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Chem. Rev., **2008**, 108 (2), 543-562 • DOI: 10.1021/cr068115u

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Radionuclide Sensors for Environmental Monitoring: From Flow Injection Solid-Phase Absorptiometry to Equilibration-Based Preconcentrating Minicolumn Sensors with Radiometric Detection

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Received March 7, 2007

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1. Introduction

The development of in situ sensors for ultratrace detection applications in process control and environmental monitoring remains a significant challenge. Such sensors must meet difficult detection limit requirements while selectively detecting the analyte of interest in complex or otherwise challenging sample matrixes. Nowhere are these requirements more daunting than in the field of radionuclide sensing for α- and β-emitting radionuclides in water. The detection limit requirements can be extremely low. Nevertheless, a promising approach to radionuclide sensing based on preconcentrating minicolumn sensors has been developed. In addition, a method of operating such sensors, which we call equilibration-based sensing, has been developed that provides substantial preconcentration and a signal that is proportional to analyte concentration, while eliminating the need for reagents to regenerate the sorbent medium following each measurement. While this equilibration-based sensing method was developed for radionuclide sensing, it can be applied to nonradioactive species as well, given a suitable on-column detection system. By replacing costly sampling and laboratory analysis procedures, in situ sensors could have a significant impact on monitoring and long-term stewardship applications.

The preconcentrating minicolumn sensor relies on a solid phase, typically a packed bed of particles or beads, to collect and concentrate the analyte species of interest within a detector. A portion, or ideally all, of the solid phase is within the detected volume. Typically the solid phase is packed in a small column with fluid flow parallel to the column axis. This can be a straight column or a column that has been coiled to fit within the detection system. Some sensors, however, are prepared with the solid phase in a disk or plate geometry with radial flow from the center to the periphery. Optical or luminescent methods predominate for the detection of analyte species, or their reaction products, captured on the solid phase. The radionuclide sensors described in this review are primarily preconcentrating minicolumn sensors that rely on the detection of scintillation photons from a dual-functionality column. The column contains selectively sorbent functionality and scintillating properties in the same material, or in materials that are in close proximity to one another.

The preconcentrating minicolumn sensor is shown schematically in Figure 1a, along with the radionuclide sensor concept in Figure 1b, where the scintillation photons are detected with a pair of photomultiplier tubes. The fluidic format is an efficient means of collecting analyte species from much larger sample volumes and for concentrating them on the solid phase for on-column detection. This precon-

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10.1021/cr068115u CCC: $71.00 © 2008 American Chemical Society
Published on Web 01/03/2008

Jay W. Grate is a Laboratory Fellow at the Pacific Northwest National Laboratory (PNNL) and an Affiliated Professor with the Chemistry Department of the University of Washington. He received a B.A. in Chemistry at Rollins College and received his Ph.D. in Chemistry from the University of California, San Diego. After postdoctoral research at the University of California Irvine, he joined the Naval Research Laboratory in 1984, moving to PNNL in 1992. He spent a sabbatical at the Scripps Research Institute prior to joining PNNL. Dr. Grate's research has focused on chemically interactive polymers and nanomaterials, chemical vapor sensors, radiochemical separations and sensing, and bioanalytical fluidics for biothreat detection. His work integrates aspects of the chemical sciences, material sciences, and measurement sciences into new microanalytical principles, methods, and systems. His work in the radioanalytical field has entailed the development of new radiochemical analysis methods using sequential injection separations, fully automated radiochemical process monitors, and sensors for radionuclides in water. He has published over 100 papers in peer-reviewed journals and numerous book chapters, and he is author or coauthor on over a dozen patents, several of which have been licensed. He received an R&D 100 Award in 2004 and an American Chemical Society Regional Industrial Innovation Award in 2007.

Prior to joining IsoRay Medical Inc. in 2005 as a Director of Research and Development, Dr. Egorov has worked as a senior research scientist at the Pacific Northwest National Laboratory. He received his Ph.D. in Analytical Chemistry from the University of Washington in 1998. In addition to his Ph.D., Dr. Egorov has an M.S. degree specializing in Radiochemistry from Moscow State University in Moscow, Russia, and an M.S. in Environmental Analytical Chemistry from the University of Washington. His research at PNNL has specialized in microfluidic systems and their application toward automation of radionuclide separations and analysis, where he has authored or co-authored several key publications, including invited review articles and book chapters. Dr. Egorov pioneered the application of flow-injection techniques for automating radiochemical analyses of nuclear wastes and process monitoring, renewable surface sensing and separations, and equilibration sensing. His research interests include radiochemical analysis, selective radionuclide sensing, nuclear waste process monitoring, medical radioisotope production, and laboratory automation.

Matthew J. O'Hara is a scientist at the Pacific Northwest National Laboratory. He received B.A. degrees in Chemistry and in Geology from the University of Montana in 1996, and a Masters degree in Business Administration from Washington State University in 2004. He has been involved in scientific research in the fields of radioanalytical chemistry and laboratory automation for over 10 years. The primary focus of his research has been the selective preconcentration, separation, and detection of actinides and radioactive fission products from various matrices using automated fluid handling and detection systems. The instrumentation he has developed has targeted specific α- and β-emitting radionuclides with the objective of activity quantification ranging from ultralow activities in environmental waters to high-level activity in nuclear waste samples. His research has resulted in the development of medical isotope separation systems, sensors for groundwater monitoring, and prototype process monitors for Hanford's nuclear waste treatment plant.

Timothy A. DeVol is a Professor of Environmental Engineering and Earth Science at Clemson University. Dr. DeVol earned a B.S. in engineering physics from The Ohio State University, and a M.S. and Ph.D. in nuclear engineering from the University of Michigan. Dr. DeVol has been teaching and conducting research at Clemson University since 1993. He teaches courses in radiation and health physics, ionizing radiation detection, and radioactive waste management. His major research interests are in the detection and measurement of ionizing radioactivity in the environment, environmental radiochemistry, and statistical analysis of monitoring data. Dr. DeVol has published over 40 papers in peer-reviewed journals and has made over 130 scientific presentations.

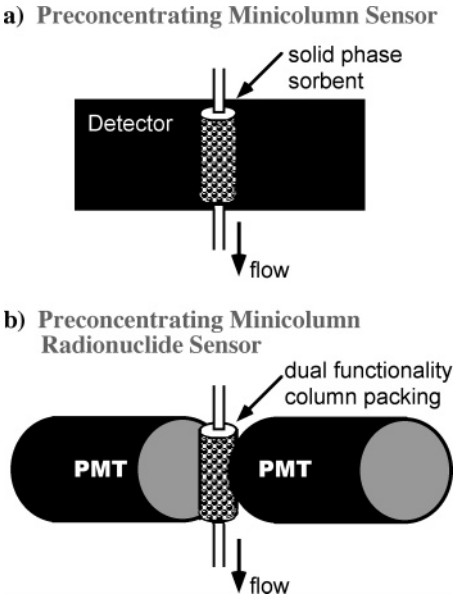


Figure 1. Schematic diagrams for (a) preconcentrating minicolumn sensors and (b) radionuclide sensors based on dual-functionality materials in preconcentrating minicolumn sensors. The column may also be a coil within the detection zone.

centration increases sensitivity and reduces detection limits. In addition, concentrating the analyte in a smaller volume can simplify and reduce the size of the detection method used. These features are all desirable for environmental sensors, where analytes are typically present at very low concentrations and the sensor should ideally be suitable for at site or in situ deployment.

In typical use, the fluidic system containing the sensor processes a sample aliquot of defined volume, and the analytical signal is taken within a defined time range of the process. In this regard, the sensor may be regarded as part of an assay system that determines the quantity of the analyte in that particular sample volume. However, as we shall illustrate with the equilibration-based radionuclide sensor to be described below, such a sensor can also function as a true sensor whose signal goes up and down with the ambient concentration. As long as the sensor is allowed to reach equilibrium, the signal is not dependent on the volume of the sample processed through the flow cell; it depends on the concentration of the analyte and its interaction with the solid phase.

The aim of this review is to cover radionuclide sensors for α- and β-emitting radionuclides that combine some form of selective sorption with a radiometric detection method and—as a primary aim—to comprehensively review preconcentrating minicolumn sensors for radionuclide detection. This work that has largely occurred from 1995 to the present.[1−18] As a secondary aim, we will cover radionuclide sensors that combine sorption and scintillation in formats other than minicolumn sensors. We are particularly concerned with the detection of α- and β-emitting radionuclides in liquids, which presents particular challenges as we shall describe below. We will not cover systems to detect γ rays or the radionuclides that emit them, since γ rays can readily pass through condensed media to radiation detectors and the γ-ray energy spectrum provides considerable selectivity. Nonetheless, preconcentrating sensor methodologies to be described in this paper can also offer advantages for low-level sensing of γ-ray emitters where preconcentration is required.

Throughout the narrative, we will focus on sensors for ^{99}Tc as the prototypical examples for illustrating the detection principles. These are the most mature radionuclide sensors to date, and ^{99}Tc is an important radionuclide to detect in environmental monitoring. It is generated from the thermal fission of ^{235}U with a high production yield of 6% and is a significant radioactive contaminant at U.S. Department of Energy sites associated with nuclear weapons production. It has a long radioactive half-life of 2.13×10^5 years, and it is highly mobile in the environment in the Tc(VII) oxidation state as the pertechnetate oxyanion, TcO_4^-. Hence, this contaminant will persist in the environment, and it must be monitored as it is unlikely to stay in one place.

As a portion of the background material, we will cite selected material on preconcentrating minicolumn sensors using transduction mechanisms other than radioactivity to detect analytes ranging from metal ions to organic pharmaceuticals and nutrients. This work has largely occurred from 1985 to the present. These types of fluidic sensors were developed within the fields of flow injection and sequential injection analysis; therefore, these topics will be introduced in the background material. In addition, the method of "bead injection" has been developed where the sorbent material is delivered to the detection flow cell for each measurement and then released. Bead injection represents a renewable surface preconcentrating sensor. Before turning our attention entirely to radionuclide sensors for water monitoring, we will also provide some background on automated radiochemical analysis.

Finally, this review is not concerned with assays that use radionuclides as labels, such as the scintillation proximity assay (SPA).[19−21] This method is used for studies of binding interactions of biologically relevant compounds, using scintillating microspheres and radiolabeled molecules of high specific activity. It is designed to discriminate between bound and unbound molecules. Although this assay combines chemical selectivity with scintillation, its purpose is not focused on environmental radiochemical analysis applications.

2. Background

2.1. Flow Injection and Sequential Injection Analysis

A large number of sensors fitting our definition of preconcentrating minicolumn sensors were developed as detectors for flow injection analysis systems.[22−24] Flow injection consists of a fluidic analysis approach where sample and reagent solutions are driven in a continuous forward flow paradigm through a progression of mixing, reaction, and/or separation steps to a flow-through detector. The prototypical assay was colorimetric with an optical absorbance detector. Figure 2a provides a schematic diagram of a flow injection system. The original fluid drive was typically one or more peristaltic pumps coupled with at least one valve for sample injection. By incorporating an appropriate solid phase within the detector, creating an optosensor, the analyte or reaction products could be captured, preconcentrated, and focused within the detection zone for greater sensitivity.

Sequential injection arose as a subsequent approach to flow-based analysis; a schematic diagram is shown in Figure 2b.[25−28] Sequential injection relies on programmed bidirectional flow. The preferred fluid drive is a digital syringe pump coupled to a multiposition valve with a holding coil

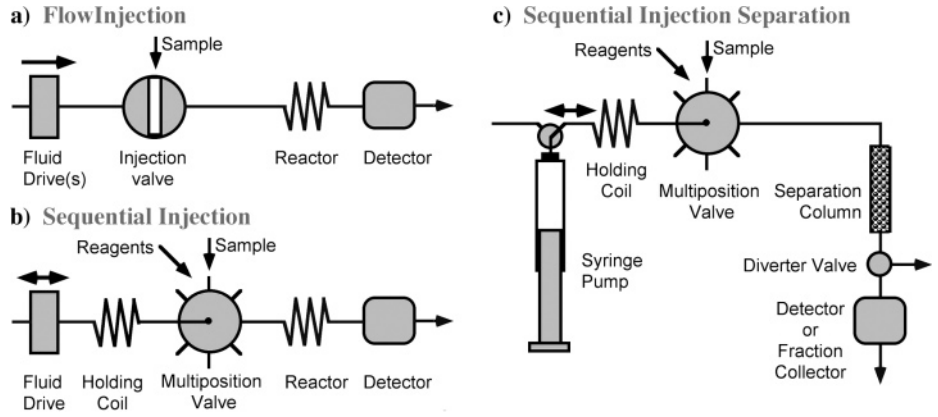


Figure 2. Schematic diagrams of prototypical (a) flow injection analysis, (b) sequential injection analysis, and (c) sequential injection separation systems.

in between. In a typical analysis, samples and reagents are pulled as zones into the holding coil using reverse flow, stepping the multiposition valve from one position to another for each solution. These zones are then propelled forward though the multiposition valve to the analysis system consisting of a reactor or separator and detector. In a simple colorimetric assay, the zones intermix by dispersion, generating reaction products for detection. Sequential injection systems are fully automated with a computer providing precise control of volumes, flow rates, and timing. The detector in some examples has been a preconcentrating minicolumn optosensor.

