm^3. The solid angle of collection is nearly 180° so f_{dir} is assumed to be 0.5.

In most of the measurements, the resin-coated fiber is allowed to come to equilibrium with a volume of sample. The fiber is removed and signal is registered while the fiber is dry (see Experimental Section). Knowing the mass of resin on the fiber, the activity and volume of the sample solution, and the distribution coefficient (D), one can compute the activity of ^{137}Cs bound to the resin. For example, most measurements were performed using a 0.35-cm^3 sample volume (V) and 3.0×10^{-4} g of resin (M). The mass of resin on the fiber was estimated by calculating the volume of the resin on the fiber and assuming a density of 1 g/cm^3 for the resin particles. The resin volume was calculated by determining the difference in volume between an uncoated fiber and a fiber coated with 5-μm resin particles. The value of D is ~490 cm^3/g (see below). Using the following relationship

$$DM/V = A_R/(A_{S,0} - A_R) \tag{5}$$

where A_R is the activity of resin bound ^{137}Cs (used as A_{abs}, eq 4)

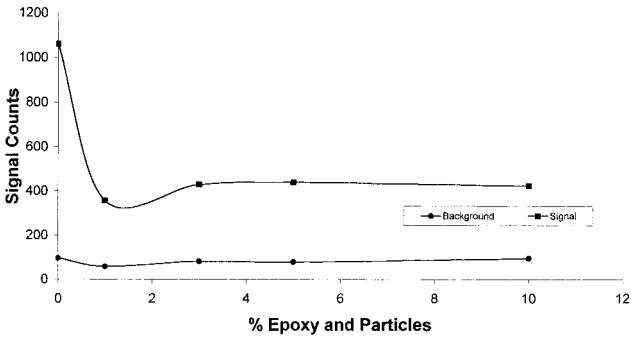

Figure 3. Signal and background versus percent epoxy and particles coating the fiber.

and $A_{S,0}$ is the initial activity of ^{137}Cs in the sample solution before uptake by the resin. Using eqs 4 and 5, a rate of 7 counts/s is calculated for the most dilute ^{137}Cs solution used in these studies (1.4 nCi in 350 μL). The observed count rate was ~5 counts/s for this solution, which is reasonably comparable considering the assumptions made in this theoretical treatment.

The photon-counting system used in this work was not ideally suited to these experiments. In particular, while the discriminator level was readily adjusted within its limits, it was not possible to read out the actual discriminator setting. Thus, optimization studies could only be performed crudely. In these studies, it was observed that signal-to-noise levels were best when there was an appreciable background (~10^2 counts/100 s count period). Presumably this is a result of the wide range of β-particle energies from ^{137}Cs emission. Although different discriminator levels were employed in these studies, a single setting is used whenever comparisons are made (e.g., in obtaining the calibration plots presented below). Another limitation of the system is the crude mode of cooling the PMT. Temperatures for the PMT probably varied slightly over long experiments or from day to day. The PMT also needed to be changed during the course of the studies due to failure of the one initially employed. It should be mentioned that the scintillation fibers are very well suited to coinicidence counting methods using the outputs from opposite ends of the fiber and the proper instrumentation. By using such instrumentation and longer fibers with greater accessible resins amounts (M in eq 5), limits of detection (LODs) lower than reported herein should be possible.

Coating Thickness Studies. The thickness of the coating applied to the scintillation fibers is of concern to prevent attenuation of β-particles from the radioactive decay of ^{137}Cs. Attenuation of β-particles before they reach the core of the scintillating fiber would increase the LOD achievable with the fibers. To study the effect of coating thickness upon signal counts, coated fibers were produced using varying percent epoxy solutions. A plot of counts above background versus the percent epoxy used for each fiber is shown in Figure 3. From this plot it can be seen that there is a steep drop in signal counts, when as little as a 1% epoxy solution is applied to the fibers. This suggests that as small a percentage of epoxy as possible should be used to prevent signal attenuation. Less occlusion of the resin is also expected for thin-film epoxy coatings. Unfortunately, coatings made from epoxy solutions below 1% were not physically stable. This lack of stability caused irreproducibility between measurements when the same fibers were regenerated by an acid rinse and reused. The signal loss from fibers coated with epoxy solutions above 1% is relatively constant. The reason for this is not clear. Coatings that employed a percent epoxy solution of ~3% were also seen to be stable, allowing better reproducibility between measurements, made with the same fibers. Profilometry measurements were used to determine the thickness of the epoxy coatings. Fibers were dipped in an epoxy solution so that there were two sections of the fiber, coated and uncoated. The fibers were coated with 3% and 10% epoxy solutions. Measurements of these two coatings showed virtually no difference in thickness, with each fiber exhibiting a step height of ~1 μm from an uncoated section of fiber to the coated section. This is consistent with the signal data plot in Figure 3.

