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Lead Principal Investigator: Dr. Jay W. Grate
Pacific Northwest National Laboratory
Box 999, Richland, WA 99352
509-376-4242 (voice); jwgrate@pnl.gov,

Co-Investigator: Dr. Oleg B. Egorov
Pacific Northwest National Laboratory
Box 999, Richland, WA 99352
509-376-3485 (voice); oleg.egorov@pnl.gov

Co-Principle Investigator: Dr. Timothy A. DeVol
Environmental Engineering & Science
Clemson University
Clemson, SC 29634-0919
864-656-1014 (voice); tim.devol@ces.clemson.edu

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 ^{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 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 1 year and 9 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, development and modeling of the scintillation and diode detection systems, and digital signal processing.

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 have completed systematic evaluation of the sorbent materials for use in equilibrium ^{99}Tc sensing in groundwater. Our studies indicate that weakly basic anion exchange materials are preferred due to better resistance towards fouling by dissolved natural organic matter (e.g. humic acids). We have completed systematic studies of the guard column materials that can be used to remove humic acids without capturing pertechnetate.

We are completing detailed evaluation of the equilibration sensing approach using mixed bed microcolumn geometry and development of the equilibration sensing theory. We have successfully demonstrated the feasibility of accurate ^{99}Tc equilibration sensing below regulatory levels in actual Hanford groundwater. The testing was conducted using both laboratory and prototypical field instrumentation developed in collaboration with Advanced Monitoring System Initiative.

In collaboration with Adherent Technologies Inc., we have conducted evaluation of the chemically selective scintillating fibers for detection of ^{99}Tc in water. The feasibility of analyte capture and detection has been demonstrated. Scintillating fiber geometry represents a promising geometry for the development of radionuclide sensors.

The research continues in the area of chemically modified diode detectors. We have completed systematic evaluation of the thin film uptake properties for actinides using several extractants and plasticizers.

In the area of dual function scintillation materials, we have conducted research directed at the synthetic preparation of macroporous scintillating yttrium silicate (YSO) with the objective of enhancing the surface area of crystalline particulates. Synthetic experiments using sol gel techniques were directed at the attempt of optimizing porosity and luminosity by controlling surfactant and sintering temperatures. A total of fifteen formulations of YSO fluors were investigated, however, we were not able to achieve material that combines high porosity and luminosity.

We have completed evaluation of the solid-state semiconductor detection using a passivated ion-implanted planar silicon (PIPS) diode for detecting beta radiation from ^{99}Tc as an alternative to scintillation detection. Strongly basic anion exchange material was used to capture and localize ^{99}Tc in a close proximity to the detector surface. The experiments were conducted both in a batch and flow regime. While this approach readily enabled detection at/below regulatory levels, our results indicate that generally PIPS diode detectors do not offer significant advantages to scintillation for detection of low energy beta-emitters due to proximity of beta signals to thermonic noise. To address this issue we have initiated investigation into the possibility of exploiting digital pulse shape discrimination to separate the alpha and beta radiation interaction from one another and electronic noise in a PIPS detector. Preliminary tests indicate that alpha and beta radiation interactions can be separated from one another. The pulse shape difference between beta radiation interactions in the PIPS detector and background exist but are minimal. It is to be determined if the difference is sufficient to be able to discriminate between the events.

We have completed light collection efficiency experiments of the heterogeneous scintillation detectors. These experiments were conducted to determine the significance of the index of refraction of the aqueous phase relative to that of the solid scintillator as well as the significance of the number of layers of resin beads that exist between the scintillation event and photodetector. These experiments gave consistent results with expectations, namely that if the index of refraction of the aqueous media is less than that of the scintillator the light output is lower than if the index of refraction of the aqueous media is greater than that of the scintillator. Also, as the number of layers between the scintillation source and the photodetector increase, the light measured decreases.

Planned activities

During the third year of this program, we will continue research directed at the development of reagentless equilibrium sensing of radionuclides using preconcentrating columns. We will complete detailed characterization of this approach as relevant to detection of ^{99}Tc in groundwater and publish results of these studies. We expect to demonstrate fully functional prototype ^{99}Tc sensor device. 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 and development of the digital signal processing techniques will be also continued. Several

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