Because sequential injection systems provide such a versatile system for fluid handling, and they scale well for handling milliliter size to microliter size samples, they have been used in a great variety of analytical approaches beyond the simple example of mixing, reaction, and detection just given. Sequential injection separations (Figure 2c) and bead injection represent two prominent examples, which will be described in more detail below. The use of solid phases in sequential injection systems has recently been reviewed.[29]

2.2. Preconcentrating Minicolumn Sensors

Early work on preconcentrating minicolumn sensors in flow-based analysis was reviewed in 1993.[30] Another review on such sensors appeared in 2004.[31] Our own surveys indicate there are over 100 papers on such sensors. Generally, these sensors are columns containing sorbent solid phases and fit the general idea shown in Figure 1a, with all or part of the column in the detection zone. In the fluidic systems shown in Figure 2, a and b, the sensor serves as the detector. Many such sensors are spectrophotometric, measuring absorbance of the packed bed in the visible or UV wavelengths. Accordingly, they have been described using terms such as optosensors, optosensing, solid-phase absorptiometry, and ion-exchanger phase absorptiometry. The flow cell may be a modified cuvette fitting in a conventional spectrophotometer, or it may be a flow cell configured with fiber optics. Luminescent methods, such as fluorescence, phosphorescence, and chemiluminescence, and luminescent methods using energy transfer processes have also been widely employed. Even photoacoustic detection has been adapted to flow cells containing sorptive solid phases.[32]

The solid phases are typically ion exchangers, ligand-loaded complexing resins, or hydrophobic phases such as C18-modified silica. Molecularly imprinted polymers have also been used. Ligand-loaded complexing resins have been reviewed.[33] The detected analyte may be the "native" ionic or molecular species, a reaction product or complex formed upstream of the flow cell, or such products formed upon interaction with the solid-phase material. The range of species detected using these methods are extremely broad, including metal ions (including the rare earths), complexes, inorganic anions such as iodide and phosphate, pharmaceuticals and metabolites, nutrients and other food components, oxygen, and aromatic hydrocarbons and phenolics.

Typically, the analyte or analyte reaction product from a certain volume of sample is captured on the solid phase, measured, and then released using a suitable reagent after the completion of the measurement. In some cases the interaction is weak enough that the species migrates down the column and is detected as it traverses the optical path. For example, Yoshimura used an ion-exchange resin in an optosensor flow cell to capture copper ions from a 0.17-mL injected sample volume.[34] Using a 0.014 M nitric acid concentration, where the distribution ratio was $D = 62000$ [mol of copper sorbed/kg of resin]/[mol of copper/L of solution], the copper ions were completely retained and were detected with a spectrophotometer at 800 nm. The sensor was regenerated by perfusion with 2 M nitric acid solution. On the other hand, if the copper ions were captured from 0.28 M nitric acid, where the distribution coefficient was $D = 340$, the ions were eluted in a "fairly short time" in additional carrier solution.

Recently, an alternative methodology for operation of a preconcentrating minicolumn sensor with optical absorption detection has been described.[18] Hexavalent chromium ions were accumulated in an equilibration-based sensing approach, where the entire bed of the anion exchange column sensor was equilibrated with the analyte in the sample by flowing an excess of sample through the column. Once the column was fully equilibrated, the entering and exiting chromium ion concentrations were the same. At trace concentrations (e.g., on the linear portion of a sorption isotherm), the amount retained on the column at equilibration is proportional to the sample concentration. Because it is dynamic equilibrium, pumping a sufficient volume of a blank solution through the column will eventually elute the analyte. This approach can be regarded as a true sensor whose response can go up and down with analyte concentration, rather than representing an assay on a specific volume of sample solution. Furthermore, reagents are not required to regenerate the sensor. The concept of equilibration-based preconcentrating minicolumn sensors will be described in more detail below for sensing the radionuclide ^{99}Tc (as pertechnetate, $^{99}TcO_4^-$).

2.3. Bead Injection and Renewable Surface Sensing

As an alternative to methods that elute the analyte from the solid phase, as just described, a methodology has been developed to automatically provide a fresh solid phase for each measurement. Renewable surface sensing using solid phases has also been dubbed "bead injection".[28,35−40] In this approach, the solid phase is again within the observed region of a detector, and most detection methods are optical or microscopic. However, fluidic procedures and specialized flow cells have been developed so that the solid phase is delivered as a liquid suspension to the flow cell, captured within the flow cell, perfused with the sample for interaction and measurement, and then removed or released from the flow cell, all under computer control. In this way, a fresh solid phase with a new surface can be provided for each sample measurement, hence the phrase "renewable surface sensing". These approaches can be used in both separation and sensing for a variety of species; however, they have been particularly useful in bioanalytical measurements where sensitive biochemical interfaces are involved. Nevertheless, renewable surface separations[41,42] and sensing[3] have both been described in the field of radiochemistry as well.

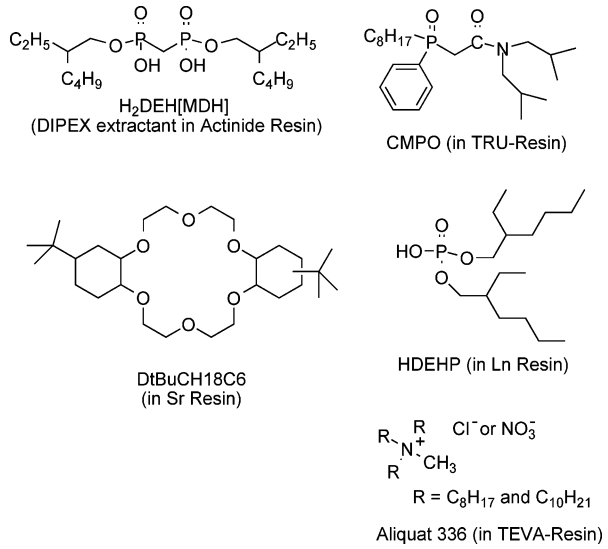
A variety of flow cells have been designed for implementing renewable surface techniques, including a "jet ring cell" with a moveable tubing end in contact with a transparent plate,[35,38,40] a machined flow cell with a moveable solid rod intersecting the flow channel,[35,38,43] and a rotating rod design where the angled end of a solid rod intersects an angular flow path in one position but allows beads to pass when rotated 180°.[44,45] Methods that can direct the flow and beads toward one channel with a frit or another channel without a frit have also been developed.[41,42,46] These will not be described in detail here. Some have been reviewed together in connection with nucleic acid-based analyses.[46]

2.4. Automated Radiochemical Separation and Analysis

Radiochemical analysis is concerned with the determination of radionuclides from a variety of sample matrixes. If the radionuclide of interest cannot be determined nondestructively by detection of a γ-ray emission and identification from the γ-ray energy spectrum, then chemical separations are normally a necessary and critical aspect of the analysis. The radionuclides of interest must be separated from the sample matrix and concentrated for determination by either radiometric or mass spectrometric techniques. The classical methods for performing such separations, including precipitation, solvent extraction, and manual ion exchange, are tedious and time-consuming.

Significant advances in separation materials for column-based separations have simplified radiochemical analysis. At the same time, fluidic and in some cases robotic methods have been developed to automate column-based radiochemical separation and detection. The fluidic automation methods have been based on flow injection and sequential injection methods as described briefly above. In particular, the coupling of sequential injection fluidics to small separation columns lead to "sequential injection separations", as shown in Figure 2c. In this approach, the sequential injection fluidics provide fluid handling to deliver samples, reagents, and eluants; the column provides selective separations based on the sorbent material in the column; and the analytes that are separated from the matrix and eluted from the column are detected downstream. Typically, the separation is based on using a separation chemistry where the radionuclide(s) are retained under the sample load conditions, the sample matrix and unretained radionuclides are removed in a wash step, and then the retained radionuclide(s) are released in one or more steps using a change in solution conditions that greatly reduces the affinity of the radionuclide for the separation material. These separations can rapidly separate individual radionuclides or groups and tolerate significant sample loading.

Scheme 1



The separation materials for automated radiochemical separations can be conventional ion-exchange resins or more recent extraction chromatography or solid-phase extraction materials. These same separation materials can be used in the development of radionuclide sensors to be described below. Extraction chromatographic materials[47] for radionuclide separations, using selective or semiselective extractants impregnated on macroreticular polymer supports, have been developed by Horwitz and co-workers and commercialized by Eichrom Technnologies, Inc.[48−52] The uptake properties and chemical selectivities of these materials are well characterized in the literature, and hence the selectivities of sensors can be rationally designed and understood. The chemical structures of the extractants in some of these resins are shown in Scheme 1. A variety of solid-phase extraction materials dubbed "SuperLig" have been developed using "molecular recognition" ligands on solid supports and commercialized by IBC Advanced Technologies (American Fork, Utah).[53−56] These ligands are covalently bound to various polymeric or silica gel supports.

Automated sequential injection separation can be illustrated with data for ^{99}Tc analysis, the same radionuclide we will use to illustrate the principles of radionuclide sensors. A system similar to that in Figure 2c was set up with a separation column containing the extraction chromatographic resin known as TEVA-resin.[9,42,57] TEVA-resin is a macroreticular polymer support impregnated with Aliquat 336, a liquid anion exchanger consisting of a mixture of long-chain quaternary ammonium ions. This resin is known to retain ^{99}Tc(VII) as pertechnetate under neutral to weakly acidic conditions and to release it in strongly acidic conditions.[50] As shown in Figure 3, the majority of the radionuclides in a nuclear waste sample pass through the column in the wash step following sample injection, resulting in a large

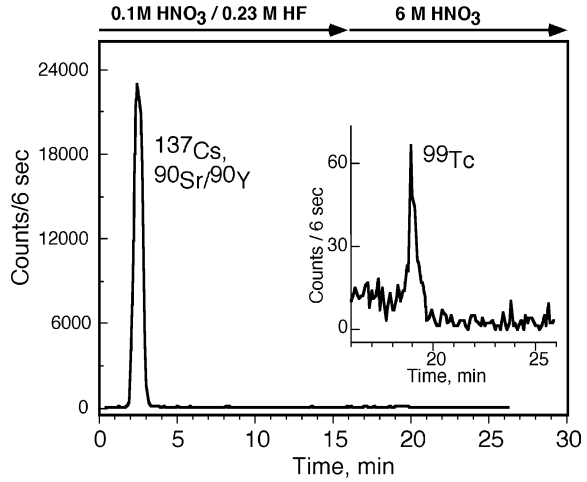


Figure 3. Detector traces from a sequential injection separation system set up to isolate ^{99}Tc as pertechnetate from a nuclear waste sample, using TEVA-resin as the separation material. Figure reprinted with permission from reference 57. Copyright 1998 American Chemical Society.

transient peak as detected by a flow-through scintillation detector. Pertechnetate is retained until a strongly acid eluant solution releases it, resulting in a small ^{99}Tc peak seen in the inset.

Flow injection and sequential injection separations using extraction chromatographic separations have been developed for a variety of radionuclides.[3,41,57−65] Automated radiochemical separation methods have been reviewed.[9,42]

3. Radionuclide Sensors

3.1. Challenges of Radionuclide Sensing in Water

Prior to the development of preconcentrating minicolumn sensors for radiochemical sensing, there had been very little development of radiochemical sensors suitable for rapid and selective quantification of β- and α-emitting radionuclides in water or process streams. Thus, although there were many radioactivity detectors, there were not any selective radiochemical sensors. This state of affairs is evident, for example, in a review of "Emerging Technologies for Detecting and Measuring Contaminants in the Vadose Zone" in the *Handbook of Vadose Zone Characterization and Monitoring*, published in 1994.[66] This review contained a section on "Radiochemical Sensors", yet it was notably lacking in any examples of such sensors. Instead, it discussed various ways of detecting and analyzing for radionuclides and heavy metals, including general radioactivity detection techniques, inductively coupled plasma mass spectrometry (ICPMS), inductively coupled plasma atomic emission spectroscopy (ICPAES), neutron activation analysis (NAA), and X-ray fluorescence (XRF) spectrometry. Radioactivity detection and instrumental analysis techniques such as these are not radiochemical sensors and have significant limitations for field analysis. The article correctly noted that radioactivity detection "usually requires some form of sample preparation to concentrate the radionuclides prior to counting to achieve a reasonable degree of sensitivity". The article further stated that "much of current analytical work is still done in fixed chemical laboratories using conventional radiochemical analysis" and that "conventional detection techniques... are confined to fixed or mobile laboratories". Thus, the conventional analytical methods for α- and β-emitting radionuclides in water consist of concentration, separation, and source preparation methods prior to either radioactivity counting or mass spectrometry, activities that are largely performed in centralized laboratories. A radionuclide sensor for water monitoring must succeed at achieving results similar to those of multistep laboratory procedures, all in a compact sensor package that operates automatically.

