Project Number: **95009 (renewed from 81923)**
Project Title: **Radioanalytical Chemistry for Automated Nuclear Waste Process Monitoring**

Date: September 2005

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Number of Graduate Students Actively Involved in the Project: 4

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, which entails integration of sample treatment and separation chemistries and radiometric detection within a single functional analytical instrument. 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.

Research Progress and Implications

This report summarizes work as of 1 years of this renewed 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, the prior work was predominantly focused on addressing scientific issues relevant to the development of chemistries and instrumentation for the analysis of total ^{99}Tc in the process streams. This research was highly successful and the fundamental understanding of the separation issues and chemistries necessary for rapid and reliable control of the analyte speciation greatly contributed to the development of the practical analyzer instrument that was selected by the Hanford contractor for the potential use at Hanford. The focus of the ongoing research activities has shifted on the development of the separation and matrix modification control chemistries for the other key radionuclides of interest such as ^{90}Sr. Development of the reliable and robust monitoring approaches for this radionuclide is critically dependent on the separation chemistries necessary for selective isolation of Sr from chemically and radiologically complex matrices, in a manner compatible with rapid automated measurements. A strontium selective solid phase extraction material was identified as a promising candidate for use as a separation media. The research has been directed at the development of the fundamental uptake characteristics of this material as relevant to the automated measurement methods. Specific challenge is the possibility of efficient separation of Sr from Ba. Numerous complexing agents were investigated in a batch contact format to obtain the selectivity data for key radionuclides as necessary for the development of the separation protocols. Initial feasibility of the automated separation procedure was demonstrated and is being characterized in detail.

We have continued research on the use of silicon diode and scintillation detectors for direct analysis of alpha emitters in liquid samples relevant to nuclear waste process monitoring. Specific emphases was placed on the side by side comparison of these detection approaches with objective of understanding the fundamental processes which determine detector responses. Our past work indicated the diode detection is feasible for the direct analysis of alpha emitters in liquid matrices however, the issues of response dependence on alpha-particle energy remain. Our initial hypothesis is that the use of thin scintillator films can alleviate these issues. The extensive experimental data for thin scintillators was acquired and is being analyzed for the development of theoretical response models.

We continued to make progress in the area of digital signal processing and modeling for use in the pulse shape discrimination. Our specific objective is to develop digital analysis techniques for simultaneous, selective detection of beta and alpha radiation. Development and characterization, and comparison of the software algorithms for processing pulses from the scintillator crystals and phoswitch detector configuration is ongoing. A novel approach using inverse value of pulse shape parameters was conceptualized and demonstrated that offers a notable enhancement in the figure of merit relative to existing methods.

The work continued on the simulation of the light output from the solid scintillator flow cells for use in process analyzers. Energy deposition and light collection efficiencies were successfully modeled to gain fundamental understanding of these processes that determine detection efficiency. This information is important to optimize detection of beta emitters (e.g. ^{99}Tc and ^{90}Sr) in process analyzer instrumentation.

Planned activities

During remaining 2 years of this project we will continue development of chemical separation and advanced radiation detection techniques relevant to detection and quantification of ^{90}Sr and TRU actinides. We will work completion and publication of several manuscripts that detail our progress in automated radiochemical measurements and development of advanced radiometric detection techniques.

Information Access

- Egorov, O.B Addleman, R.S., O'Hara, M.J., Marks, T., Grate, J.W.., "Direct Measurement of Alpha Emitters in Liquids using Passivated Ion Implanted Planar Silicon (PIPS) Diodes", *Nuclear Instruments & Methods In Physics Research, Section A*, **2005**, 573(3), 600-609.

- Egorov, O.B., O'Hara, M.J., Grate, J.W., "Automated Radiochemical Analysis of Total ^{99}Tc in Aged Nuclear Waste Processing Streams", *J. Radioanal. Nucl. Chem.,* **2005**, Vol. 263, No. 3, 629-633.

- J. W. Grate, O.B. Egorov, and M.J. O'Hara, " Sensors and Automated Analyzers for Radionuclides, in "Susbsurface Contamination Remediation: Accomplishments of the Environmental Management Science Program", ASC Symposium Series 904, Oxford University Press, 322-341, **2005** (INVITED)

- R. S. Addleman, O. B. Egorov, M. J. O'Hara, B. Busche, T. S. Zemanian, G. Fryxell "Preconcentration and Assay of Radionuclides with Self Assembled Monolayers on Mesoporous Supports"; *J. Radioanal. Nucl. Chem.,* **2005**, Vol. 263, No. 1, 59-64.

- Addleman, R.S., O'Hara, M.J., Grate, J.W., Egorov, O.B., "Chemically Enhanced Alpha Energy Spectroscopy in Liquids", *J. Radioanal. Nucl. Chem.,* **2005**, Vol. 263, No. 2, 291-294.

- Addleman, R.S., Egorov, O.B O'Hara, M.J., Zemanian T. S., Fryxell. G., Kuenzi D.,., "Nanostructured Sorbents for Solid Phase Microextraction and Environmental Assay", in "Nanotechnology and the Environment: Applications and Implications" ASC Symposium Series 890, Oxford University Press, 186-193, **2005** (INVITED)

- Addleman, R.S., O'Hara, M.J., Marks, T., Grate, J.W., Egorov, O.B., "Direct Actinide Assay with Surface Passivated Silicon Diodes", *J. Radioanal. Nucl. Chem.,* **2005**, Vol. 263, No. 2, 295-300.

- Egorov, O.B., O'Hara, M.J., Grate, J.W., "Microwave-Assisted Sample Treatment in a Fully Automated Flow-Based Instrument: Oxidation of Reduced Technetium Species in the Analysis of Total Technetium-99 in Caustic Aged Nuclear Waste Samples", *Analytical Chemistry*, **2004,** 76(14), 3869-3877. (Highlighted on the US DOE office of Science Web Page)
- Ayaz, B., DeVol, T.A., "Experimental-Theoretical Response of ZnS(Ag) Scintillating Discs for Gross Alpha-Measurements of Aqueous Radioactivity," IEEE Transactions on Nuclear Science, Vol. 51, No. 4, 1688-1692 (2004).