Project Number: 81923
Project Title: Radioanalytical Chemistry for Automated Nuclear Waste Process Monitoring
Publication Date: 06/09/2003
DOE Report Number: CU-EES-06003

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

Co-Investigator:
Dr. Jay W. Grate
Environmental Molecular Sciences Laboratory
Pacific Northwest National Laboratory
Box 999, Richland, WA 99352
509-376-4242 (voice); jwgrate@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

This research program is directed toward rapid, sensitive, and selective determination of beta- and alpha-emitting radionuclides such as ^{99}Tc, ^{90}Sr, and trans-uranium (TRU) elements in low-activity waste (LAW) processing streams. The overall technical approach is based on automated radiochemical measurement principles. Nuclear waste process streams are particularly challenging for rapid analytical methods due to the complex, high-ionic-strength, caustic brine sample matrix, the presence of interfering radionuclides, and the variable and uncertain speciation of the radionuclides of interest. As a result, matrix modification, speciation control, and separation chemistries are required for use in automated process analyzers. Significant knowledge gaps exist relative to the design of chemistries for such analyzers so that radionuclides can be quantitatively and rapidly separated and analyzed in solutions derived from low-activity waste processing operations. This research is addressing these knowledge gaps in the area of separation science, nuclear detection, and analytical chemistry and instrumentation. The outcome of these investigations will be the knowledge necessary to choose appropriate chemistries for sample matrix modification and analyte speciation control and chemistries for rapid and selective separation and preconcentration of target radionuclides from complex sample matrices. In addition, new approaches for quantification of alpha emitters in solution using solid-state diode detectors, as well as improved instrumentation and signal processing techniques for

use with solid-state and scintillation detectors, will be developed. New knowledge of the performance of separation materials, matrix modification and speciation control chemistries, instrument configurations, and quantitative analytical approaches will provide the basis for designing effective instrumentation for radioanalytical process monitoring. Specific analytical targets include ^{99}Tc, ^{90}Sr and TRU actinides.

Research Progress and Implications

This report summarizes work as of 1 year and 8 months into a 3-year program. Because of the immediate relevance to our applied effort in the development of an on-line ^{99}Tc process monitor for the Waste Treatment Plant at Hanford, we have continued research efforts directed at the development of chemistries and instrumentation necessary for the development of the ^{99}Tc process analyzer prototype. Specific scientific challenges that have been investigated include 1) chemistry for rapid, automated ^{99}Tc speciation control; 2) ^{99}Tc separation chemistry; and 3) radioanalytical chemistry of Hanford tank waste. A major emphasis has been placed on the separation chemistry for rapid ^{99}Tc analysis. In the area of radiation detection, our effort has been directed at the use of diode detectors for direct alpha analysis of liquids and digital signal processing techniques.

In order to enable *total* ^{99}Tc analysis in process solutions, oxidation chemistries and automated procedures must be available which convert all of the Tc species to pertechnetate. Successful development and testing of a microwave assisted oxidation process using sodium peroxidisulfate was accomplished during the previous reporting period. During the second year of this program, we have continued a detailed development and investigation of the column separation chemistries for separating ^{99}Tc(VII) from radioactive interferences in aged waste. A specific separation format selected for a detailed evaluation is based on the use of strongly basic anion exchange functionality. Our results to date indicate that rapid and selective separation of ^{99}Tc from major radioactive interferents and stable matrix is readily achievable using anion exchange sorbent material. Nevertheless, experimentation with various LAW samples from the Hanford site revealed an issue of potential interferences from less abundant anionic species. Using low energy photon spectroscopy, we identified ^{121m}Sn and ^{106}Ru/^{106}Rh as radionuclides that could result in a positive analysis bias in high organics wastes, unless reliably separated from ^{99}Tc(VII). The separation of ^{99}Tc from anionic species using anion exchange material has been characterized in detail. We successfully developed a sequence of column wash steps comprising complexants and acid and caustic washes that enable reliable separation of ^{99}Tc from anionic interferents. The automated separation procedure was successfully evaluated with Envelope A, B, and C Hanford wastes. We conducted studies directed at evaluating Tc(VII)-selective solid phase extraction material (Superlig 639 is this the right number for Tc-02?, IBC Advanced Technologies) as an alternative sorbent for developing a rapid automated separation protocol. Batch uptake and column studies indicated that this sorbent can be used to capture ^{99}Tc from acidified oxidized samples. This sorbent exhibited excellent selectivity for ^{99}Tc(VII) over cationic and anionic species in high ionic strength solutions. Moreover, captured Tc(VII) was elutable from the column using deionized water. Nevertheless, experiments with on-line radiometric detection revealed slow elution kinetics that resulted in unacceptably broad elution profiles, even at elevated column temperatures (60°C) and when using flow reversal technique.

