

Radionuclide Sensors for Water Monitoring

(Project Number: 70179)

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Number of Graduate Students Actively Involved in the Project:	2
Number of Undergraduate Students Involved (part-time) in the Project:	1
Number of Post-Doctoral Scholars involved (part-time) in the Project:	1
Number of Ph.D. degrees granted involved in the Project:	1
Number of M.S. degrees granted involved in the Project:	1

Research Objective

Radionuclide contamination in the soil and groundwater at U.S. Department of Energy (DOE) sites is a severe problem requiring monitoring and remediation. Radionuclide measurement techniques are needed to monitor surface waters, groundwater, and process waters. Typically, water samples are collected and transported to the analytical laboratory where costly radiochemical analyses are performed. To date, there has been very little development of selective radionuclide sensors for alpha- and beta-emitting radionuclides such as ^{90}Sr , ^{99}Tc , and various actinides of interest.

The objective of this project is to investigate novel sensor concepts and materials for sensitive and selective determination of beta- and alpha-emitting radionuclide contaminants in water. To meet the requirements for low-level, isotope-specific detection, the proposed sensors are based on radiometric detection. As a means to address the fundamental challenge of short ranges of beta and alpha particles in water, our overall approach is based on localization of preconcentration/separation chemistries directly on or within the active area of a radioactivity detector using automated microfluidics for sample manipulation and sensor regeneration or renewal.

The outcome of these investigations will be the knowledge necessary to choose appropriate chemistries for selective preconcentration of radionuclides from environmental samples, new materials that combine chemical selectivity with scintillating properties, new materials that add chemical selectivity to solid-state diode detectors, new preconcentrating column sensors, and improved instrumentation and signal processing for selective radionuclide sensors. New knowledge will provide the basis for designing effective probes and instrumentation for field analytical chemistry.

Research Progress and Implications

This report summarizes work as of 2 years and 8 months of a 3-year program. The ongoing effort is directed at the investigation of the preconcentration column sensor concepts, development and characterization of the selective scintillating microspheres (SSMs), development and characterization of the chemically selective diode detectors, and development/modeling of the new scintillation detection systems.

The preconcentrating minicolumn radionuclide sensor is based on the use of dual-functionality bead materials. These materials are designed to incorporate both selective separation chemistry for analyte preconcentration and localization within the detector, and scintillating properties, so that radioactivity of retained species can be converted to a measurable light output. To date, we have achieved progress in SSM materials prepared by co-immobilization of selective organic

extractants and scintillating fluors within inert macroporous polymeric beads, immobilization of selective organic extractants on scintillating glass, and by physically mixing sorbent and scintillating bead materials to yield a mixed-bed, composite sensor column. Various scintillating sensor materials selective for Tc, Sr, and actinides were prepared and evaluated during the course of this work.

Using pertechnetate-selective scintillating beads prepared by co-immobilization of selective extractants and scintillating fluors, we have demonstrated the application of SSM resins for the on-line characterization of $^{99}\text{TcO}_4^-$ (pertechnetate) in acidified groundwater. For on-line measurements, the resin is used in conjunction with an on-line flow-cell scintillation detector and an automated fluid handling system. The results of these tests clearly indicate that pertechnetate can be readily detected in acidified groundwater samples below the U.S. Safe Drinking Water Act maximum concentration level of 900 pCi/L. Nevertheless, these studies indicated that long-term material stability and analysis of the unacidified groundwater are still problematic when using sensor materials prepared by co-immobilization of scintillator dyes and organic extractants within the polymeric bead.

To address sensor stability challenges, we have been investigating more robust sensor designs based on a composite or mixed-bed sensor column configuration. In this configuration, sensor column is comprised of a heterogeneous mixture of scintillating and selective sorbent sub-materials that have stability in solution media. We determined that composite bed sensor configuration is efficient for capture and on-column detection of beta emitters such as ^{90}Sr and ^{99}Tc . For example, for the ^{99}Tc sensing, absolute detection efficiency that can be obtained using a composite bed column can be as high as 30%, and the chemical stability is much improved.

Progress has been made in the area of reagentless, equilibrium-sensing approaches. The reagentless sensing approach is particularly well suited for the development of field-deployable, long-term monitoring probes. Using a composite bed sensor with anion exchange sorbent functionality, we have demonstrated the feasibility of reagentless equilibrium ^{99}Tc sensing. As expected from the theoretical model, equilibrium sensor responses were proportional to the sample activity, and the magnitude of the signal was dependent on the sorbent uptake affinity. Reagentless sensing in chemically untreated Hanford groundwater at or below regulatory drinking water levels was possible. The issue of sensor fouling over long periods of operation in chemically untreated groundwater was identified and is being investigated. Presumably, it is due to the fouling of the anion exchange materials with natural organic acids.