The detection and quantification of α- and β-emitting radionuclides in water present a number of basic challenges: the required detection limits are typically extremely low, the particles emitted have short penetration ranges in condensed media, and the α/β decay events in condensed media provide limited spectroscopic information for distinguishing one radionuclide from another (i.e., for selectivity).

Detection limit requirements determined by regulations such as drinking water standards or maximum contaminant levels,[3] typically defined in radioactivity units, translate into chemical detection limits that are well below parts per billion (ppb) levels. For example, the 33 Bq/L (900 pCi/L) drinking water standard for ^{99}Tc[67−69] translates to 0.05 μg/L , which is the same as 0.05 ppb. Required mass detection limits for other radionuclides such as ^{90}Sr, ^{129}I, and various transuranic actinides are from 1 to 6 orders of magnitude lower. Consequently, chemical detection with a sensor is simply not feasible; radiometric detection methods are required for measurement at and below the standards-based requirements. In addition, chemical detection alone does not distinguish between stable isotopes (that may be natural) and radioactive isotopes of concern. Uranium is an exception to this conclusion, since detection at the required tens of ppb is feasible with chemical sensing approaches, such as stripping voltammetry.[70−72]

Taking radiometric detection as a given, the properties of α and β emissions in water must then be considered. In contrast to γ rays, which are characterized by relatively long mean-free paths through solid and liquid media, β and especially α particles are characterized by short ranges and rapid energy dispersion in condensed media. For example, the ranges in water for β particles emitted by ^{90}Y (E_{max} = 2282 keV), ^{90}Sr (E_{max} = 546 keV), and ^{99}Tc (E_{max} = 294 keV) are 1.1 cm, 1.8 mm, and 750 μm, respectively. The range of a 5.5 MeV α particle emitted by ^{241}Am is only 47 μm in water. Furthermore, the energies of α and β particles detected in liquids do not provide well-resolved energy spectra that can be used for selective radionuclide identification. β particles are emitted with broad energy spectra, the β spectra of different radionuclides are not well separated, and the particles lose energy as they travel through water or other condensed media. Although α particles are emitted with characteristic energies, detection by scintillation does not provide adequate energy resolution for selective individual detection of α emitters, and again, the particles lose energy as they travel through water. High-resolution α spectroscopy requires preparation of very thin counting sources placed in a close proximity to a solid-state diode detector, typically in vacuum. Even then, radiochemical separations are required to overcome α energy peak overlap problems and interferences from the sample matrix.

The challenges listed above lead to a number of requirements for radiometric sensors for α and β emitters in water. (1) Due to the short radiation travel distances, the species of interest must be spatially localized within a detector volume of well-defined geometry in close proximity to the transducing medium. Localization can be achieved by sorbing the species in a material that is in close proximity to the transducing medium. Typically this transducing medium is a scintillating material, although semiconductor diodes may

also be used. (2) Due to insufficient energy information for discrimination, the method for localizing the analyte must also be selective for particular species and separate them from potentially interfering radionuclides. (3) Due to the challenging detection limit requirements, the species must be collected from a large sample volume and preconcentrated.

The preconcentrating minicolumn sensor configuration meets these requirements. The flow-based sensor comprising the sensing material in combination with the radioactivity detection method captures the analyte from the matrix, does so according to its selectivity, and can achieve very low detection limits. This approach achieves the same preconcentration and separation results that would conventionally be obtained as the result of a multistep, manual procedure. In terms of the automated radiochemical methods described above, the preconcentrating minicolumn sensor combines the separation column and the radioactivity detection, as shown in series in Figure 2c, into a single functional unit as shown in Figure 1b.

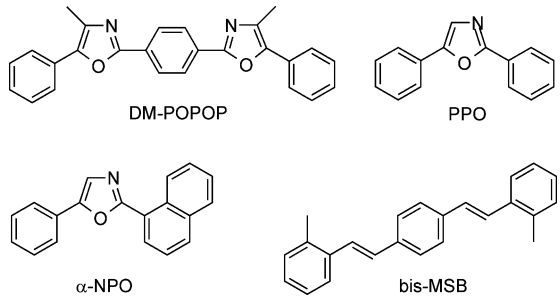
3.2. Minicolumn Sensors Based on Extractive Scintillating Resins

Using a preconcentrating minicolumn sensor for radionuclide detection via scintillation requires that the column have dual functionality. It must provide chemical selectivity for capture and separation of the radionuclide of interest, and it must scintillate. Given the short ranges of the α or β particles, these functions are most readily achieved by (1) creating a column packing where the packing medium has dual-functionality or (2) combining and intimately mixing scintillating media with selectively sorbent media in one column. The latter approach, which we call a composite bed column, will be described in the next section.

The creation of polymeric beads with both ion-exchange and scintillating properties was reported over 40 years ago;[73] however, there was practically no follow-up related to radiochemical analysis. The collection of radionuclides from the sample and subsequent counting were performed manually in separate steps; consequently, this did not yet represent a sensor. In 1994, the oxidation of a scintillating plastic to create ion-exchange sites was described.[74] The purpose of this work was to create a tool for studying ion exchange, where the β particles from ^{45}Ca (simulating Ca in hard water) would result in a signal when they were absorbed.

The creation of dual-functionality materials for radiochemical analysis and sensing was pursued in the late 1990s by independent teams at Clemson University and Pacific Northwest National Laboratory. An investigation by DeVol et al. into the adsorption of uranium ions onto CaF_2:Eu scintillator particles (Eu-doped CaF_2) represented a combination of sorption and scintillation in a flow cell.[1] Detection efficiencies of 60% were reported, and scintillation pulse height spectra were measured. Detection efficiency, E_d, is the ratio of observed counts to the number of decay events that occur within the detector. Subsequently, these authors described scintillating glass beads coated with organic extractants for the detection of radionuclides.[2] These investigators also reported impregnation of polymer beads with extractants and scintillators for radionuclide sensing.[75] Similarly, Egorov and co-workers described impregnation of both extractant and scintillating fluors in polymer beads, and characterized the analytical performance of the material in minicolumn sensors for ^{99}Tc.[3] Both groups now have a number of publications, sometimes jointly, on dual-functionality, preconcentrating minicolumn sensors for radionuclides.[2−18]

Scheme 2



The separation properties of extractive scintillating resins were modeled after the extraction chromatographic resins used for radiochemical separations. Scintillating properties could be obtained by co-impregnating the resins with fluor molecules. For example, the fluor 2,5-diphenyloxazole, PPO, has been used as a primary fluor which captures energy deposited in the polymeric material and subsequently emits light. It has been combined with 1,4-bis(2-methylstyryl)-benzene, bis-MSB,[3] or with 1,4-bis(4-methyl-5-phenyloxazol-2-yl)benzene, DM-POPOP,[4] as a secondary fluor to shift the emitted wavelength. Alternatively, resins have also been prepared with 2-(1-napthyl)-5-phenyloxazole, α-NPO, as the primary fluor, without a secondary fluor. The chemical extractant is chosen according to the radionuclide to be retained and detected. Structures of the fluors used in developing extractive scintillating resins are shown in Scheme 2.

Egorov et al. described a sensor for technetium based on co-impregnating macroreticular acrylic polymer beads with Aliquat 336, PPO, and bis-MSB.[3] The Aliquat 336 is a liquid anion exchanger, as noted above, for pertechnetate separations. Its use for an automated SI separation of ^{99}Tc was shown in Figure 3. Characterization results for the dual-functionality material are shown in Figure 4. Analyte retention, shown as the capacity factor, k',[76] in the upper plot, is very high in low acid to neutral conditions, which is favorable for uptake from groundwater. At higher acid concentrations, pertechnetate is released; hence, acidic solutions can be used to regenerate the sensor. These results are consistent with the known uptake characteristics of Aliquat 336.

The lower plot in Figure 4 shows the instrumental pulse height spectra of ^{99}Tc obtained using the selective sensor material (trace A) in a static liquid scintillation spectrometer. This result is compared with the ^{99}Tc spectrum in liquid scintillation cocktail (trace B). The luminosity of the sensor material is lower than that of the liquid scintillator, but the detection efficiency remains sufficiently high (56%) for practical analytical applications.

This sensor material was packed into a minicolumn flow cell which was placed between the photomultiplier tubes of a Packard Radiomatic 515A flow-through scintillation detector. In this configuration the detection efficiency E_d (observed counts divided by the radioactive events from ^{99}Tc quantitatively captured on the column) was 45%. The sensor flow cell was configured as part of a computer controlled sequential injection fluidic system for sample and reagent delivery.

Detector traces illustrating selective ^{99}Tc sensing are shown in Figure 5. Analyte capture and measurable scintillation light output are observed upon injection of an aliquot of ^{99}Tc standard (duplicate traces shown as A) in dilute acid. The signal persists as the sensor column is washed with dilute

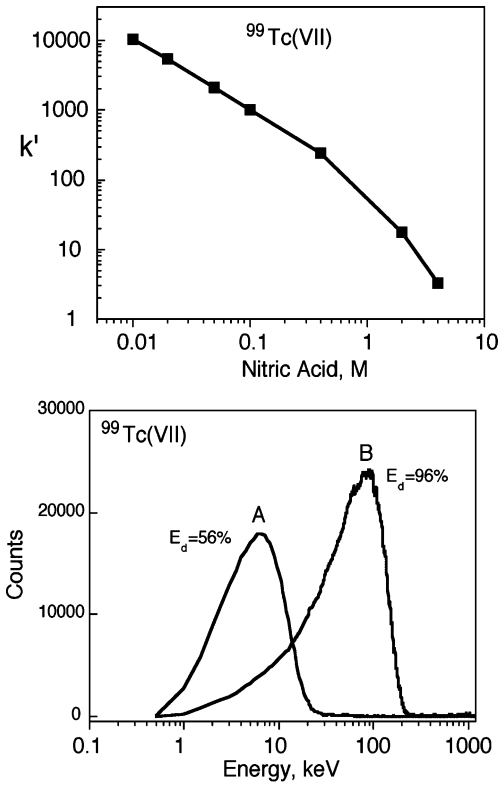


Figure 4. Analyte uptake and scintillation properties of a dual-functionality sensor material for ^{99}Tc. (Top) Plot of the sensor material capacity factor as a function of nitric acid concentration. (Bottom) Pulse height spectra for the dual-functionality sensor (A), and liquid scintillation spectrometer (B). Figures reprinted with permission from reference 3. Copyright 1999 American Chemical Society.

acid. By contrast, radioactive species that do not have a high affinity for the sensor material appear as only transient peak signals, and are promptly removed from the system using a small volume of wash solution. This is illustrated with ^{137}Cs in Figure 5 (trace C).

In the presence of interferences, the light output integrated over time after the wash step provides a quantitative measure of the ^{99}Tc in the sample. If interferences are not a problem, the analyte can be quantified from either the slope of the uptake signal or from the steady-state signal as shown in the calibration traces in the middle plot of Figure 5. Each standard was measured using a freshly packed column followed by release of the packing after the measurement, as in a renewable column sensor. The lower plot in Figure 5 illustrates detection of ^{99}Tc in actual groundwater from the Hanford nuclear site. The water was acidified to pH 2 and analyzed with and without a spike. The detection limit for this sensor was estimated to be 6.2 Bq/L (167 pCi/L) or 0.0098 ppb, based on a 50-mL sample size and a 30-min signal accumulation. This detection limit is well below the 33 Bq/L (900 pCi/L) drinking water standard for ^{99}Tc.[67−69,77] These results illustrate the extremely low detection limits that can be achieved with a preconcentrating minicolumn radiometric sensor. Because the sensor material exhibits high binding affinity toward pertechnetate, large sample volumes can be preconcentrated using a small sensor column.

DeVol et al. investigated a wide range of dual-functionality column packing materials for on-line and off-line radionuclide measurements.[4] Subsequent studies examined these materials in greater detail and introduced additional materials.[5−7,12−14,17] These studies included a number of extractive scintillating materials, extractant-coated glass scintillator particles, and a heterogeneous mixture of plastic scintillator beads with extraction chromatographic resin. The extractive scintillator materials were prepared by impregnating acrylic or styrene-based polymer beads with PPO and DM-POPOP, followed by impregnation with the extractants of interest. Extractive scintillating materials developed for radionuclide sensors are summarized in Table 1.

