Sensors and Automated Analyzers for Radionuclides

Jay W. Grate and Oleg B. Egorov
Pacific Northwest National Laboratory,
Box 999, Richland, WA 99352
jwgrate@pnl.gov

Introduction

The production of nuclear weapons materials has generated a legacy of nuclear waste and contaminated environmental sites. The remediation of radiochemically contaminated sites and processing of stored wastes into stable waste forms will require characterization procedures throughout all phases of these activities. Consequently the demands for radiochemical analysis will increase rapidly in the future. Methods are required to do these analyses rapidly and precisely. To meet these characterization needs, new automated techniques are required in order to provide improved precision, consistent analytical protocols, reduced worker exposure to toxic and/or radioactive samples, greater sample throughput, reduced costs, and reduced secondary waste generation. Furthermore, methods are required that provide automatic analyses in settings other than analytical laboratories.

Analyses of radionuclide content are needed at-site or *in situ* for monitoring surface waters, groundwater, and process waters. The greatest concern is radionuclides that are mobile in the environment and cannot be practically detected and identified using gamma spectrosopy. Radionuclide measurements are required to support baseline monitoring of surface and subsurface waters; to support characterization of contaminant migration; to assess efficacy of remediation processes in the field (e.g., pump-and-treat and barriers); to support operation of remediation processes (e.g., column breakthrough); and in long term stewardship. In current practice, water samples are collected and transported to the analytical laboratory where costly radiochemical analyses are performed. Sample turnaround times are several days to several weeks.

In addition, new automated radiochemical analysis techniques will be required to enable rapid characterization of the nuclear processing streams, for example, during radionuclide removal steps. These analyzers must operate continuously within the nuclear waste processing plant. Such new monitoring techniques would facilitate more precise and reliable control of waste processing operations, and offer considerable cost savings. For example, replacement of separation resins in radionuclide removal steps is very costly due to the expense of the selective resins. Monitoring of column performance will allow replacement only when needed, rather than scheduled periodic replacement at arbitrary intervals. In addition, treated waste that does not meet specifications will have to be run through the treatment process again, at considerable cost. Using automated monitors to assure effective process operations will avoid such costs and schedule delays.

Although there are many radioactivity detectors available, there has been very little development of analytical instruments or radiochemical sensors suitable for rapid and selective quantification of beta- and alpha-emitting radionuclides such as Tc-99, Sr-90 and TRU actinides in process streams. Current baseline analytical methods for these analytes are based on tedious manual radiochemical analysis methods performed in centralized laboratories. This represents a significant technical gap that has been identified in several technology needs throughout the DOE complex. Moreover, significant scientific challenges exist in order to meet these technical needs.

Considerable progress has been made in developing automated methods for radiochemical analysis using sequential injection fluidics and extraction chromatography separations.[1-9] These separation processes capture radionuclides of interest while washing away matrix components and interferences. The captured radionuclides are then released

selectively by sudden changes in the solution composition passing through the column. Automated analytical separations for Sr-90, Tc-99, and actinides have been described, using flow through scintillation counting or inductively-coupled-plasma-mass-spectrometry for detection and quantification. The present paper turns its attention to new approaches for sensing and monitoring.

Methods and Results

Preconcentrating Minicolumn Sensors for Radionuclides

The fundamental challenges in radionuclide sensing of alpha- and beta-emitters are the short ranges of these particles in condensed media (e.g. water) and the ultra-trace analytical detection limit requirements. Chemical sensing methods may be applicable only to those radionuclides where the required detection limits are not too stringent, such as uranium. For other radionuclides of interest, where the required detection limits are far beyond the capabilities of any known or conceivable chemical sensing method, radioactivity detection is necessary. Radioactivity detection is also required when radioactive isotopes of concern must be distinguished from stable natural isotopes.

For detection on the basis of alpha or beta emissions, some method of separating the radionuclide of interest from interfering species and localization in the detection volume of a detector must be incorporated into the sensing mechanism. We have developed a preconcentrating minicolumn concept for a radionuclide sensor that is based on dual functionality minicolumns. The materials in these columns incorporate selective separation chemistry to capture and retain the radionuclides of interest, and scintillating fluors so that radioactivity of the captured species results in a measurable light output. These two functions can be incorporated into the column using a single material. For example, "selective scintillating microspheres" (SSMs) have been developed for this purpose. Alternatively, intimate mixtures of chemically selective microspheres and scintillating microspheres can be packed into the minicolumn The minicolumn is located between two photomultiplier tubes of a scintillation detection system to collect the signal. The selectivity is determined mainly by the separation chemistry used to preferentially capture and preconcentrate the analyte of interest.