Reproducibility. The reproducibility of the chelating, scintillating fibers was studied by coating seven fibers with the DMBP using a 3% epoxy solution. Each of these fibers was then used to measure the signal from a 400 nCi/mL solution of ^{137}Cs. The RSD for the seven fibers was 11.0%. This RSD represents not only the reproducibility in the coating of the fibers but also the positioning of the fiber within the PMT housing. This relatively low RSD value indicates that the fiber coating procedure used produces consistent resin coatings. However, it is possible to regenerate fibers. The fibers are regenerated by rinsing in 1 M HCl for 10 min to remove ^{137}Cs from the DMBP. The fibers are then rinsed with water for 10 min and dried. To ensure that ^{137}Cs was removed, the signal from a regenerated fiber is compared to the signal from an unused fiber. If the background signal measured with the regenerated fiber is within a standard deviation of the background measured with an unused fiber, then the regeneration is considered complete; if not, the rinsing procedure is repeated. In some cases, particularly with repetitive regeneration, it was visually observable that this process resulted in the loss of resin from the fiber. It is believed that the loss of the resin is caused by degradation of the epoxy used to secure the resin to the fiber surface during rinsing with HCl. The loss of resin from the fiber makes it difficult to use one fiber for a set of experiments and still achieve a linear response. We did not conduct studies to find more reliable rinsing procedures. While it is desirable to be able to regenerate the fibers to reduce experimental costs and deviations between fibers, the inability to do so reliably is not detrimental to their use because the fibers are inexpensive to produce and it has been shown that the reproducibility from fiber to fiber is sufficient for many applications. For these reasons, most experiments reported herein were performed using new fibers for each sample solution.

Fiber Uptake Kinetics:without and with Potential Interferences. The rate of uptake of ^{137}Cs into the polymer matrix was studied to determine an appropriate equilibration time for the fibers in solution. A factor of the rate of uptake of ^{137}Cs into the polymer is the ion-exchange process. This process may be limited by the concentrations of interfering cations in the sample matrix. With increased concentrations of interfering cations, ion exchange with the target ion may be reduced through competition for ion-exchange sites. This effect should be mitigated by the fact that in most experiments the capacity of the coated resin far exceeded the metal ion content of the sample (exclusive of Na(I)). Figure 4 shows the counts measured in 350 μL of a 400 nCi/mL solution of ^{137}Cs versus time. The measurements were made in a realistic matrix with an alkaline pH and a large (~10^7-fold) excess of