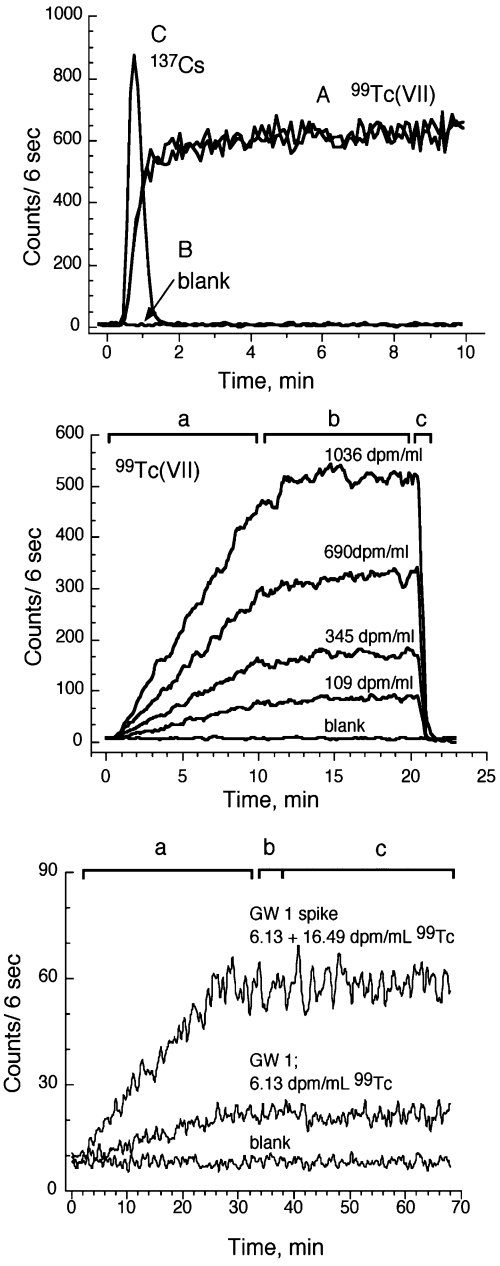


Figure 5. (Top) Sensor response to ^{99}Tc(VII) analyte and a potentially interfering species (^{137}Cs) unretained by the sensor material. Flow rate 1 mL min^{-1}, injected sample volume 0.1 mL. Following the injection the sensor bed is washed with 10 mL of 0.02 M nitric acid. (Middle) Calibration traces for ^{99}Tc sensing. (a) Sample load step (10 mL), (b) sensor wash step (10 mL), and (c) ejection of the sensing material from the column. (Bottom) Detector traces from the analysis of acidified Hanford groundwater (GW 1) sample. Flow rate used was 2 mL min^{-1}; (a) sample load step (50 mL); (b) sensor wash step using 5 mL of 0.05 M HNO_3; and (c) 30-min stopped-flow counting interval. Time zero corresponds to the beginning of the sample load step. Figures reprinted with permission from reference 3. Copyright 1999 American Chemical Society.

Table 1. Scintillating Extractive Resins for Flow-Cell Minicolumn Sensors

fluor or scintillator	extractant	support	analyte	refs
PPO, bis-MSB	Aliquat 336	macroreticular acrylic polymer	^{99}Tc	3,5
PPO, DM-POPOP	Aliquat 336	macroporous styrenic polymer	^{99}Tc	4,5
α-NPO	Aliquat 336	macroporous styrenic polymer	^{99}Tc	14
PPO, 9,10 diphenylanthracene	MnO_2	polyvinyltoluene	U	14
PPO, DM-POPOP	"ABEC" Me-PEG-2000	macroporous styrenic polymer	^{99}Tc	4,5
PPO, bis-MSB	HDEHP	macroreticular acrylic polymer	^{90}Sr	3
PPO, DM-POPOP	crown ether DtBuCH18C6	macroporous acrylic polymer	^{90}Sr	6
PPO, DM-POPOP	crown ether DtBuCH18C6	macroporous styrenic polymer	^{90}Sr	4,6
PPO, DM-POPOP	CMPO/TBP	macroporous styrenic polymer	actinides	4,7, 12,17
PPO, DM-POPOP	CMPO/TBP	macroporous acrylic polymer	actinides	4
α-NPO	H2DEH[MDP]	macroporous styrenic polymer	actinides	13
PPO, 9,10 diphenylanthracene	H2DEH[MDP]	polyvinyltoluene	actinides	13
GS-20 scintillating glass	H2DEH[MDP]	GS-20 scintillating glass	actinides	2,4
GS-20 scintillating glass	crown ether DtBuCH18C6	GS-20 scintillating glass	^{90}Sr	2,4,6

Materials for ^{99}Tc detection were developed based on two extractants, Aliquat 336 and a monomethylated-polyethylene glycol ("ABEC"). The latter is known to bind pertechnetate from certain high ionic strength solutions which is useful in the analysis of nuclear waste or waste-processing streams.[78] Resins with bifunctional organophosphorus extractant octyl-(phenyl)-*N*,*N*-diisobutylcarbamoylmethylphosphine oxide (CMPO) in tri-*n*-butyl phosphate (TBP) were investigated for actinide retention and sensing. These were modeled after Eichrom TRU-resin.[48,79] In later work,[13] another material for actinide detection was developed based on bis(2-ethylhexyl)-methane-diphosphonic acid, which is abbreviated as H2DEH-[MDP] and also known as Dipex. This material is modeled after Eichrom Actinide Resin.[80] For ^{90}Sr sensing, the crown ether4,4′(5′)-bis(*tert*-butylcyclohexano)-18-crown-6(DtBuCH18C6) was used. This material was modeled after Eichrom Sr-resin, which contains the crown ether in 1-octanol solution impregnated in a polymeric resin.[49,81−85] This material selectively binds strontium from nitric acid solutions as $Sr(NO_3)_2$(DtBuCH18C6). In separate work, 2-ethylhexyl-phosphoric acid, HDEHP, was used in a prototypical ^{90}Sr sensor with uptake from 0.001 M HCl.[3]

These various extractive, scintillating resins were evaluated for the efficiency with which radionuclides were captured, the efficiency with which the radionuclides were recovered from the column by elution, and the detection efficiencies.[4] Values from 30 to 100% were found for the detection efficiencies in the initial study,[4] which are all suitable for development of sensors. A number of these were further investigated and tested against groundwater, synthetic groundwater samples, or nuclear waste samples.[5−7,12−14,17]

For example, further studies of ^{99}Tc sensing were carried out using Aliquat 336 as the sorbent.[5] The fluors, PPO and bis-MSB, were diffused into the macroporous acrylic-based (Amberchrom CG-71t2) polymer beads in a separate step prior to impregnation with the extractant. This resin in minicolumn format was used to analyze six contaminated groundwater samples from the Hanford site. The samples were acidified to pH 2 prior to analysis, and quantification was carried out using standard addition methods. Each measurement involved analysis of the following solutions: (1) reagent blank (0.01 M HCl or 0.02 M HNO_3, depending on acid used for sample acidification), (2) acidified groundwater sample, and (3) spiked acidified groundwater sample. All solution delivery steps were performed at 2-mL min^{-1} flow rate, delivering 50-mL sample aliquots, and washing the flow cell with 5 mL of 0.02 M HNO_3. Then the flow was stopped, and the count rate was determined over a 30-min counting interval. Analysis results obtained using the flow-cell sensor and standard radiochemical methods were in excellent agreement. The minimum detectable concentration (MDC) of the flow-cell procedure was calculated with the Currie equation,[86] using average background levels and analyte loading and detection efficiencies. For the 50-mL groundwater samples and 30-min counting interval, the MDC was reported to be 6 Bq/L.

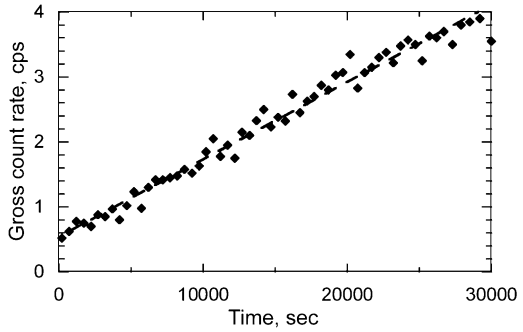


Figure 6. ^{99}Tc sensing in Paducah groundwater, acidified to 0.1 M nitric acid, using a preconcentrating minicolumn sensor in portable detection instrumentation. Volumetric flow rate of ~1 mL min^{-1} results in a measured slope of 8.26 cps/L. Results are replotted from data published in reference 87.

An additional pertechnetate-selective resin was prepared by co-immobilization of the α-NPO fluor with Aliquat 336 extractant within an inert macroporous polystyrene resin. This resin was used in combination with portable and transportable instruments to demonstrate these sensors as potential field screening tools.[14,87,88] A Hidex Triathler field portable scintillation counter was modified with a sensing flow cell containing a small coil of Teflon tubing containing the resin. The detection efficiency measured for this sensor instrument was ~30%. Figure 6 illustrates the Triathler instrument response obtained during loading of a 400-mL quantity of acidified ^{99}Tc-contaminated groundwater from the Paducah site. These data were collected by recording the count rate of the detector in 100-s intervals while the groundwater was continually pumped through the flow cell. A ^{99}Tc activity of 26.8 Bq/L was determined from the slope of the count rate, in reasonable agreement with an independent radiochemical measurement of 22.0 Bq/L. In addition to the experiments with the Triathler, a minicolumn, flow-cell detection system was designed around an Eberline E-600 survey meter and a modified photomultiplier tube (PMT) housing. The advantage of this configuration is portability, but the disadvantage is the low detection efficiency of about ~2%.

Preconcentrating minicolumn sensors for radiostrontium were prepared using a crown ether chemistry (DtBuCH18C6) to concentrate the radioactive ions of interest.[6] The polymeric resins (both acrylic and styrenic resins were investigated) were impregnated with PPO, DM-POPOP, and DtBuCH18C6

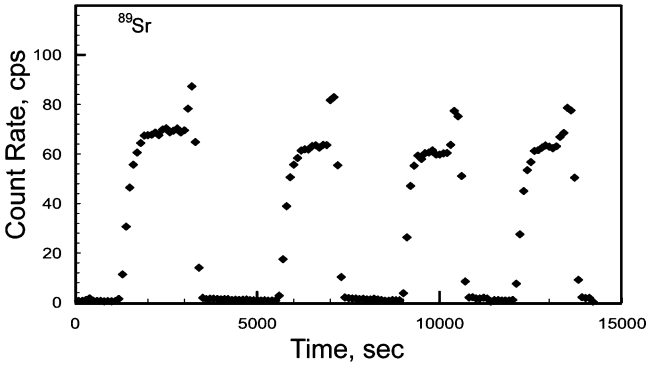


Figure 7. Repeated loading and regeneration of a Sr-selective extractive scintillating resin. ^{89}Sr was loaded in 4 M nitric acid and released in water.

in 1-octanol. Packed flow cells were monitored, and the signal was quantified using a commercially available scintillation detection system, the IN/US Beta-Ram model 1. Strontium ions were captured from 4 M nitric acid solutions with efficiencies of 99−100% and released in water, which is consistent with the known extraction chromatographic separation chemistry of DtBuCH18C6. Regeneration capability was demonstrated through multiple loading/elution cycles with ^{89}Sr and ^{90}Sr. Repeated capture and release of ^{89}Sr are shown in Figure 7. There was only a slight degradation in the detection efficiency (59.7 ± 2.97% for ^{89}Sr) over time. The detection efficiency for ^{90}Sr was lower than that for ^{89}Sr because ^{90}Sr has a weaker β energy. Detection of ^{89}Sr was demonstrated at concentration as low as 120 Bq/L. Lower minimum detectable concentrations would require (1) that the detection efficiency be higher, (2) that the detection system background count rate be lower, (3) the use of longer count times, and/or (4) replacement of the extractant with one which has a higher distribution coefficient so that analyte can be collected from a larger sample volume without breakthrough.

For uptake of ^{90}Sr from weakly acidic to neutral solutions, a scintillating extractant resin was created based on HDEHP extractant. In this case, both ^{90}Sr and its daughter product ^{90}Y were extracted from 0.001 M HCl.[3] However, they could be individually determined by selective elution of the ^{90}Sr using 0.2 M HCl, leaving the ^{90}Y on the column. Finally, ^{90}Y was eluted with 4 M HCl to regenerate the column. These steps are shown in Figure 8. Assuming 100% efficiencies of the capture and elution procedures, the individual absolute detection efficiencies, E_d, for ^{90}Sr (E_{max} = 546 keV) and ^{90}Y (E_{max} = 2282 keV) were determined to be 46 and 99% respectively. Thus, co-retention and selective elution steps can be used to quantify individual radionuclide species.

