

Project Number: 70179

Project Title: Radionuclide Sensors for Water Monitoring

Publication Date: 06/02/2003

DOE Report Number:

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Number of Graduate Students Actively Involved in the Project: 3

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: 0

Number of M.S. degrees granted involved in the Project: 0

Research Objective

Radionuclide contamination in the soil and groundwater at U.S. Department of Energy (DOE) sites is a severe problem that requires monitoring and remediation. Radionuclide measurement techniques are needed to monitor surface waters, groundwater, and process waters. Typically, water samples are collected and transported to an 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 ⁹⁰Sr, ⁹⁹Tc, 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 the 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. Automated microfluidics is used 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 and in situ measurements.

Research Progress and Implications

This report summarizes work after 8 months of the renewed 3 year program. The ongoing effort is directed at the investigation of the reagentless equilibration sensing concept for the purpose of ^{99}Tc in situ sensing, characterization of the sorbent and sensor materials, investigation of the chemically modified diode detection, and development and modeling of the scintillation and diode detection systems.

The preconcentrating column sensor concept is based on the use of dual function materials that enable selective sorbent and scintillating properties attained within the sensor column. The quantification method is based on achieving complete sensor equilibrium with the sample solution, at which point no further preconcentration occurs, and the analyte concentration on the sensor is proportional to the analyte concentration in the sample. Because the sensor re-equilibrates with the next sample, no sensor regeneration is necessary. This forms the basis for reagentless operation, which is well suited for the development of long term in situ probes. Challenges and scientific issues associated with this novel sensing approach are one of the key areas of this research program.

We are in the process of conducting a systematic study of sorbent materials for use in equilibrium ^{99}Tc sensing in groundwater. A range of sorbent materials is being characterized in a batch uptake regime to determine uptake affinity and selectivity in the presence of ubiquitous anions. Additional studies were carried out to determine resistance of this material towards fouling by natural organic matter. We determined that quaternary ammonium solid phase extraction materials (strongly basic anion exchangers) exhibit excellent affinity towards pertechnetate in groundwater, but are subject to severe fouling by humic acids. The degree of fouling was determined to be dependent on the nature of the bead substrate, and is less severe for acrylic supports relative to polystyrene divinylbenzene matrixes. Tertiary amine functionalities (weakly basic anion exchangers) were found to exhibit weaker affinity towards pertechnetate. Nevertheless, these materials were found not to be irreversibly fouled by the humic acid. We are conducting research directed at the identification and selection of a prefilter material that would selectively remove organic matter but not anionic analyte species. Various inorganic and organic materials are being evaluated for this purpose. Our research to date indicates that suitable materials do exist and can be used to mitigate the issue of sensor fouling.

We have conducted further evaluation of the equilibration sensor and had demonstrated the feasibility of ^{99}Tc equilibration sensing in actual Hanford groundwater. Results of the sensing were in good agreement with independent laboratory analysis. With the supplementary funding provided through Advanced Monitoring System Initiative (EM), and in collaboration with

Bechtel Nevada scientists, we performed the initial design and a successful demonstration of the prototypical sensor probe compatible with a 3.5 inch well casing.

The research continues in the area of chemically modified diode detectors. We are in the process of completing 1) systematic evaluation of the thin film uptake properties for actinides; and 2) tradeoffs between preconcentration, sensitivity, and energy resolution capabilities for in situ detection of alpha emitters.

In the area of dual function scintillation materials, the ongoing research is directed at the characterization of chemical selectivity of two inorganic scintillators yttrium silicate (YSO) and calcium fluoride ($\text{CaF}_2\text{:Eu}$) for uptake and preconcentration of Uranium from natural waters (pH 8). Batch uptake and flow experiments indicate the feasibility of U uptake and preconcentration. The detection efficiency for captured U ranged from 3-22%, depending on particle size. We have initiated research directed at the synthetic preparation of macroporous scintillating YSO with the objective of enhancing the surface area of crystalline particulates. Synthetic experiments using sol gel techniques are directed at the attempt of optimizing porosity and luminosity by controlling surfactant and sintering temperatures.

Solid-state semiconductor detection using a passivated ion-implanted planar silicon (PIPS) detector of beta radiation from ^{99}Tc is being investigated as an alternative to scintillation detection. The background count rate and detection efficiency were measured at 0.76 cps and 5.1%, respectively. These detection parameters are inferior to those that can be obtained from the heterogeneous mixed-bed scintillation flow-cell.

Experiments were conducted and then modeled with Monte Carlo methods to evaluate the impact of optical and geometrical properties on light collection efficiency of heterogeneous scintillation flow-cell detectors. Light collection measurements were made by placing a photon source, ZnS(Ag) scintillator attached to an ^{241}Am alpha point source, at a fixed distance from a photomultiplier tube (PMT). Non-scintillating glass beads, contained in a mobile phase to simulate a flow-cell detector, were positioned between the photon source and the PMT. The index of refraction, n , of the mobile phase, and the number of layers of glass beads were investigated. The three mobile phases chosen were air ($n=1$), water ($n=1.33$) and methylnaphthalene ($n=1.62$); and the diameter of the glass beads ($n=1.5$) was $115\text{ }\mu\text{m}$. We observed that as the number of bead layers between the photon source and the PMT increased, the normalized collection efficiency decreased. As the index of refraction of the aqueous medium surrounding the beads increases, so does the light collection efficiency. The optical transport Monte Carlo computer code, DETECT, is being used to model the experimental set-up. Simulations of a sphere with a ground surface indicate that photons will not be totally internally reflected due to the random surface. These results have important consequences in the detection of alpha and low-energy beta radiation with scintillating spheres, where the energy, and hence the light, will be generated close to the surface of the bead because of the short range of the radiation in matter.

Planned activities

During the second and third year of this program, we will continue research directed at the development of reagentless equilibrium sensing ~~or~~^{of} radionuclides using preconcentrating columns. We plan to continue exploring chemical modification of diodes for the purpose of low level monitoring of alpha emitters. Modeling and optimization of the scintillation detection will also continue.

Information Access

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