We had initiated research on the feasibility of direct TRU detection and quantification in liquids using diode detectors. In order to improve the overall robustness of the sensor, the diode was placed above the surface of the sample, rather than being in direct contact with the sample solution. This approach was determined feasible and we observed characteristic “thick source” alpha energy spectra, comparable to those reported for a direct contact geometry. The sensitivity was determined to be sufficient to meet the analytical requirements of process monitoring. The effects of the air gap and sample density on sensitivity and energy resolution were examined in detail. Both parameters were found to affect spectral shape, signal intensity, and apparent energy resolution. We investigated the effect of high beta/gamma fields on detection of low intensity alpha radiation. This effect was characterized in detail using commonly occurring fission products, such as ^{90}Sr/^{90}Y, ^{137}Cs, and ^{99}Tc. This study confirmed that diode detectors do exhibit a certain degree of sensitivity towards beta and gamma radiation, and that beta/gamma signals could overlap with a low energy component of the alpha signal. Nevertheless, selection of the appropriate low energy discriminator level allows virtually complete elimination of beta/gamma contribution in the alpha region. In this manner, direct low-level TRU assay is possible in the presence of high levels of beta/gamma emitters. Additional research has been directed at the feasibility of alpha energy or isotopic analysis using thick source spectral responses. We developed a spectrum deconvolution mode and algorithm that enabled reliable deconvolution of individual alpha energy spectra from a mixture of alpha emitters with different energies. This approach enables simultaneous detection of individual isotopes (e.g. ^{241}Am and ^{239}Pu), as opposed to gross alpha measurement. Direct TRU assay using diode detection was validated with the analysis of actual nuclear waste samples from Hanford and Savannah River sites.

Research in radiation detection methodologies has continued in the following areas: 1) preliminary evaluation and single-PMT analysis of pulse shape discrimination with digital signal processing; 2) evaluation of digital signal processing techniques to evaluate improvements in the signal to noise ratio available from solid state radiation detectors; 3) evaluation of ZnS(Ag) for gross alpha measurements of aqueous solutions ; 4) evaluation of "long range alpha (L-Rad)" detection technique for quantification of alpha radioactivity in aqueous waste streams.

A Digital Gamma Finder (DGF-4C, X-ray Instrumentation Associates) was purchased and set up as a fully digital data acquisition system. The DGF-4C offers the possibility of hardware implemented real-time digital signal processing. The negative output pulses from the photodetectors will be digitized at a rate of 40 MHz with 12-bit precision using the XIA's DGF-4C digital spectrometer and waveform digitizer. All four channels of the DGF-4C will be used to digitize up to four signals from various radiation detectors. This arrangement allows for numerous combinations of coincidence and anti-coincidence detection of radiation interactions in the detector assembly. The work in progress is directed at the characterization of pulse shape discrimination algorithms contained within the DGF-4c for separation of alpha/beta as well as beta/gamma-ray events with phoswich style detectors. The beta/gamma-ray phoswich detector is being arranged to quantify the beta events in a gamma-ray background. We have begun to investigate the impact of digital filtering of the data as a means to increase the signal to noise ratio from the radiation detector. The digital data acquisition systems have the advantage of being versatile in the quantification of the radiation interaction in the detector. We have been evaluating photomultiplier tubes as well as avalanche photodiodes as photodetectors and passivated ion-implanted planar silicon semiconductor detectors for direct charged particle

detection. Currently, the means to increase the signal to noise is to use two photodetectors in coincidence as a means of recording a single scintillation event. A similar option does not exist for the direct measurement of charged particles; hence the pursuit of digital filtering techniques to enhance the signal-to-noise ratio.

A ZnS(Ag) scintillator was evaluated as a gross "alpha-only" sensor of alpha radioactivity in aqueous solution as an alternative to diode detection. In this work, experiments were performed for ^{233}U and ^{237}Np a-contaminated wastewaters at various concentrations with a ZnS(Ag) disc coupled to a photomultiplier tube (PMT). The experiment showed that a lower level discriminator setting could be adjusted to discriminate alpha particles from beta particles. Detector responses were compared with the theoretical model and were in satisfactory agreement.

Planned activities

During the third year of the project we will complete research on automated ^{99}Tc measurement in LAW streams and use of the diodes for direct detection of alpha emitters in solution. Per earlier discussions with Savannah River personnel, we will proceed with the research on detection of ^{90}Sr in the presence of high levels of ^{137}Cs. The challenge there is high degree of separation of Sr and Ba. We will continue the research directed at the use of digital filtering for use with diode detectors.

Information Access

Addleman, R. Shane; Egorov, Oleg B.; O'Hara, Matt; Grate, Jay. "Direct measurement of actinides in liquids with PIPS diodes". Abstracts of Papers, 225th ACS National Meeting, New Orleans, LA, United States, March 23-27, 2003 (2003)

Grate, Jay W.; Egorov, Oleg B.. "Sensors and automated analyzers for radionuclides." Preprints of Extended Abstracts presented at the ACS National Meeting, American Chemical Society, Division of Environmental Chemistry (2003), 43(1), 1195-1198.

O. Egorov, M. O'Hara, J. Grate. Automated Radiochemical Analysis of Total Tc-99 in Aged Nuclear Waste Processing Streams, *Journal of Radioanalytical and Nuclear Chemistry*, submitted (2003)

R. Shane Addleman, Matthew O'Hara, Todd Marks, Jay Grate, Oleg B. Egorov. "Direct Actinide Assay with PIPS Diodes"; *Journal of Radioanalytical and Nuclear Chemistry*, submitted (2003)

Grate, J.W. and O. Egorov, "Automated Radiochemical Separation, Analysis, and Sensing," in Handbook of Radioactivity Analysis, Elsevier, 2003, pp. 1129-1164.

B. Ayaz and T. A. DeVol, "Experimental-Theoretical Response of ZnS(Ag) Scintillating Discs for Gross a-Measurements of Aqueous Radioactivity," abstract and summary submitted to the IEEE Nuclear Science Symposium and Medical Imaging Conference, 2003.