Research has commenced on radionuclide sensors based on chemically modified diode detectors. We were successful in developing packaging approaches that resulted in minimal noise in the alpha region and reliable diode operation in solution. Diode leakage current and alpha noise are not significantly affected upon surface modification and packaging for use in solution. Selective

films of reproducible and controlled thickness can be deposited on the surface of diode detectors using a spray coating technique. We obtained actinide-selective thin films by modifying PVC polymer with actinide-selective organic extractants (HDEHP and DIPEX). Uptake characteristics of the thin films as a function of solution composition are being investigated in detail. Initial results indicate that selective thin films exhibit high distribution coefficients for the uptake of actinides from groundwater matrixes acidified to pH 2. For example, Am and U distribution coefficient values exceed 10^6 in Hanford groundwater at pH 2. Initial batch contact results indicate that good energy resolution (~ 100 keV FWHM) can be obtained for <0.5 - μm -thick films. However, energy resolution is degraded significantly for > 2 - μm -thick films. Nevertheless, alpha particle energy resolution for 3 to 5- μm -thick films exceeds practical energy resolution capabilities of scintillation detection. In addition, noise (alpha background) of the diode detectors is much superior to that of scintillation detection.

Research has commenced on the development of modeling approaches for the preconcentrating column sensors. Specifically, we conducted Monte-Carlo computer modeling of the light collection efficiency as well as the beta-particle charge deposition in a heterogeneous scintillation flow-cell. From the charged-particle interaction model, the percentage of electron energy deposited in the scintillator as a function of electron energy was determined. The energy deposited in the scintillator varies with scintillator granule size, packing geometry (porosity), the scintillator material, and the initial location of radioactivity within the flow-cell. The simulation results of electron interactions showed higher packing density and smaller scintillator spheres would result in greater energy deposition in the scintillator, but the absolute effects also depend on the energy and location of electrons within the flow-cell at the time of the decay. This energy deposited in the scintillator has a strong dependence on the initial energy if it is below ~ 200 keV. The spatial energy distribution for electron interactions provided insight into determining the appropriate size of flow-cell tubing for a given energy. The simulated geometrical detection efficiency was shown to be comparable to the experimental absolute detection efficiency. It was concluded that the charged particle interaction process has greater effect on overall detection efficiency than the photon transport process within the constraints of this study. The light collection efficiency modeling needs further work. The light collection efficiency is shown to be affected more by optical properties including the indices of refraction of scintillator, aqueous phase, and the Teflon tubing; the reflection coefficients of the internal surfaces of the flow-cell holder; and the surface treatment of scintillator granules than by geometrical properties such as the scintillator granule size, the flow-cell volume, and the packing geometry (porosity). Reduced light collection efficiency was observed for scintillator spheres with polished surfaces compared to spheres with ground (rough) surfaces due to losses from total internal reflection. There is currently an inconsistency between the model and the experiments in light collection efficiency as the number of spheres in the flow-cell increase. This discrepancy is due to the discrepancy in the absorption coefficient of the scintillator used in the model. We plan to conduct specific

experiments to elucidate the effects of light collection efficiency as a means of refining the model.

We continued further development of the dual functionality sensing media, with particular emphasis on detection of uranium and actinides. Resins were investigated with bis(2-ethylhexyl)methane-diphosphonic acid (H₂DEH[MDP], Dipex[®]) extractant, which has a strong affinity for tri-, tetra-, and hexavalent actinides in dilute acids. Extractive scintillating resins were manifested 1) as a mixed bed of scintillating resin and extraction chromatographic resin and 2) by diffusing the organic fluor 2-(1-naphthyl)-5-phenyloxazole (α NPO) into macroporous polystyrene chromatographic resin, then coating with H₂DEH[MDP] or by coating H₂DEH[MDP] on scintillating polyvinyltoluene (PVT) beads. The average detection efficiencies were 51.7 \pm 2.6 % and 65.8 \pm 10.1 % for natural uranium and ²⁴¹Am, respectively, for the extractant-coated scintillator. The resin was stable for solution flow of up to 1000 mL resulting in rapid real-time screening of alpha radiation in natural groundwaters at or below the alpha concentration set forth in the U.S. Safe Drinking Water Act.

Manganese dioxide-coated plastic PVT scintillator and Aliquat 336-based extractive scintillator (ES) resins were prepared and applied toward environmental screening of ⁹⁹TcO₄⁻ and uranium in groundwater, respectively. Off-line screening using a commercially available liquid scintillation counter (LSC), and on-line screening using a modified hand-held survey meter, were evaluated in the laboratory for quantification of ⁹⁹TcO₄⁻ and uranium in groundwater. The detection efficiencies for uranium with the MnO₂-coated PVT resin were determined to be from 17% to 37 % and from 7% to 27 % for the LSC and survey instrument, respectively. The loading efficiency of the uranium out of groundwater ranged from 16% to 26 %. In contrast, the detection efficiencies for ⁹⁹Tc with the ES resin were determined to be from 2% to 14% and from 2% to 3% for LSC and the hand-held survey meter, respectively, while the loading efficiency of the ⁹⁹TcO₄⁻ in groundwater acidified to pH 2 was nearly 100%. It was shown in this work that it is possible to use MnO₂-coated PVT scintillator resin (MnO₂-PVT) and ES resin with a hand-held survey meter to simultaneously separate and quantify radioactivity in aqueous solutions. This hand-held survey meter can be applied toward environmental screening applications in the field.

Planned Activities

During the remainder of the third year, our activities will be directed at completing experimental work directed at the initial feasibility of ⁹⁹Tc reagentless sensing in groundwater and developing and testing the chemically modified diode detectors. We plan to complete initial demonstration of the hand-held field survey equipment for detection of U and ⁹⁹Tc in groundwater. In addition, we are beginning to work with the DOE Nevada office and Bechtel Nevada on the development of the prototype ⁹⁹Tc sensor probe suitable for long term/in-situ monitoring.

Information Access

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