The method of selective uptake of a group of radionuclides with selective elution steps has also been demonstrated in actinide sensing. The extractive scintillating resin containing fluors PPO and DM-POPOP was impregnated with CMPO in TBP.[7] The resin was packed in an FEP Teflon tubing flow-cell coil and placed into a dual photomultiplier tube coincidence detection system to obtain pulse height spectra and time-series data. Loading and elution experiments were conducted with ^{241}Am (9.8 Bq), ^{239}Pu (7.4 Bq), and ^{233}U (10.2 Bq) as illustrated in Figure 9, where on-line sensor detection results are shown in plot A (top) along with the eluted radionuclides in plot B, as determined by fraction collection and liquid scintillation counting. The data shown in Figure 9, a and b, are complementary and were obtained essentially simultaneously using the same column. The intervals when

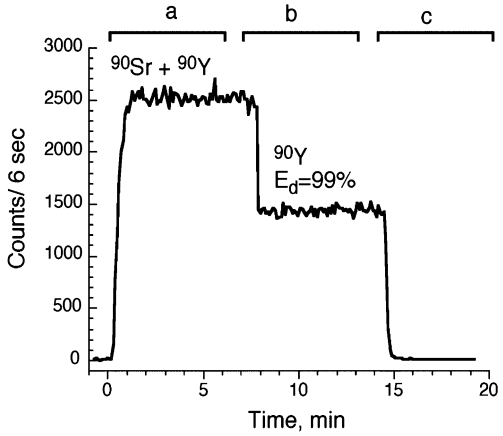


Figure 8. Detector traces for ^{90}Sr/^{90}Y separation experiments using HDEHP-based scintillating extraction resin. The sample was 100 μL of 1.57 × 10^4 dpm ^{90}Sr/^{90}Y standard in 0.001 M HCl. Flow rate was 1 mL min^{-1}; (a) sample injection and sensor wash step using 6 mL of 0.001 M HCl; (b) ^{90}Sr elution step using 6 mL of 0.2 M HCl; (c) ^{90}Y elution using 6 mL of 4 M HCl. Figure reprinted with permission from reference 3. Copyright 1999 American Chemical Society.

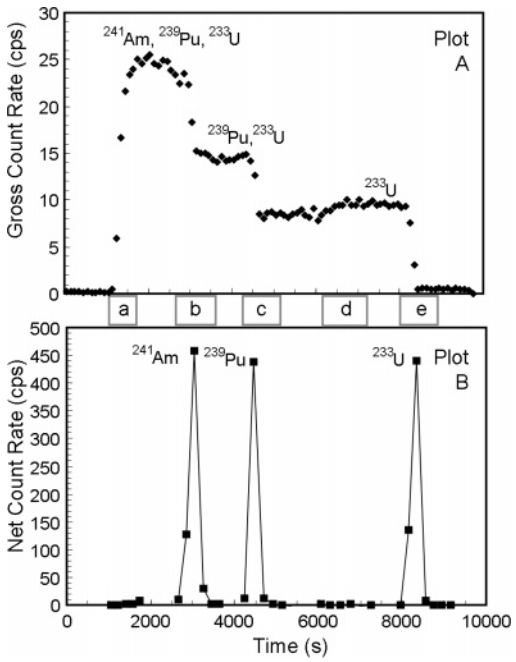


Figure 9. Detection of actinides ^{241}Am, ^{239}Pu, and ^{233}U in the mixed actinide solution with selective elution in a dual functionality sensor (Plot A), and the chromatogram of the eluents as determined by fraction collection and counting (Plot B). Results are replotted from data published in reference 7.

solutions were pumped through the column are indicated by the lettered boxes along the *x*-axis between the plots, where interval "a" is the sample load in 2 M nitric acid. The captured actinides produce a counting plateau corresponding to the total actinide count rate of 24.88 cps for a 10-min counting time. Trivalent actinides were eluted with 4 M hydrochloric acid (e.g., ^{241}Am during interval "b"). A solution 0.02 M $TiCl_3$ in 4 M hydrochloric acid was applied during interval "c" to reduce the plutonium and elute it from the resin. After a column rinse with 2 M hydrochloric acid during interval "d", uranium-233 was eluted with 0.1 M ammonium bioxalate during interval "e". The count rate difference divided by the detection efficiencies for ^{241}Am, ^{239}Pu, and ^{233}U (96.5%, 77.5% and 96.6%, respectively) constitute the

Table 2. Composite Bed Minicolumn Sensors

scintillator	selective chemistry	solid phase	analyte	refs
BC-400	Aliquat 336	TEVA resin	^{99}Tc	4,5
BC-400	crown ether DtBuCH18C6	Sr-resin	^{90}Sr	6
GS-20	crown ether DtBuCH18C6	Sr-resin	^{90}Sr	6
BC-400	H2DEH[MDP]	Actinide resin	actinides	13
yttrium silicate (YSO)	H2DEH[MDP]	Actinide resin	actinides	13
BC-400	anion exchange, strongly basic	AGMP1	^{99}Tc	8−11
BC-400	anion exchange, weakly basic	AG 4-X4	^{99}Tc	16,18
BC-400	SuperLig 620 solid-phase extraction material	silica gel-based solid-phase extraction material	^{90}Sr	10,18

measured activity and were within 10% of the expected values. One advantage of this system is that quantification can be accomplished at low activities because long count times can be obtained by extending the time between eluents. This sensor resin was also applied to a digested high-level waste sludge and high-activity drain tank samples where the agreement between the on-line and off-line analyses was within 35%. The extractive scintillating resin and detection system just described was subsequently applied to low-level uranium concentration determination in acidified groundwater.[12]

Using Dipex extractant, a scintillating extraction resin containing α-NPO fluor was demonstrated for monitoring natural uranium in groundwater.[13] This resin was packed into a flow cell designed for a modified Hidex Triathler. The average detection efficiencies were 51.7 ± 2.6% and 65.8 ± 10.1% for natural uranium and ^{241}Am, respectively. The resin was stable for sample load volumes of up to 1000 mL, resulting in rapid real-time quantification of natural uranium in groundwater down to 30 μg/L, which is sufficient to meet the standard established in the U.S. Safe Drinking Water Act.

In summary, extraction chromatographic materials containing organic scintillator fluors were developed and demonstrated in preconcentrating minicolumn sensors for uptake and detection of a variety of radionuclides, including ^{99}Tc, ^{90}Sr, actinides, and natural uranium. The uptake characteristics are similar to those of the extraction chromatographic materials without the fluors, and detection efficiencies were good. Accurate detection in Hanford groundwater samples was demonstrated for ^{99}Tc, and it could be detected to below drinking water standard limits. Detection of uranium in groundwater to drinking water standard levels was demonstrated. and samples up to at least one liter volume could be preconcentrated.

Nevertheless, extractive scintillating materials have some potential drawbacks related to their stabilities under repeated or long-term use. The impregnated extractants can leach out. Under some conditions, chemiluminescence signals from the scintillating fluors are observed, which can interfere with the radiochemical measurement. In addition, the scintillating fluors are quenched or damaged and may lose their scintillating properties in the presence of some of the acid reagents used. It was noted, for example, that attempts to elute pertechnetate from resins that were co-impregnated with Aliquat 336 and the PPO/bis-MSB fluor combination, using 4 M nitric acid, resulted in a significant chemiluminescence signal and loss of scintillating properties in subsequent sensing experiments.[3] Fluor impregnation methods based on diffusion or synthesis yield sensors with greater stability for sequential sensing experiments, but long-term stability remains a concern.

The best combination of fluor and support for the extractive scintillating resin of the variations tested is the α-NPO fluor impregnated into the macroporous polystyrene resin. For the combination of fluor and support to respond like a scintillator there needs to be good energy transfer from the support, which is the bulk of the scintillator, to the fluor. This π-electron energy transfer is more efficient with the polystyrene support. The procedure for producing the scintillating resin results in some fluor diffusing into the polystyrene and some just being retained within the pores of the resin. In the latter case, the fluor can interact with reagents and eluants, and may be leached out. Of the fluors evaluated, α-NPO resulted in little to no leaching from the polystyrene resin.

3.3. Composite Bed Scintillating Minicolumn Sensors

Composite bed columns, consisting of a heterogeneous mixture of scintillating particles and chemically selective particles, represent an alternative to the extractive scintillating resins described above. Composite bed column materials are listed in Table 2. In most cases, the scintillating component consists of Bicron BC-400 beads, which are poly(vinyltoluene) scintillating plastic beads. These nonporous scintillating beads were found to have high chemical stability in sample and regeneration solutions. A further advantage of the composite bed sensing approach is that it facilitates the use of existing extraction chromatographic, ion-exchange, or solid-phase extraction materials for the chemically selective sorbent component of the bed.

Given an intimate mixture of the sorbent particles and the scintillating particles, the α or β emission from a radionuclide captured on a sorbent particle has a reasonable probability of colliding with a neighboring scintillating bead, provided the travel distance of the radiation in the condensed phases is large enough in comparison to the distance across column pore spaces (in between particles) and particle diameters. Higher ratios of scintillating particles to sorbent particles increase this collision probability, increasing the detection efficiency, at the cost of reduced sorbent material for radionuclide capture in the composite bed. This approach is particularly well suited to detection of radionuclides that emit β particles, which have longer ranges in condensed media than typical α particles. For example, the β particle from ^{99}Tc has an estimated maximum range in water of 750 μm, which is greater than typical sorbent particle sizes in the 20−200 μm size range.

A number of composite bed columns were demonstrated for mixtures of extraction chromatographic resins and BC-400 beads (100−200 μm), including those based on TEVA resin for ^{99}Tc sensing,[4,5] Sr-resin for ^{90}Sr sensing,[6] and Actinide resin for actinide measurements.[13] Composite bed approaches were also developed using conventional anion-exchange materials for ^{99}Tc sensing.[8−11,16,18]

For example, a composite bed flow cell was prepared by mixing equal masses of TEVA extraction chromatographic resin (100−150 μm) and BC-400 plastic scintillating beads (100−200 μm).[5] The mixture was packed into a flow cell, and responses to ^{99}Tc were quantified using an IN/US Beta-Ram model 1. The detection efficiency of ^{99}Tc ranged from 7.5% to 16.4% during the subsequent performance tests. The uptake of ^{99}Tc was quantitative. In addition to characterizing responses to ^{99}Tc, tests to evaluate potential inference by ^{137}Cs, ^{90}Sr, and ^{239}Pu were investigated. Typically, the column was first exposed to a ^{99}Tc standard, followed by an injection of a potential radioactive interference. A statistically significant increase in the sensor count rate after loading and washing the interference, while the ^{99}Tc remained captured, was defined as an interference. For example, after loading the sensor with 5 mL of 24 Bq/mL ^{99}Tc standard, resulting in a measurable steady-state signal, 1 mL of a 7200 Bq/mL ^{137}Cs standard was loaded and subsequently washed with additional carrier solution (2 M HCl for standards and wash). A transient peak was detectible while the ^{137}Cs progressed through the flow cell, but no interference was detectable after washing. A trace amount of ^{137}Cs was detectable in the eluant when the ^{99}Tc was released in 8 M nitric acid. Interference trials with ^{90}Sr and ^{239}Pu at 54 and 240 Bq/mL, respectively, resulted in no detectable interference nor were these radionuclides detected in the final ^{99}Tc eluant. At a higher activity of 24,000 Bq/mL, ^{90}Sr resulted in a slight interference.

Composite bed columns using conventional ion-exchange resins were demonstrated using AG MP-1, a strongly basic anion-exchange resin that has very high uptake affinity and good selectivity toward Tc(VII) ions in basic to weakly acidic media. The weight/volume distribution coefficient (K_d) for ^{99}Tc(VII) on AG MP-1 was 2.5 × 10^5 mL/g for ^{99}Tc(VII) in unacidified Hanford groundwater. As a result, small volumes of the sorbent material can be used to preconcentrate analyte from large volumes of groundwater. A composite sensor bed was prepared by mixing 200−400 mesh AG MP-1 material (particle size about 40−70 μm) with BC-400 plastic scintillator beads (particle size 100−250 μm) at a 30:1 weight ratio of scintillator to sorbent.[8,10] The total bed volume was just 50 μL. The absolute detection efficiency of the composite sensor column was 34%, and analyte loading efficiency was 97%. This sensor was demonstrated to be effective in capturing ^{99}Tc(VII) in unacidified Hanford groundwater; up to 60 mL of the groundwater sample could be preconcentrated without analyte breakthrough using this very small sensor column.[9,11] The ^{99}Tc(VII) selective composite bed sensor can be regenerated using a small volume of 2 M nitric acid solution, resulting in rapid elution of the retained analyte without loss of the scintillation properties.[8,10]

Composite bed sensor columns have also been prepared using the weakly basic anion-exchange resin AG 4-X4.[16,18] The uptake affinity of this material for pertechnetate in weakly acidic to weakly basic conditions is substantially lower than that of the AG MP-1. Nevertheless, it has sufficient uptake to collect and preconcentrate pertechnetate, and it offers other practical advantages. The weakly basic anion exchanger is less prone to irreversible uptake of soil organic matter, such as humic acids, and pertechnetate can be readily eluted with sodium carbonate solutions, an environmentally benign reagent that provides an alternative to the use of strong acids for regeneration.[16]

It should be noted that high ratios of scintillator to sorbent (as was used in the AG MP-1 studies) are not necessary to obtain satisfactory detection efficiencies. This high ratio was motivated in part by the extremely high affinity of the strongly basic anion exchanger AG MP-1; dilution with a high ratio of scintillator reduces the overall retention volume of the column for such a high-affinity sorbent. The effect of ratio on detection efficiency was examined in more detail for weakly basic anion exchanger AG 4-X4. Various mixtures of 100−200 mesh (75−150 μm) AG 4-X4 and 100−250 μm beads of BC-400 were prepared. Detection efficiencies from 20 to 60% were found for scintillator to sorbent ratios of 1.5 to 14 (dry weight to dry weight) as shown in Figure 10. Sensing results using composite bed sensors based on AG 4-X4 will be described in more detail in connection with equilibration-based sensing below.

