**Project Number:** 81923
**Project Title:** Radioanalytical Chemistry for Automated Nuclear Waste Process Monitoring

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## 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 2 years and 9 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 addressing scientific issues relevant to the development of chemistries and instrumentation for the analysis of total $^{99}$Tc in the process streams. Specific scientific challenges that have been successfully addressed include 1) chemistries and instrumentation for rapid, automated $^{99}$Tc speciation control; 2) separation chemistries for $^{99}$Tc(VII); 3) radioanalytical chemistry of Hanford tank waste, and 4) quantification and calibration approaches. In the area of radiation detection, we continued the work on the use of diode and scintillation detectors for direct analysis of total alpha and individual isotopes in liquid samples. We continued work on advanced photodetectors for scintillation applications 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. We were successful in development of rapid microwave assisted method for oxidation of non-pertechnetate using sodium peroxydisulfate oxidation chemistry. The detailed study has been completed. The manuscript detailing automated oxidation technique has been prepared and accepted for publication in Analytical Chemistry. We have completed detailed development and investigation of the column separation chemistries for separating $^{99}$Tc(VII) from radioactive interferences in aged waste. Several sorbent materials were investigated and characterized. Strongly basic anion exchange sorbent chemistry showed optimal performance and was characterized in detail for the separation of $^{99}$Tc(VII) from stable and radioactive interferences in LAW samples. The issues of removing interfering anionic species such isotopes of Sn, Sb, and Ru have been successfully addressed. The separation procedures were developed and successfully tested with various Hanford LAW samples. Detailed analytical testing of the integrated total $^{99}$Tc analyzer instrument has been completed and feasibility of accurate analysis of Hanford LAW samples have been demonstrated. The manuscript detailing the development and testing of the integrated analyzer instrument is in preparation for submission to Analytical Chemistry

We have completed research on the use of silicon diode detectors for direct analysis of alpha emitters in liquid samples. Effects of the sample/detector geometry and issues associated with interferences were characterized in detail. The sensitivity of this approach was determined sufficient for practical applications. Calibration and quantification strategies have been developed for analysis of liquid samples and we have demonstrated accurate analysis of total alpha activity in Hanford and Savannah River Site samples. A manuscript has been submitted and accepted for publication. In addition to total alpha analysis we have successfully demonstrated feasibility of individual isotopic analysis of alpha emitters in liquid samples. We developed and characterized spectrum deconvolution algorithm that enabled reliable quantification 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. A total alpha detection method using zinc sulfate scintillator coupled to a photomultiplier tube (PMT) was evaluated for direct analysis of total alpha activity in liquids as an alternative to diode detector. Continuum pulse height spectrum was observed for analysis of liquid thick alpha sources. However, in contrast to diode detectors, this approach does not exhibit significant dependence of the counting sensitivity on the energy of alpha particle. Scintillator detector responses for analysis of infinitely thick liquid

samples were compared with the theoretical model and were in satisfactory agreement. A manuscript has been submitted and accepted for publication.

We have developed and characterized a flow-cell detector utilizing a cell packed with granular scintillator which uses silicon photodiodes (PD) for detection of the scintillation light. Digital signal processing was used for analysis of detector pulses. The detector system was used for simultaneous detection of beta and alpha radiation. Our studies have indicated that despite higher quantum efficiency of PD relative to the PMT, PD did not offer significant advantages in figure of merit for sensitivity and pulse shape discrimination.

In the area of digital signal processing, we have made significant progress in development and characterization of the software algorithms for use in pulse shape discrimination. A novel approach using inverse value of pulse shape parameters was conceptualized and demonstrated that offers a 3 fold enhancement in the figure of merit relative to existing methods.

The work continued on the simulation of 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 3 months of this project we plan to work on completion and publication of several manuscripts that detail our progress in automated radiochemical measurements and advanced radiometric detection techniques.

**Information Access**

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