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

Date: November 2006

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Number of Graduate Students Actively Involved in the Project: 6

Research Objective

This research program is directed toward radioanalytical chemistry for rapid, sensitive, and selective determination of beta- and alpha-emitting radionuclides in very complex sample matrixes such as nuclear waste processing streams. Matrix modification, speciation control, and separation chemistries are required for use in automated process analyzers in order to address the challenges related to nuclear waste matrixes. The overall technical approach is based on automated radiochemical measurement principles and fluid handling techniques, which entail 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. Radionuclides such as ^{99}Tc, ^{90}Sr, and transuranium (TRU) elements in waste processing streams are of particular interest. 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 processing operations. This research is addressing these knowledge gaps in the areas of separation science, nuclear detection, analytical chemistry and instrumentation. In addition, new approaches for radiometric quantification of alpha emitters in solution and improved instrumentation and signal processing techniques for use with solid state and scintillation detectors are being developed.

The outcome of these investigations is 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 matrixes. 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, have been developed. New knowledge of the performance of separation materials, matrix modification and speciation control chemistries,

instrument configurations, and quantitative analytical approaches provide the basis for designing effective instrumentation for radioanalytical process monitoring.

Research Progress and Implications

This report summarizes work as of the second year of renewal. Due to the cancellation of the High Level Waste EMSP program, this potentially represents the final year of work under this program. The research under this program has focused in two major areas: 1) radioanalytical chemistry for automated fluidic process analyzer instruments, and 2) new radiometric detection approaches and sensors for radionuclides in solution.

Our initial work on nuclear waste analyzers focused on automated sample treatment necessary to convert nuclear waste process samples in the as-received matrix to samples containing the analyte in a suitable speciation and matrix for the subsequent automated separation and analysis. Focusing on the determination of total ^{99}Tc in caustic aged nuclear waste , we developed fully-automated microwave-assisted sample acidification and oxidation procedures using peroxydisulfate that enable rapid and reliable conversion of reduced forms of ^{99}Tc to ^{99}Tc(VII), i.e. pertechnetate. Separation chemistries to quantitatively capture and purify total Tc require that the Tc be in the pertechnetate state; nonpertechnetate species are not retained by anion exchange, extraction chromatographic or solid-phase extractant materials useful in the analytical separation of ^{99}Tc. This sample treatment system and separation became part of an integrated ^{99}Tc automated radiochemical analyzer system that processes and analyzes nuclear waste samples in 15 minutes or less, using anion exchange chemistry to separate Tc from other radioactive species and a flow through solid scintillator detector. The effectiveness of the automated instrumentation and sample treatment procedures was demonstrated using actual aged nuclear waste solutions with high content of organic and nonpertechnetate species.

The analyzer appproach just described was selected in a competitive reviewed process to be incorporated in the Hanford Waste Treatment Plant as part of the technetium removal process, where substantial cost savings were projected if on-line analyzers were used to monitor process performance.

In developing this analyzer concept we investigated approaches for microwave assisted sample pretreatment and oxidation, with automated sample delivery to the microwave cavity and automated retrieval to send the sample forward to a separation scheme. We developed chemistry and procedures to overcome difficulties with uneven heating, violent bumping, gas evolution, foaming, and precipitate formation in digesting these complex sample matrixes, ultimately achieving successful pretreatment and complete conversion of technetium to pertechnetate.

We further investigated separation chemistry to isolate pertechnetate from the complex sample matrixes. Several sorbent materials were investigated and characterized. Using a particular anion exchanger, reliable separation was possible at high flow rates (up to 7.5 mL/min) as required for the development of rapid analytical procedures. In the course of this work, we discovered that some nuclear waste samples contained isotope ^{121m}Sn in significant quantities. This isotope was previously undetermined in the aged waste matrixes. We found that it can be present in aged waste at activity levels exceeding those of ^{99}Tc, especially in waste with a high content of organics. A comprehensive separation procedure was developed that successfully

addressed the challenge of separating anionic radionuclides (isotopes of Sn, Sb, and Ru) which were initially found to interfere with ^{99}Tc analysis in aged wastes. The effectiveness of the separation procedure was verified in the numerous experiments with actual Hanford nuclear waste samples.

The microwave assisted pretreatment and pertechnetate separation chemistry were integrated with a flow-through solid scintillation detector, which provides adequate sensitivity to meet required detection limits. An automated calibration approach using standard addition technique was developed and verified using simulants and actual wastes samples. The instrument was extensively tested with all envelopes of Hanford waste using waste simulants and actual AN-107, AN-102, AZ-101, AZ-102, and AP-104 Tc decontaminated waste matrixes. The instrument was fully automated and demonstrated in unattended operation. It met or exceeded all Hanford-specified requirements, with a total analysis time of 12.6 minutes per sample.

After our success with pertechnetate analysis chemistry and methodology, the focus of the research shifted to the development of separation and matrix modification control chemistries for the other key radionuclides of interest such as ^{90}Sr. Two solid phase extraction materials, SuperLig 620 and Dowex 50, were identified as being promising candidates for use as separation media for ^{90}Sr from other radioactive tank waste constituents. The greatest challenge in developing a rapid ^{90}Sr process monitor is the separation of the analyte from the highly complex chemical and radiochemical composition of the waste material. Since the ^{90}Sr is a pure beta emitting radionuclide, radiochemical purity of the analyte must be attained for accurate quantitation by radiometric detection. Most challenging is the separation of ^{90}Sr from the ^{137m}Ba daughter product of ^{137}Cs, which exists at extremely high activities in tank waste. Chemically, Sr and Ba are highly similar. Therefore, chemical conditions in which Sr has an affinity for the sorbent media will typically exhibit affinity for Ba. Since the metastable state of ^{137}Ba has a ~2.5 minute half-life, a process monitor requiring rapid sequential analysis of the tank waste stream would likely not have the luxury of waiting for the ^{137m}Ba to decay. Therefore, an efficient means of chromatographically separating Sr from Ba needed to be developed, and the column-based technique needed to be conducive to automation. Additionally, ^{90}Y, the daughter product of ^{90}Sr, needed to be separated from its parent on the column.