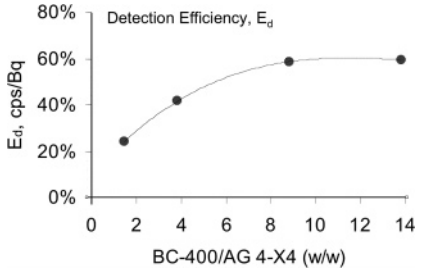


Figure 10. Detection efficiency for ^{99}Tc as a function of the dry scintillator to sorbent ratio for a composite bed sensor column. Scintillator is BC-400 (100−250 μm); sorbent is AG 4-X4 (100−200 mesh).

BC-400 plastic scintillator beads have been mixed with solid-phase extraction material SuperLig 620 for the development of ^{90}Sr sensors.[18] Using a 1:1 weight ratio, a detection efficiency of 63% was reported. It was anticipated and observed that a higher detection efficiency could be obtained for ^{90}Sr than ^{99}Tc because the former has a higher-energy β emission.

3.4. Sensor Regeneration or Renewal

Much like the preconcentrating minicolumn sensors developed in flow injection analysis, the radionuclide sensors described above are based on quantitative capture of the analyte from a certain volume of sample. Typically, the sensor is regenerated by passing a solution over the sensor such that the distribution coefficient between the stationary phase and mobile phase is significantly decreased and the analyte is released from the column and washed away. Then the sensor is ready for another sample.

The chemistry used for radionuclide elution and sensor regeneration is typically taken directly from the elution conditions developed for extraction chromatographic purification of radionuclides in radiochemical analysis. Examples of analyte elution and sensor regeneration are shown in Figures 7 and 8 for ^{90}Sr sensing. As described above, pertechnetate that is retained on anion-exchange materials at neutral to low pH can be released using more acidic solutions. However, an alternative approach based on the use of sodium carbonate was demonstrated for pertechnetate release from weakly basic anion-exchange materials.[16] This environmentally benign reagent was proposed to be compatible with groundwater sensing applications.

The alternative to elution or regeneration reagents is to replace the entire column packing using renewable, surface-sensing techniques as described above. This approach was proposed in one of the early examples of radionuclide sensing.[3] No liquid reagent solutions would be required for

elution in this approach, but it would require a supply of sensing material to be delivered in suspension to the flow cell. One advantage of this approach is that some of the typical concerns associated with reusing sensor materials or layers, such as long-term stability, reversibility, degradation, fouling, and potential analyte carryover from sample to sample, are also alleviated.

3.5. Equilibration-Based Sensing

As just noted, the preconcentrating minicolumn sensors for flow injection and for radionuclides relied on quantitative capture of analyte and subsequent regeneration with reagents. While this approach provided new radionuclide sensors for water monitoring and succeeded at meeting stringent detection limit requirements, the use of reagents to regenerate the sensor column for each and every measurement is a potential drawback for in situ monitoring applications. In addition, as discussed above, this approach represents an assay on a sample volume, as opposed to a sensor that responds to changes in sample concentration.

To address these issues, a new modality for the preconcentrating minicolumn sensor was developed that we call "equilibration-based" sensing.[8−11,16,18] The equilibration-based approach sets out to deliberately achieve full breakthrough conditions where the analyte concentration exiting the column is the same as the analyte concentration entering the column. Under these conditions, the sensing material in the column has equilibrated with the analyte concentration in solution. At low concentrations typical of trace detection applications, the linear portion of the sorption isotherm applies, and the amount captured on the column material is proportional to the analyte concentration. The sorbent material is not "saturated"; it is equilibrated. The amount of analyte collected has not reached the total capacity of the sorbent (as would be the case at higher concentrations corresponding to the plateau of the sorption isotherm).

The key features of the equilibration-based approach are: (1) a steady-state response once the sorbent phase is equilibrated, (2) a response that varies with the analyte activity or concentration, and (3) reversibility of the response because it is based on dynamic equilibrium. When a sample containing a different analyte concentration or activity is pumped through the column, the phase will re-equilibrate, and the signal will go up or down accordingly. If this sample is blank, the signal will go down as if the column were regenerated with a reagent. Thus, in principle at least, no consumable reagents are required in this equilibration-based approach.

The responses of a ^{99}Tc sensor using this approach are shown in Figure 11. All three key features just mentioned are apparent in this figure. Steady-state responses are obtained while pumping 225 mL samples through the column, and a final blank shows the reversibility. The sensor response levels and the calibration curve in the inset illustrate how the signal varies with sample activity. The activity of the lowest level standard is equivalent to the drinking water standard for ^{99}Tc.

The column in this case had internal dimensions of 4 mm i.d. × 29 mm length for a bed volume = 0.364 mL. The experimentally determined retention volume, V_r, was 81 mL. Retention volume is equivalent to the sample volume containing the same quantity of analyte as the fully equilibrated sorbent phase in the column. Comparison of the retention volume with the column bed volume illustrates the high degree of preconcentration achieved with this sensor (a factor greater than 200). The experimentally determined column theoretical plates, N, was 12, and the detection efficiency, E_d, was 38%.

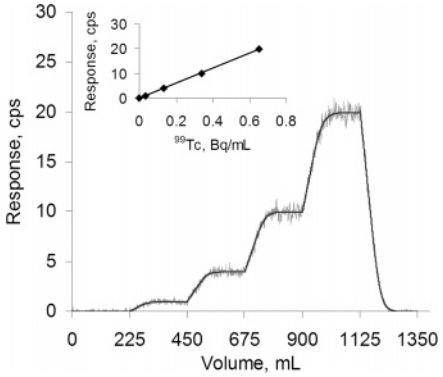


Figure 11. Responses of a composite bed (1:4 w/w ratio AG 4-X4: BC-400) preconcentrating minicolumn sensor to samples at increasing activities of ^{99}Tc standards (in 0.01 M nitric acid) in the pertechnetate form, followed by a final blank sample. The data were obtained by delivering 225-mL aliquots of the following solutions at 2-mL min^{-1} syringe pump flow rate: (1) blank sample, (2) 0.033 Bq/mL; (3) 0.13 Bq/mL; (4) 0.34 Bq/mL; (5) 0.65 Bq/mL; (6) blank sample. Figure reprinted with permission from reference 18. Copyright 2006 American Chemical Society.

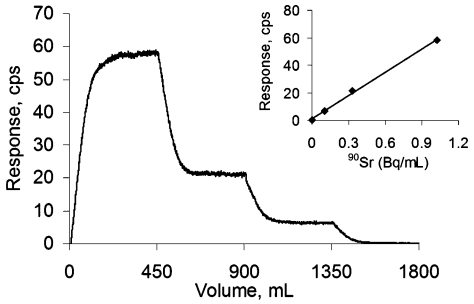


Figure 12. Detector trace showing responses of the ^{90}Sr sensor column (1:1 w/w ratio SuperLig 620:BC-400) to ^{90}Sr standards in Hanford groundwater acidified to pH ~2.1 with nitric acid: (1) 1.02 Bq/mL; (2) 0.33 Bq/mL; (3) 0.10 Bq/mL; (4) blank sample. Figure reprinted with permission from reference 18. Copyright 2006 American Chemical Society.

Whereas the ^{99}Tc column sensor was based on anion-exchange chemistry, a sensor for ^{90}Sr was developed using a solid-phase extraction sorbent, SuperLig 620, which consists of a silica support with covalently bound crown ether ligands. A composite bed sensor was created with a 1:1 ratio of the SuperLig sorbent to BC-400 scintillating plastic beads. The sorbent is capable of ^{90}Sr uptake from neutral or acidic solutions. However, because the daughter product ^{90}Y is also slightly retained at neutral conditions and unretained under acidic conditions, experiments to illustrate equilibration-based sensing were carried out in samples acidified to pH 2 with nitric acid. The sensor responses to sequential 450-mL sample volumes of acidified groundwater containing ^{90}Sr are shown in Figure 12. The detection efficiency E_d of this composite bed sensor was 63%, and the column theoretical plates were just N = 3.4. These results illustrate how a different sorbent chemistry can be used to tailor this sensor concept to different radionuclide analytes, and that even with a column of rather low theoretical plates, a satisfactory sensor can be created.

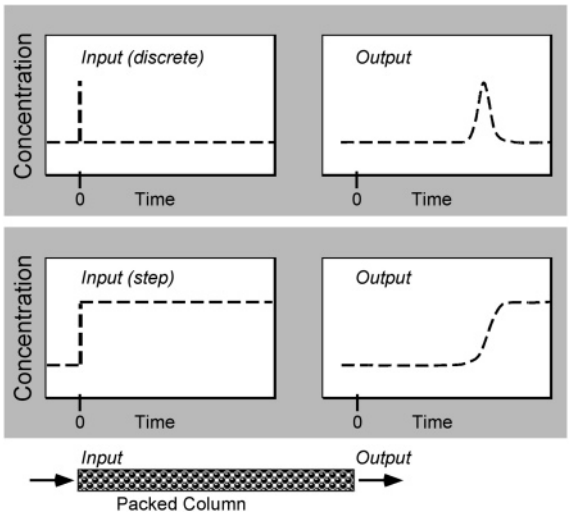


Figure 13. Schematic illustration of column chromatography concepts. A discrete injection and subsequent Gaussian peak illustrates conventional chromatography in the upper pair of plots. A step function input with a subsequent sigmoidal breakthrough profile is shown in the lower pair of plots illustrating frontal chromatography.

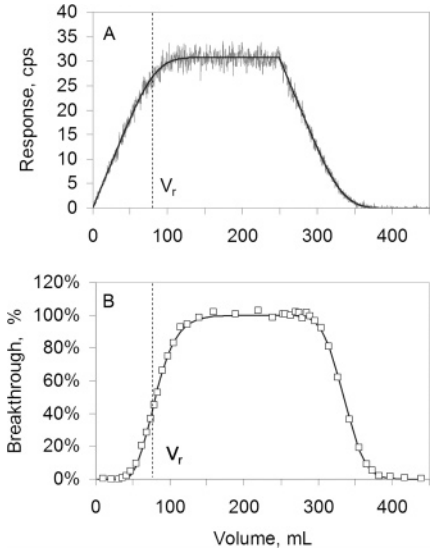


Figure 14. (A) Trace showing sensor equilibration with 1 Bq/mL ^{99}Tc solution followed by a reequilibration to a blank solution in a matrix of 0.01 M nitric acid. Sensor cell (dimensions 4 mm i.d. × 29 mm height) is composed of a 1:4 dry w/w ratio AG 4-X4/BC-400. (B) Fractions collected immediately downstream of the sensor cell show the breakthrough profile of ^{99}Tc from the sensor column. Both the Gaussian model (black lines in each plot) and low plate model (not shown) provide a good fit to the observed data. Figure reprinted with permission from ref 18. Copyright 2006 American Chemical Society.

3.6. Chromatographic Theory for Equilibration-Based Sensing

The characteristics of the preconcentrating minicolumn sensor in equilibration-based sensing mode, and the attainment of the steady-state response, can be understood in terms of concepts from chromatography. In conventional chromatography with a discrete injection, the analytes are sorbed to the stationary phase in a dynamic process and migrate down the column until they elute with a typically Gaussian peak. This discrete input and the peak-shaped output are shown schematically in Figure 13. The peak shape results from a normal distribution of the velocities with which individual molecules traverse the column length, all starting at essentially the same time. Individual molecules or ions have different net velocities due to random factors including the path through the packed bed, diffusion in various directions while in the mobile phase, and variations in the amount of time each molecule or ion spends being immobilized in the stationary phase. In frontal chromatography, and in the operation of the preconcentrating minicolumn sensor in equilibration-based mode, the input is a step change in analyte concentration, as shown in the lower plots of Figure 13. As analytes migrate down the column, the step input is transformed into a sigmoid-shaped concentration profile in the column effluent.[89] In this mode, the analyte molecules or ions still traverse the column with a distribution of individual velocities, but they do not all start at the same time. The sigmoid shaped effluent concentration profile is typically represented by an integral of the Gaussian distribution function.[89,90] The inflection point of the sigmoidal breakthrough profile corresponds to the maximum in the Gaussian distribution. In practical terms, this inflection point also corresponds to the retention volume, V_r.