This configuration meets all the functional requirements for effective radionuclide sensors. The packed column format provides for efficient fluidic processing of the sample for preconcentration. The detection method is radiometric via the process of scintillation. Selective chemistry is in very close proximity to the scintillation material and retains the radionuclides for counting. These new column sensors represent a novel and advantageous approach for detection of radionuclides when selective preconcentration is required. When necessary, the sensing material can be regenerated or renewed.

Using pertechnetate-selective scintillating beads prepared by co-immobilization of selective extractants and scintillating fluors, we have demonstrated the application of SSM resins for the characterization of Tc-99 in the pertechnetate oxidation state in acidified groundwater.[10,11] The resin is used in conjunction with a scintillation detector flow-cell and an automated fluid handling system. The results of these tests clearly indicate that radioactive pertechnetate can be readily detected in acidified groundwater samples below the U.S. Safe Drinking Water Act maximum concentration level of 900 pCi/L. We have also evaluated sensor configurations based on a mixed-bed column of anion exchange and polymer scintillator beads. Using mixed-bed sensor columns, we demonstrated the feasibility of Tc-99 sensing in unacidified groundwater with detection efficiency of 25% and excellent long-term sensor column stability. This approach appears especially promising for the development of a Tc-99 sensor probe suitable for down-well groundwater monitoring.

Automated Radionuclide Analyzer

Determination of non-gamma emitting radionuclides in process streams is a significant challenge. The combination of the sample matrix, the characteristics of the species to be detected, and the detection limit requirements preclude

most existing analytical methods. The process streams to be analyzed are caustic brine solutions. Thus, the sample matrix is difficult, and furthermore, it will be variable. The basicity, nitrite content, organics, complexants, and aluminum ion concentrations will depend on the feed. Radionuclides such as Tc-99 may not be present as a single chemical species, and in some cases the actual speciation is not known.

Our specific emphasis has been on the process monitoring needs associated with the operation of the chemical pretreatment or low activity waste (LAW) processing operations. The major chemical processing steps include a Tc removal process based on a semi-continuously operated ion-exchange column. For the analysis of total Tc in nuclear waste, it is necessary to fully oxidize the Tc present so that it is all in the pertechnetate state. We have developed an automated fluidic analyzer system that takes a complex nuclear waste stream sample, acidifies it, and oxidizes Tc to pertechnetate in an automated microwave digestion system using peroxidisulfate. It then performs a chemical separation and detects the purified Tc-99 by radioactivity detection. The monitor determines total Tc to the required detection limits and the total analysis time is less than 15 minutes. Furthermore, it is fully automated for continuous operation.

Tests were conducted on high organic content AN107 waste in which the majority of Tc is present in reduced oxidation states. The fully automated instrument correctly quantified the Tc in these challenging samples, as demonstrated by comparisons with independent analysis by ICP-MS.

Discussion

Our initial work in automating laboratory analysis of radionuclides in nuclear waste has now advanced to the development of sensors and instruments for nonlaboratory settings. Our sensor for Tc-99 in ground water was selected for prototype engineering development, and a field test was conducted at the Hanford site in September 2002. This unit successfully quantified the Tc-99 activity in Hanford ground water samples. The automated Tc analyzer has been under development for use at the Hanford site, and was selected for incorporation into the Hanford Waste Treatment Plant.

References

[1] J. W. Grate and O. B. Egorov, Anal. Chem., 70 (1998) 779A-788A.
[2] J. W. Grate, R. S. Strebin, J. Janata, O. Egorov and J. Ruzicka, Anal. Chem., 68 (1996) 333-340.
[3] O. Egorov, J. W. Grate and J. Ruzicka, J. Radioanal. Nucl. Chem., 234 (1998) 231-235.
[4] O. Egorov, M. J. O'Hara, J. W. Grate and J. Ruzicka, Anal. Chem., 71 (1998) 345-352.
[5] O. B. Egorov, M. J. O'Hara, J. Ruzicka and J. W. Grate, Anal. Chem., 70 (1998) 977-984.
[6] J. W. Grate and O. Egorov, Anal. Chem., 70 (1998) 3920-3929.
[7] J. W. Grate, S. K. Fadeff and O. Egorov, Analyst, 124 (1999) 203-210.
[8] J. W. Grate, O. B. Egorov and S. K. Fiskum, Analyst, 124 (1999) 1143-1150.
[9] O. B. Egorov, M. J. O'Hara, O. T. Farmer, and J. W. Grate, Analyst, 126 (2001) 1594-1601.
[10] O. B. Egorov, S. K. Fiskum, M. J. O'Hara and J. W. Grate, Anal. Chem., 71 (1999) 5420-5429.
[11] T. A. DeVol, O. B. Egorov, J. E. Roane, A. Paulenova and J. W. Grate, J. Radioanal. Nucl. Chem., 249 (2001) 181-189.