Using the selected solid phase extraction materials, we characterized the uptake of Sr, Ba, and Y radiotracers in various uptake and complexing solutions. As both solid phase sorption media had high affinity for Sr and Ba from acidified tank waste stimulant, the challenge was to identify a complexant solution which was capable of separating Sr from Ba. Numerous complexing agents were investigated in a batch contact format to obtain the uptake data for key radionuclides as necessary for the development of the separation protocols. Ultimately, we developed a separation scheme using SuperLig 620 and tested it in a packed column format using automated fluidics. We were able to obtain baseline separation of Sr from Ba, as determined by a flow-through scintillation spectrometer coupled to the automated fluidic system. We further evaluated our selected separation approach for its ability to separate Sr from the multitude of other inorganic ions in the tank waste stimulant, leading to load / elute profiles for many elements. This data was invaluable to show which tank waste constituents were easily washed from the column versus elements which would co-elute with the Sr. None of the elements found to be retained and co-eluted with Sr should have radioactive isotopes in sufficient concentration in

tank waste to bias the ^{90}Sr measurement. Furthermore, no chemical interferences were identified.

The development of functional radiochemical analyzers capable of meeting analysis time and detection limit requirements necessitates improvement in flow-through radiometric detectors. The research on new radiometric detection approaches and sensors for radionuclides in solution has proceeded with multiple aspects in parallel: 1) solid state diode detectors for quantification of alpha-emitters in liquids, 2) total alpha activity measurements in liquids using thin films scintillators, 3) advanced photodetectors for scintillation applications, 4) digital signal processing, and 5) simulations of solid scintillator flow cells.

Improved scintillation detection methodologies, light detection techniques and detector configurations are required for quantification of beta emitting ^{99}Tc and ^{90}Sr in the process analyzers using flow-through radiometric detectors. In addition, the development of novel detection methodologies based on diode and thin film scintillation detectors is necessary to enable rapid and sensitive analysis of alpha emitters. Digital signal processing offers the potential to improve the sensitivity of scintillation and solid state detectors.

Both diode detectors and thin films scintillators were investigated as a means to detect alpha emitters in thick liquid sources for process monitoring applications. Diode detection can be used for total alpha analysis and provide alpha energy information to discriminate among individual radionuclides. Scintillation can be used in total alpha analysis only. In addition, several instrumental aspects of detection were investigated including digital signal processing for pulse shape discrimination, light detection devices, and flow cell design.

Solid state diode detectors for the detection of alpha emitters in liquid samples were investigated with the detector in direct contact with the liquid, or with small separations between the liquid and detector surface were examined. Total alpha measurements were made, as well as alpha energy spectra with spectral deconvolution to determine individual isotopes in mixtures. Modern passivated ion implanted planar silicon (PIPS) detectors were found to be robust and practical for operation in these geometries. Diodes were also investigated with thin film extractants to collect and localize alpha emitters at the surface, yielding detectable signals and characteristic alpha energy spectra. The direct measurement of alpha emitting radionuclides from high activity liquids would be highly beneficial as a means of rapidly determining activity of actinides in a process waste stream.

Thin film scintillators were also investigated for total alpha activity measurements in liquids. A ZnS(Ag) detector was successfully used in the direct detection of alpha particles from aqueous solutions and the results were compared to the PIPS diode. The large detection area available to the ZnS(Ag) detector proved to be a valuable characteristic in the detection of liquids. The beta and gamma interference did not significantly spillover into the alpha region of interest. Total alpha analysis using scintillation detection was demonstrated for detection of ^{233}U in waste simulant matrixes containing ^{90}Sr. Experimental detection efficiencies for analysis of infinitely thick sources were compared with the model values and were in satisfactory agreement

Also in the area of radiometric detection instrumentation, solid state photon detectors were compared with conventional photomultiplier tubes. Photodiodes offer higher quantum efficiencies, smaller size and reduced power consumption. A flow detection system using two silicon PIN-photodiodes (PD) operated in coincidence was developed and demonstrated for detection of alpha and beta activities in liquids, and digital signal processing of the PD was demonstrated for discrimination of alpha and beta events.

Using digital data acquisition systems to record and process individual detection pulses, several software algorithms were developed and optimized to execute pulse shape and pulse height processing of signals to separate individual radiation events. Using a combination of plastic and inorganic scintillators, a digital signal processing system was successfully applied to the simultaneous detection of beta and gamma events. A *new* digital signal processing algorithm using an inverse of pulse shape parameter was developed and evaluated against a pair of metrics and a figure of merit for pulse shape discrimination. These approaches to discriminate events due to different types of radiation events will enable greater selectivity in the measurement of radionuclides of interest in complex radiation backgrounds.

In addition, energy deposition and light collection in solid scintillator flow cells were successfully simulated using Monte Carlo methods and compared with experimental measurements. These models provide fundamental understanding of the processes that govern detection efficiency, and important trade off parameters relevant to flow-cell design were identified.

Planned activities

The remaining budget from this program will be utilized preparing manuscripts describing the various scientific advancements which were made possible by the EMSP HLW program. This includes development of automated process monitoring systems, thin film coating and surface functionalization of PIPS diodes, and direct alpha measurements using PIPS and ZnS(Ag) detectors.

Information Access

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