These characteristics are shown in detail for the ^{99}Tc sensor in Figure 14.[18] The ^{99}Tc activity in the input is first stepped from 0 to 1 Bq/mL for a 250-mL sample volume and then stepped back down from 1 to 0 Bq/mL. This sample volume is clearly more than that which is necessary to equilibrate the column in each step. The sensor response shown in the upper trace indicates the amount of ^{99}Tc captured on the column. Initially the ^{99}Tc is captured quantitatively, resulting in a linear increase in the signal. As ^{99}Tc begins to break through, the response begins to level out. The lower plot shows the sigmoid-shaped output profile, i.e., the effluent concentration profile as a function of time or volume, as determined by analyzing collected fractions on the sensor output. The amount accumulating on the column, leading to the sensor response, is the total amount that has been delivered to the column minus the total amount that has broken through and exited the column. When the output concentration equals the input concentration, the amount accumulated on the column stops increasing. After the 250-mL sample load, the input was stepped from the 1 Bq/mL ^{99}Tc activity back down to zero. The sensor signal begins to drop and the effluent concentration also begins to drop, until the retained ^{99}Tc is completely removed from the column.

Frontal chromatography theory in equation form has been adapted to derive theoretical equations that express the effluent concentration as a function of volume or time (i.e., the breakthrough curve), and similarly the sensor response as a function of the solution volume or time. The derivation and equations are given in detail in ref 18. The total amount that has exited the column is the integral of the effluent concentration profile, as shown in the first half of Figure 14b, which is itself the integral of a normal distribution (an integral of an integral). The amount that has accumulated on the sensor column, as a function of volume or time, is the amount delivered to the column minus the amount that has exited. While the plot in Figure 14 illustrates step changes from zero to one and one down to zero, the equations can be derived for step changes from any arbitrary concentration to another, and converted to radiometric count rates on the sensor.

In equation form, the function $f(V)$ is used to represent the normalized analyte concentration profile in the column

effluent, i.e., the breakthrough curve as shown schematically in the lower right plot in Figure 13 and the first half of the lower plot in Figure 14. For an input step with concentration changing from initial concentration $C_0 = 0$ to subsequent concentration C_1 ($C_1 > 0$), the effluent concentration as a function of volume, $C_{ef}(V)$, can be expressed as

$$C_{ef}(V) = C_1 f(V) \quad (1)$$

where $f(V)$ goes from 0 to 1.[89] In conventional linear frontal chromatography with a sufficient number of theoretical plates, the shape of function $f(V)$ is usually assumed to be represented by an integral of a Gaussian distribution:[89−91]

$$f(V) = \frac{1}{2} + \frac{1}{2} erf\left(\left(\frac{V}{V_r} - 1\right)\sqrt{\frac{N}{2}}\right) \quad (2)$$

where $erf(x)$ is the error function defined as $erf(x) \equiv 2/\sqrt{\pi} \int_0^x e^{-t^2} dt$, and N is the number of theoretical plates. The parameter V_r is the analyte retention volume, as usual.

The amount of the analyte that has exited the sensor column after delivering sample volume V, $M_{el}(V)$, is given by the integral of the effluent concentration,

$$M_{el}(V) = C_1 \int_0^V f(V) dV \quad (3)$$

Then the amount of analyte, $M_{s,C_1}(V)$, present on the sensor column as a function of the sample volume can be calculated as the amount delivered C_1V minus the amount that has exited the column:

$$M_{s,C_1}(V) = C_1V - C_1 \int_0^V f(V) dV = C_1V - C_1F(V) \quad (4)$$

where the integral of the normalized breakthrough profile is expressed by the simplified notation:

$$F(V) = \int_0^V f(V) dV \quad (5)$$

For an arbitrary step input with prior and subsequent analyte concentrations equal to C_0 and C_1 the amount of analyte present on the sensor column as a function of the sample volume with analyte concentration C_1 can be expressed as:

$$M_{s,C_0,C_1}(V) = C_0V_r + V(C_1 - C_0) - (C_1 - C_0)F(V) \quad (6)$$

where, V is the volume of the sample solution with concentration C_1.

In radiometric detection, the number of radioactive decay events per second is proportional to the number of analyte atoms, while the fraction of the total decay events being detected is expressed as the absolute detection efficiency, E_d. Therefore, the radiometric sensor response can be expressed by using the following equations:

$$R_{c/s,eq} = E_d A_a V_r \quad (7)$$

$$R_{c/s,C_0,C_1} = E_d[A_0V_r + V(A_1 - A_0) - (A_1 - A_0)F(V)] \quad (8)$$

Equation 7 expresses the radiometric count rate, R_{eq}, in counts/second (c/s) of a sensor column that is fully equilibrated with a sample containing analyte activity, A_a , in Bq/mL. Equation 8 gives the sensor count rate, $R_{c/s,C_0,C_1}$, as a function of sample volume for an arbitrary activity step with initial and subsequent activities A_0 and A_1, respectively.

Recalling that $F(V)$ is an integral of $f(V)$ (see eq 5), which depends on the column parameters V_r and N (see eq 2), it follows that the sensor response as a function of volume depends on the column chromatographic parameters, i.e., the retention volume V_r and number of theoretical plates N, and the detection efficiency E_d. In turn, the retention volume V_r depends on the volume of the stationary phase, V_s, and the analyte partition coefficient, $K = C_s/C_a$, where C_s and C_a are the concentrations of the analyte in the sorbent and aqueous phases at equilibrium, respectively. It is the dependence on the partition coefficient that accounts for the capture of the analyte from the aqueous phase due to interactions between the analyte and sorbent, while variations in the partition coefficient among analytes and potential interferences provide the sorbent selectivity.

The sensor responses in Figure 14 for each step change in input concentration were fit to the models using a nonlinear least-squares optimization with the detection efficiency, E_d , retention volume, V_r , and column theoretical plates, N, as regression parameters. A Gaussian function was used to model the normal distribution. These fits are shown as solid lines in Figure 14, where fits were determined for the step change from zero to the sample concentration, and separate fits were determined for the step change from sample concentration to zero. The experimental data can be fit extremely well, and one obtains important sensor and column chromatographic parameters. The fit parameters were in excellent agreement with independent experimental determinations of these parameters. Fits to the model were also used to create the solid lines in Figure 11 for the ^{99}Tc sensor.

Strictly speaking, the Gaussian distribution assumption is valid only for columns with relatively high numbers of theoretical plates.[90] The sensor columns do not have high numbers of theoretical plates. However, for plate numbers greater than 5 or 10, the Gaussian model provides satisfactory fits and extracts parameters that are in agreement with other measurements. For lower numbers of theoretical plates, the Gaussian model still provides reasonable looking fits to the sensor response, but the fit parameters are unreasonable. Lövkvist et al. reviewed several breakthrough profile equations and proposed an alternative function that can be used to describe the breakthrough profile in low plate number frontal chromatographic systems.[90,91] This function was also integrated into the theory for the equilibration-based column sensors and dubbed the Low Plate Model.[18] When applied to experimental data from columns with plate numbers of about 3, it was found to give good fits and parameters.

It is not surprising that the composite bed minicolumn sensors generally have low numbers of theoretical plates, given that they have short lengths and the bed itself contains the sorbent diluted by the plastic scintillator beads. In addition, the sorbent materials have relatively big particle sizes, and linear flow velocities through the column are high. Nevertheless, such columns do make effective sensors and can be modeled.

In general, extremely low numbers of theoretical plates (e.g., less than two) are undesirable because the volume in excess of the retention volume that is necessary to equilibrate the column becomes rather large, i.e., the sigmoid-shaped elution profile becomes extended horizontally. Thus, the

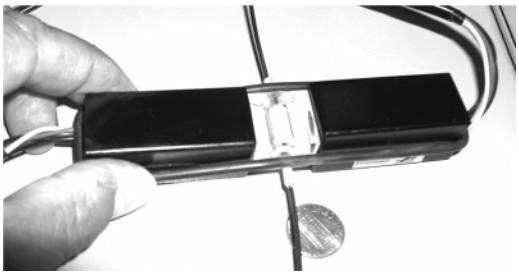


Figure 15. Sensor flow cell and PMTs of the first-generation prototype ^{99}Tc(VII) preconcentrating minicolumn sensor for equilibration-based sensing.

design of the sensor requires a balance between theoretical plates and the volumes required to equilibrate it, and these must be balanced with the required detection limits. The fact that sensors can be characterized in terms of chromatographic parameters and modeled theoretically can help to guide decisions about sensor design.

3.7. Engineered Radiometric Preconcentrating Minicolumn Sensors for Groundwater Measurements

The preconcentrating minicolumn sensor for radiometric detection of ^{99}Tc has been engineered into a sensor probe in a rod-shaped form suitable for monitoring in groundwater via well bore holes. Images of the sensor flow cell with two PMTs is shown in Figure 15, while images of first- and second-generation prototypes are shown in Figure 16.

The first-generation prototype, which incorporates an anticoincidence shield around the sensing flow cell to reduce background counts, has been described in some detail.[16] Using AG 4-X4 anion exchanger and BC-400, the performance of this sensor in equilibration-based sensing mode was investigated with chemically unmodified Hanford groundwater that was spiked with known amounts of ^{99}Tc(VII). Sample volumes of 150 mL, pumped at 3 mL min^{-1}, were used to equilibrate the column, followed by a 30-min counting interval. A linear calibration curve was obtained. Actual contaminated Hanford groundwater samples were also analyzed with results that were in agreement with independent laboratory analysis results, using the method of standard addition for calibration. It was shown in this study that a hydroxyapatite prefilter could be used to extend the life of the sensor by reducing fouling by colored impurities (likely soil organic matter) in the groundwater. No change in sensor response was evident after pumping a volume equivalent to 36 samples of 150 mL each.

For a radionuclide sensor in equilibration-based sensing mode, the time required to obtain a measurement depends on the amount of sorbent material, the flow rate, the volume of sample required to equilibrate the sorbent phase, and the time to devote to counting once the sensor has equilibrated. Although one may spend minutes to hours equilibrating the column and counting the captured radionuclides, fast response time is typically not required for subsurface monitoring applications and long-term environmental stewardship. Changes occur slowly in the subsurface, and the interval between taking data points is long. The Hanford Site's groundwater-monitoring program typically requires the sampling and analysis of monitoring wells on a quarterly basis.

A deployed sensor could be equilibrated and the signal determined and then sealed until the next measurement. At a later date, a new sample could be introduced and equilibrated to get another measurement. A reversible equilibration-based sensor requiring no reagents could potentially work in the field for tens of measurements or years of use if it is sufficiently selective within the sample matrix and it does not become fouled with organic matter or bacteria.

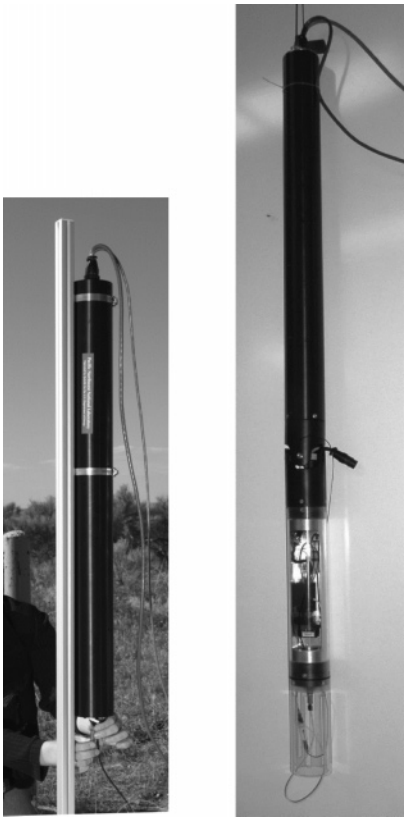


Figure 16. (Left) First-generation package for the engineered ^{99}Tc(VII) sensor. Hands at the bottom where the water intake is located provide a scale. (Right) Second generation prototype, with a water intake, filtration, and pumping components at the bottom in clear plastic, linked to the sensor module and electronics in black with a universal joint to provide some flexibility. The diameters of the two prototypes are the same, the second is longer overall.

