Surface and Groundwater Analyses Using Solid Phase Extraction Disks

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Abstract

The Savannah River Site (SRS) has been using commercial and test solid phase extraction (SPE) disks to prepare samples for radiochemical analysis. Two projects where the new techniques have been deployed are at the F&H Groundwater Treatment Facility for rapid radiochemical screening of samples, and along surface streams around the SRS for environmental monitoring of radionuclides. The SPE disks used for these projects are the 3M Empore™ RAD disks; technetium, strontium, radium and a test disk for cesium. Each application will be discussed separately below.

Introduction

Empore™ RAD disks are a combination of 3M Empore™ Membrane technology and selective adsorption resin technology. Empore™ disks contain chromatographic particles enmeshed in a network of PTFE fibrils to form a strong porous sheet, or membrane. The properties of the membrane are determined by the sorptive or reactive properties of the chosen particle. Initially, membranes were prepared containing hydrophobic octyl- and octadecyl-bonded silica particles for reversed-phase extractions of environmental pollutants[1] and used to replace liquid-liquid extractions. This technology was then expanded to include membranes that were selective for the extraction of radionuclides from solution.

The Sr RAD disk makes use of IBC Advanced Technologies, Inc., AnaLig™ Molecular Recognition Technology, such that the AnaLig™ adsorbent particles (Superlig 620) in the Sr disk allow selective adsorption of strontium. The Ra RAD disks contain another AnaLig™ particle, Superlig 640, which is selective for radium. The Tc RAD disks contain GD-1 sorbent for the selective adsorption of technetium. The test disk for Cs contains potassium cobalt ferrocyanide (KCFC). Hexacyanoferrate compounds have often been used for the environmental analysis of radiocesium[2,3].

Laboratory testing of the Empore™ RAD disks[4] demonstrated that the disks were highly selective for the specific analyte, had a large capacity for the chosen analyte, and could maintain quantitative extractions at flow rates up to 100 mL per minute. Only minimal volumes of unfiltered surface water could be pumped through the disks before complete physical clogging, however, over 10 liters of water could be pumped through a membrane if the water was first filtered through a 0.45μm particle filter. These characteristics of the

Empore™ RAD disks were exploited in the two technology deployments at the SRS, discussed below.

F&H Groundwater Treatment Facility

The present mission of the Savannah River Site, a Department of Energy nuclear production facility, is one of nuclear waste stabilization and environmental restoration and remediation. Due to previous practices of disposing radioactive waste to seepage basins located near the center of the Site, some of the groundwater has become contaminated with radioactive species. A water treatment facility has been installed to remediate the groundwater below the F&H area seepage basins, which had previously received waste discharges.

Groundwater is pumped from the contaminated aquifer through a series of filtration, ion exchange and reverse osmosis steps, and when cleaned is reinjected back into the aquifer. Prior to reinjection the water must be analyzed to ensure the radioactivity levels are below established criteria. In order to minimize turn around time, an on-site lab is going to be installed near the treatment facility; rapid analytical procedures have therefore been developed for determining sample activity in the on-site lab. The required analyses include tritium, gross alpha, gross beta (excluding tritium), Sr-90, Tc-99, Cs-137 and Ra-226/228. Currently, the analyses are performed in an SRTC lab and counted in the Environmental Monitoring Section counting room until the on-site lab counting equipment is installed.

Tritium is determined using standard liquid scintillation spectrometry methods; a 3 mL aliquot of the sample is mixed with 19 mL of Packard Opti-Fluor® liquid scintillation cocktail. The sample is then counted on a calibrated Tri-Carb® 2200 liquid scintillation spectrometer for activity determination. Gross alpha and beta activities are determined using a batch extraction incorporating EIChroM's Actinide and TEVA resins, followed by simultaneous alpha/beta liquid scintillation detection on a Packard Tri-Carb® 2700TR with pulse decay analysis to discriminate alpha and beta particles.

The isotope specific analyses are completed using 3M Empore™ solid phase extraction disks. In order to minimize turnaround time and minimize sample size, therefore exposure, all four elements are determined on the same sample aliquot. For influent water, a 500 mL sample size is used while a one liter sample is processed for the effluent/injection sample. Based on laboratory studies[4], the sample is first passed through the Ra disk, followed by the Sr disk, the Cs disk and lastly the Tc disk. Stacked in this manner only the analyte of interest is retained on the specific disk without interfering with the following disks. The water is pulled through the stacked disks under vacuum using a Milli-pore filter housing. Prior to counting, the disks are dried in an oven set at 70°C for 20-30 minutes. The disks are counted on a low background alpha/beta gas-flow proportional counting system for 20 minutes each.

In the contaminated influent waters we found that Th-234 or Co-60 may also be extracted on the Cs disk, biasing the Cs-137 activity determination. If this is suspected, the Cs disk may be counted by gamma spectrometry to uniquely identify the individual components. In the effluent water, we have seen only minimal residual activity on the Cs disk; attributing all the activity to Cs-137 does not cause the resultant activity calculation to exceed the reinjection criteria.

Environmental Monitoring of Surface Streams

Commercially available ISCO, Inc., 3700 series portable samplers were modified by ISCO, Inc. to collect aqueous samples from surface streams and process the sample through 3M Empore™ solid phase extraction (SPE) disks at the time of collection. The modified samplers were placed at routine monitoring locations and set to collect a composite sample over the course of a week. Six to eight liters of water were processed through the Tc RAD, Sr RAD and Cs RAD SPE disks in the field during each sampling period.

Data collected during the first field trial[5] compared favorably with historical and standard analysis results but could not be easily compared to laboratory analyses due to differences in the start and end dates of the sample collection period, and due to the more sensitive detection limits achieved by the new field method (due to larger sample volumes processed) as compared to the detection limits of the routine laboratory based method. A second field trial was therefore undertaken. Samples were collected for the same time periods, and the laboratory counting times or sample volumes were increased in order to achieve lower limits of detection comparable to the detection limits achieved by the field analyses.

The field based Tc-99 and Sr-90 results agreed in most cases with the lab based results; 95% of the Tc-99 results agreed at 2 sigma with no bias seen in the data; over 70% of the Sr-90 results agreed at 2 sigma with slight negative bias in the field results. The Cs-137 results were harder to compare as the field method generated a dissolved and particulate result and the lab an unfiltered result. The particulate Cs-137 activity was often over 50% of the total field determined activity, however the field dissolved Cs-137 result often was similar to the lab total result. 80% of the field dissolved results agreed at 2 sigma with the lab total result, with a positive bias in the lab total result, as might be expected.

A significant emphasis has been placed on the DOE labs to work "faster, better and cheaper." Data generated by the field method were available within a week of sample collection. One technician was able to prepare all the disks for counting in a few hours. Each laboratory based analysis was performed by a different technician, with results often not available for several weeks. The laboratory based analyses had to be modified to meet the detection limits achieved by the field method. Overall, the field based method meets the "faster, better, cheaper" criteria, and has been implemented as part of the routine environmental monitoring program at the SRS.

References

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