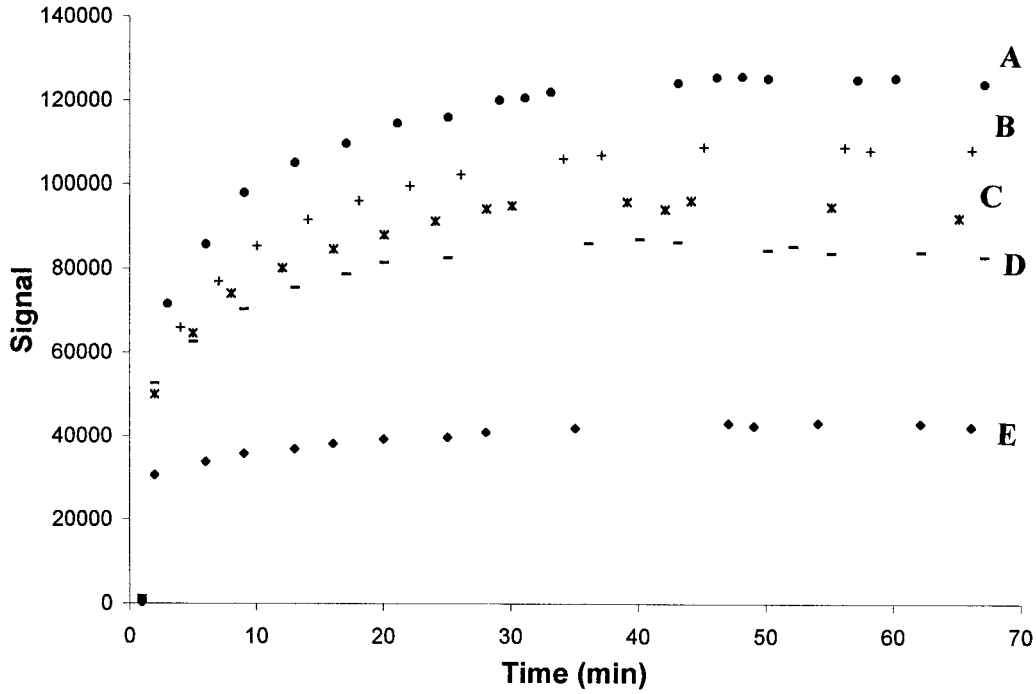

Figure 4. Signal counts versus equilibration time (min) within several sample matrixes that contain interfering metal ions: (A) 10^{-5} M Al(III) in 1 M NaOH; (B) 10^{-5} M Sr(II) in 1 M NaOH; (C) 1 M NaOH; (D) 10^{-5} M Cs(I) in 1 M NaOH; (E) 5-fold-diluted tank waste simulant.

Table 1. Hanford DSSF 101-AW Stock and Diluted Diluted 101-AW Simulant, MSimulant Composition

species	stock 101-AW simulant, M	diluted 101-AW simulant, M
Na	7.00×10^{0}	1.4×10^{0}
Al	6.95×10^{-1}	1.39×10^{-1}
Ba	8.28×10^{-7}	1.66×10^{-7}
Ca	3.62×10^{-4}	7.24×10^{-5}
K	6.65×10^{-1}	1.33×10^{-1}
Sr	1.00×10^{-7}	2.00×10^{-8}
SO_4	1.52×10^{-2}	3.04×10^{-3}
OH	5.82×10^{0}	1.16×10^{0}
OH (free)	3.04×10^{0}	6.08×10^{-1}
theoretical pH	1.51×10^{1}	
Cl	9.10×10^{-2}	1.82×10^{-2}
CO_3	1.96×10^{-1}	3.92×10^{-2}
F	6.07×10^{-2}	1.21×10^{-2}
NO_2	1.23×10^{0}	2.46×10^{-1}
NO_3	2.09×10^{0}	4.18×10^{-1}
PO_4	2.45×10^{-2}	4.90×10^{-3}

Na(I). As the figure shows, a plateau in signal is reached after 35 min of exposure. Similar plots were constructed for solutions containing 20, 40, 80, and 200 nCi/mL ^{137}Cs. Each of these plots showed that a plateau was reached by 35 min of exposure to the respective solutions. From this study, an equilibration time of 35 min was set for all subsequent measurements.

Figure 4 also shows the uptake process in the presence of potential interferences including uptake in a 5× diluted mock DSSF Hanford waste. The composition of the Hanford simulant and a 5-fold dilution used in these studies are shown in Table 1. The simulated Hanford tank waste sample was made by the procedure described by Carlson of Pacific Northwest Laboratories.[14] The chosen simulant approximates a DSSF supernate from Hanford Tank 241-AW-101 with the exception that the total sodium concentration is lower than the actual tank waste (7 M rather than 10 M). The initial rate of uptake of ^{137}Cs is not significantly altered in the presence of these other metals (see initial slopes in the figure). However, the equilibrium signals (in the 30−60-min range) are different in some instances. Given its extreme complexity, it is not surprising that equilibrium signal levels in the Hanford matrix are significantly lowered. In a matrix such as this, the possibility of complicated secondary equilibria exists. Secondary equilibria would effectively alter (in many cases decrease) the concentration of free metal ions in the sample. Since we are far from exceeding the capacity of the resin, the equilibrium signal in the presence of 10^{-5} M Cs (nonradioactive) should not be altered. The slight decrease relative to the 1.0 M NaOH matrix (without other metal ions) may simply reflect the reproducibility in preparing the fibers. The presence of 10^{-5} M concentrations of other metal ions showed an increase in the measured signal for all metals evaluated. Part of this increase may be attributed to the reproducibility in preparing the fibers. However, these metals appear to be enhancing the steady-state equilibrium of Cs with the resin. This signal enhancement is believed to be due to an increase in the uptake of ^{137}Cs, since β-emission should not be affected. The reason for this enhancement in ion-exchange equilibria can be linked to several effects including ion-pair formation, salting-out, and repulsion due to like charges.[15] It has been reported that as ionic strength of the sample matrixes increases, so does sorption of electrolytes onto the ion exchanger.[16] Increased sorption of ^{137}Cs into the resin used in our studies would lead to an increase in observed signal. Hydrolysis of cations can alter the concentrations of free metal ions in

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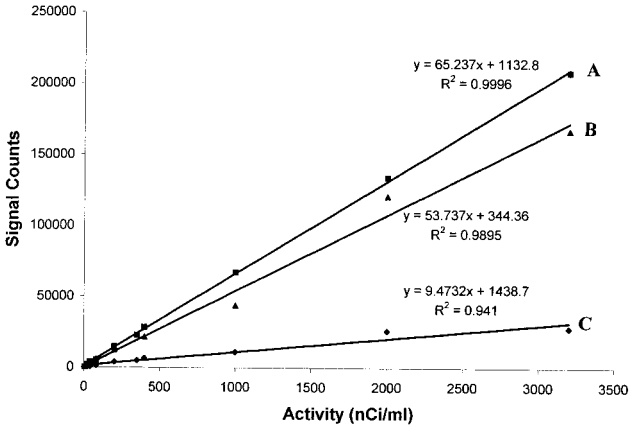

Figure 5. Signal counts versus activity (nCi/mL) for fibers measuring ^{137}Cs in solutions of 1 M NaOH: (A) coated fibers measured in solution; (B) coated fibers measured out of solution; (C) uncoated fibers measured in solution.

solution, as well as the pH of unbuffered solutions.[16] The presence of higher valence cations in solution can create exchange sites in the resin that contain higher valence ions than the analyte ion which may effect the uptake of the desired ion.

It also has been reported that there is often a measurable difference in selectivity factors determined by single-species experiments and those determined by competitive studies.[17,18,19] Thus, selectivity enhancement observed in the presence of other cations is not unprecedented. The mechanisms that lead to these enhancements however are not well understood, nor well documented in literature. If the general composition of the major components of the waste tank sample are known (often the case), then calibration should be possible. In some real situations, calibration by a standard addition method may be desirable because it allows the analyte to be measured within the true sample matrix.

Calibration Plots: without and with Potential Interferences. A series of calibration plots were made to compare the signal achieved with an uncoated and a resin-coated scintillation fibers. These calibration curves are shown in Figure 5. The ^{137}Cs samples were made up in 1 M NaOH with activities from 4 to 3200 nCi/mL (3.4×10^{-10}–2.7×10^{-7} M ^{137}Cs). Three different curves are represented, coated fibers in and out (dry condition) of the ^{137}Cs-containing solutiod and an uncoated fiber in the ^{137}Cs solution. The slopes of the three curves show that the sensitivity of the coated fibers in or out of solution is much greater than an uncoated scintillation fiber in solution. The decrease in the counts between the calibration curves of the coated scintillation fibers measured dry and in solution verifies that the epoxy–polymer coating does not lead to excessive attenuation of the β-particles. The fiber appears to be able to measure β-particles both in the resin and in the surrounding solution. Sensitivity (slope) and regression data for the plots appear in the figure. The LOD achievable with the uncoated fibers was 13.10 nCi/mL (1.11×10^{-9} M ^{137}Cs) while the coated fibers measured in solution and in the dry state were 1.83 and 3.65 nCi/mL (1.54×10^{-10} and 3.08×10^{-10} M ^{137}Cs), respectively. These LOD values are based on a S/N of 2 with the noise value determined by the rms of the measured background signal.

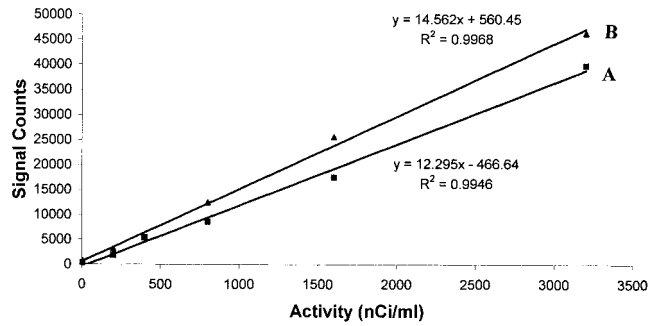

Figure 6. Signal counts versus activity (nCi/mL) for fibers measuring ^{137}Cs in the presence of 10^{-5} M each of Cs(I), Rb(I), and Al(III) (A) and in the presence of Hanford tank waste simulant (B).

The DMBP used in these studies has been shown to selectively bind Cs(I) in the presence of Na(I), but no other selectivity studies had been performed.[8] A calibration plot for ^{137}Cs in the presence of 10^{-5} M each of Cs(I), Rb(I), and Al(III) is shown in Figure 6. Although the number of counts has decreased dramatically from the calibration plot produced in 1.0 M NaOH, the plot does remain linear with a sensitivity that is ~4-fold lower that in Figure 5. In the presence of these interfering metal ions, the LOD is 6.3×10^{-10} M. Samples of ^{137}Cs with concentrations from 5.3 to 3200 nCi/mL were also made so that they were in a 5-fold dilution of the stock DSSF simulant (composition is shown in Table 1). These solutions were measured as before, and the calibration curve is also shown in Figure 6. The calibration curve was linear, with a sensitivity that was again ~4-fold less than in Figure 5. The LOD achievable in the simulated tank waste is 7.1×10^{-10} M.

The distribution coefficient (D) was calculated using data collected from uncoated fibers. By subtracting the counts from uncoated fibers measured in the original solution from the counts of an uncoated fiber measured in the same solution after uptake of ^{137}Cs by a coated fiber, the concentration of Cs in the resin can be determined. Then, using the estimated mass of resin on a coated fiber (300 μg), we can calculate the distribution coefficient by eq 6. For solutions of 3200, 2000, 1000, and 400 nCi/mL, the

$$D = \frac{(\text{mmol of Cs in resin/mass resin})}{(\text{mmol of Cs in soln/soln volume})} \qquad (6)$$

distribution coefficients were calculated to be 493, 490, 430, and 551 mL/g, respectively. This gives an average of 490 ± 50 mL/g, which is consistent with the reported value being greater than 400 mL/g.[8] Using this value of D, the mass of ^{137}Cs on the fiber (dry state) is ~6 pg at the LOD.

Nonspecific Resin Studies. The selectivity of the DMBP resins was compared with that of an ion-exchange resin (Amberlite IRP-69). The ion-exchange resin particles were ground down to match the particle size of the DMBP using a ball mill. The fibers were coated with the ion-exchange resin in the same manner as with the DMBP. Fibers were first used to measure the signal from 1600 nCi/mL solutions in 1 M NaOH, containing no interfer-

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ences, and then the signal from a 1600 nCi/mL solution in a 5-fold diluted tank waste simulant. Signal level for the ion-exchange fiber was comparable to resin fibers. However, the former retained only 2% of the original signal observed in the 1 M NaOH matrix, when measured in the tank waste simulant. The signal retention was a factor of 7 greater for the DMBP resin, under the same conditions, demonstrating the enhanced selectivity of the DMBP over a strong cation-exchange resin.

CONCLUSIONS

This study has demonstrated chelating scintillation fibers for use in quantifying activities of radioactive metals in alkaline, aqueous samples and in simulated tank waste. The use of these fibers allows for simplified sampling, extraction, concentration, and introduction into an analytical instrument. Reducing these typically separate steps into one step is advantageous to reducing sample handling by workers, which in turn reduces worker exposure to radiation sources. The coating of the scintillation fibers with a Cs-selective DMBP has shown to substantially improve the sensitivity over uncoated scintillation fibers. Calibration curves are necessary to accurately quantitate the activity of ^{137}Cs within a sample matrix. General matrix conditions are known for most waste tanks making calibration of the fibers possible. The DMBP showed good selectivity for Cs(I) over other metals. With the use of other highly selective coating materials, fibers could be created to quantitatively monitor an array of analytes. For example, a DMBP resin in the diphosphonic acid rather than diphosphonate form has been shown to extract both Cs(I) and Sr(II) from alkaline solutions.[20]

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