3.8. Planar Dual-Functionality Radionuclide Sensors

The column format for preconcentrating radionuclide sensors is convenient but not required. DeVol et al. have described a radial flow format for a disc-shaped composite bed with scintillation detection.[15] The flow-cell was based on a planar fountain cell design,[92] shown in Figure 17, which introduces solution flow from the center of the resin bed to the periphery. The sensor was interfaced with a single photomultiplier tube (PMT). This design initially concentrates most of the retained activity in the center, where the PMT has the highest sensitivity. For ^{99}Tc capture and detection, a number of sorptive scintillating media were investigated, including (1) an extractive scintillator (dual-functionality beads) combining a porous polystyrene resin with the extractant Aliquat-336 and fluor α-NPO, (2) a composite bed of plastic scintillator beads (BC-400) and Tc-selective TEVA resin, and (3) a composite bed of inorganic scintillator particles (CaF_2:Eu) with either TEVA resin or strongly basic anion-exchange resin (Dowex1 × 8-400(Cl^-)). These sensors were operated in a quantitative capture mode (as opposed to the equilibration-based modality just discussed), and the capture efficiencies with these materials in this flow-cell

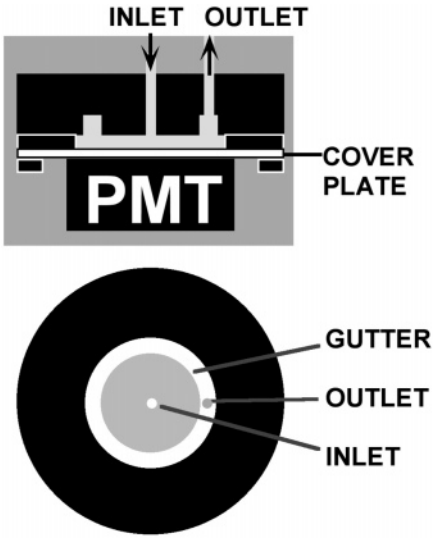


Figure 17. Planar flow cell (fountain cell) coupled to a PMT detector for a dual functionality preconcentrating radiometric sensor. The upper image with a gray background shows a side cross-sectional view, while the lower image represents a top cross-sectional view.

configuration were all above 98%. The detection efficiencies ranged from 10% for the extractive scintillator resin to 50% for the CaF_2:Eu/Dowex.

These results show that this alternative geometry provides both effective capture and reasonable detection efficiencies, even using just one photomultiplier tube. Planar configurations offer flexibility in the geometry of the selective materials and transducing materials, as well as creating opportunities for placing permeable membranes between the sample and the separation/transduction materials. Such a membrane could allow diffusion of ions to the resin bead while stopping suspended particles, thus preventing sensor fouling.

3.9. Planar Radionuclide Sensors Based on Diodes

Semiconductor diode detectors represent an alternative to scintillation for radiometric detection. The principles of α and β radiation detection using silicon semiconductor diodes have been described in detail previously.[93,94] The diode device necessarily leads to planar sensor formats. For sensors in liquids, the requirement to capture the α- and β-emitting radionuclides close to the transducing medium remains. This can be achieved by placing a selective thin film on the diode surface and using a flow cell like the fountain cell in Figure 17.

Diode detectors offer a number of potential benefits. First, they offer superior energy resolution compared to scintillation detectors. For α particles the resolution can be as good as 20 keV FWHM, as opposed to several hundred keV for scintillation detectors. Thus, sensors based on diode detectors have the potential to offer α energy spectra of radionuclides, which could be useful for distinguishing actinides that are co-retained in a semiselective film. Second, diodes for α detection offer much lower background noise levels than scintillation approaches for α detection. Third, diodes offer the potential to discriminate α particle detection from β and γ radiation.

Diode detectors with a selective layer to capture α emitters have been described recently.[10,95] Polymeric layers containing extractants were applied to thicknesses from 0.25 to 5 μm. Thin polymeric films containing supported extractants have been extensively used in preparation of ion-selective electrodes. Typically, high-molecular weight PVC is the matrix, but other materials such as polyacrylates have been utilized.[96,97] Extractant-loaded PVC membranes for radioactive cesium and strontium have also been described.[98] Similar layers can be used to create radionuclide sensors.

Using a surface passivated ion-implanted silicon diode, actinide sensors were demonstrated using bis(2-ethylhexyl)-phosphoric acid (HDEHP) as the extractant and plasticizer in a PVC film on the surface.[10,95] This extractant effectively binds actinides from aqueous solutions of low acidity, and the capture of ^{241}Am on the diode from dilute acid was demonstrated. The analyte remained on the diode surface during a wash step, but the diode sensor can be regenerated by eluting retained ^{241}Am with 4 M nitric acid. The absolute analytical efficiency was ~30%. Using layers of 0.25 μm thickness, characteristic α energy peaks were obtained for ^{241}Am and ^{233}U with peak widths of 35 keV FWHM.

In an alternative format, DeVol et al. used a planar silicon diode in combination with ion-exchange beads for the detection of ^{99}Tc.[99] The sample was mixed with a small volume of these beads, which were then allowed to settle on the diode surface at the bottom of the flow cell. This process captured ^{99}Tc from solution and brought it into close proximity to the diode. The experimental results indicated that this approach could detect to levels below the drinking water standards. In these experiments, the passivated ion-implanted planar silicon semiconductor detector was spray coated with a layer of Teflon AF to make the surface resistant to contact with aqueous solutions.

3.10. Fiber-Based Sensor

Scintillating fibers have a significant history in radiation detection. One example of their use as a radiation detector in environmental monitoring is the direct detection of ^{90}Sr and ^{238}U in soil using a "blanket" of scintillating fibers, a method developed by Schilk and co-workers and marketed by Beta-Scint Company.[100] This radiation detector responds to high-energy β particles from ^{90}Y and ^{234m}Pa as an indication of ^{90}Sr and ^{238}U contamination in soil.

Scintillating fibers were combined with a selective sorbent resin to create dual-functionality sensors for ^{137}Cs in aqueous samples.[101] The resin contained phenol-formaldehyde oligomers grafted on a polystyrene backbone with diphosphonate ligands along the chain. Particles of this resin (3−5 μm diameter) were bonded to Bicron BCF-12 scintillating fiber with an epoxy resin layer approximately one micrometer thick. In typical experiments, the fiber was allowed to equilibrate with a volume of sample. Radiometric measurements were made separately, after removing the fiber from the sample. Detection of ^{137}Cs in alkaline simulated Hanford tank waste samples was demonstrated with selectivity over a number of other metals.

3.11. Whole-Column Chromatographic Sensor

Whole-column radiometric detection was demonstrated in the chromatographic retention and separation of positron-emitting analytes.[102] Link and Synovec created a column flow cell out of BC-400 scintillating plastic materials and packed it with Dionex C14 media. Thus, the device as a whole was a dual-functionality sensor although the packing itself served

only as the sorbent functionality. The planar column geometry was just 0.5 mm thick, while positrons from the analyte were emitted with a distribution of energies with an energy maximum of 0.96 MeV, and a maximum range of 3.5 mm. Using two photomultiplier tubes, a detection efficiency of 96% could be obtained. A flow-through scintillation detector without a packing was placed downstream from the packed column in order to compare on-column radiometric detection with downstream radiometric detection.

Injected analytes on this system were concentrated by the sorbent medium and then released using a gradient elution, resulting in chromatographic migration down the column. Counts were recorded for the entire elution period. A plateau in the detector count rate was observed while the entire quantity of injected analyte was within the column sensor. By contrast, the downstream flow-through detector produced typical transient peaks of much lower area. The whole-column chromatographic sensor improved detection limits by a factor 50 compared to the downstream flow-through detector. Moreover, upon injection of samples with two or three components, a chromatographic separation was observed, enabling detection and quantification of multiple components in a single injected sample.

3.12. Dual-Functionality Sensor for Tritiated Water in Air

While all the selectively sorbent sensors described above were directed toward the detection of radionuclides in water, the combination of sorptive and scintillating properties in a material has also been used to develop a novel sensor for tritiated water in air.[103] Tritium has a low-energy β emission. The sensor material in this case is a Eu-doped zeolite of molecular sieve type 13X, where the zeolite structure provides the sorptive properties for water. The zeolite is also intrinsically a scintillator whose scintillation efficiency is increased by the Eu doping. A disk of the zeolite material was combined with a PMT and an air flow system for tritiated water monitoring. Because tritiated hydrogen gas is not adsorbed like water, the detector can distinguish between the oxidized (tritiated water) and elemental (tritiated hydrogen gas) forms.

4. Discussion

The key concept of the preconcentrating minicolumn sensor is that analytes can be efficiently collected from a large sample volume into a small detection volume on a solid-phase sorbent in a flow-cell. The macroscopic quantity of sorbent has a capacity for a significant accumulation of analyte. By filling such a flow cell with a radionuclide-selective material and a method for transducing radiation events into detectable light pulses, this approach has been demonstrated to provide very sensitive radionuclide sensors for water monitoring. These sensors potentially have applications in monitoring radionuclides in nuclear fuel reprocessing or nuclear waste processing plants, or for radionuclides in environmental matrixes such as groundwater.

Using quantitative capture of radionuclide analytes with subsequent regeneration of the columns, these sensors were similar to the optosensors originally developed as detectors for flow injection analysis systems. These sensors assayed the quantity of analyte in a particular volume of solution, or the rate of analyte uptake as a function of sampled volume.

With the development of equilibration-based sensing approach, the preconcentrating minicolumn sensors for radionuclides became true sensors whose signals rise and fall with the ambient analyte concentration, albeit with a time constant determined in part by the time necessary to equilibrate the column. In this approach, the signal magnitude is no longer dependent on the volume of the sample once the minimum equilibration volume has been delivered.

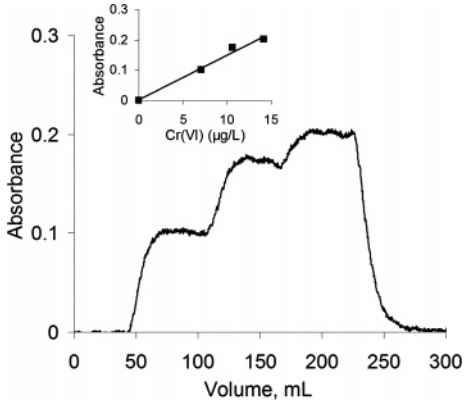


Figure 18. Optical detector response to the hexavalent chromium column sensor in response to chromium standards in Hanford groundwater matrix; data was obtained by pumping at ~1.5-mL min^{-1} net flow rate: (1) 45-mL blank sample, (2) 60 mL of 7.1 ppb Cr(VI); (3) 60 mL of 10.6 ppb Cr(VI); (4) 60 mL of 14.2 ppb Cr(VI); (5) 100-mL blank sample. Figure reprinted with permission from ref 18. Copyright 2006 American Chemical Society.

Although developed primarily for radionuclide sensors, the method can also be applied to other aqueous analytes where an on-column detection method of sufficient sensitivity is available. For example, hexavalent chromium can be captured in an anion exchange-based preconcentrating minicolumn sensor and observed with spectrophotometric detection.[18] (This was mentioned briefly in the Background section on Preconcentrating minicolumn sensors.) This sensor can be operated in the equilibration sensing modality as shown in Figure 18. The three key features of this sensing modality are seen, with steady-state responses, reversibility, and a signal that varies with sample concentration.

Equilibration-based sensing is well-known for sorbent thin films on microsensor device surfaces, but has not been widely practiced for minicolumn-type sensors. Thin films minimize the equilibration time by creating a short diffusion distance within the sorbent material, but the amount of analyte that can be captured is limited by the small amount of sorbent material. A thin film sensor, for example, may have a film mass in the scale of a few micrograms or less, while a preconcentrating minicolumn sensor may have tens of milligrams of sorbent. Thus, a thin film may have a very low capacity compared to a packed column. In addition, a thin film sensor creates a potentially long diffusion distance from the solution to the sorbent film for very low analyte concentrations. The preconcentrating minicolumn sensor overcomes long diffusion distances from solution to sorbent by actively pumping the sample through the column so that all portions of the solution pass within close proximity to the sorbent.

The equilibration-based approach maximizes the extent of preconcentration for a given column material and geometry, and the performance can be modeled using chomatographic concepts. This approach can also alleviate the need for column regeneration solutions. All these features are advantageous for environmental sensing and monitoring applications. The additional time required to reach equilibration of

a macroscopic amount of sorbent material is not a significant disadvantage in groundwater monitoring because changes in the subsurface occur slowly, and monitoring intervals are long. Thus, one obtains high sensitivity and operational simplicity in return for a response time penalty that is not important. A reversible equilibration-based sensor requiring no reagents could work in the field for tens of measurements or years of use if all other practical issues with regard to selectivity and stability in the particular application scenario are addressed. To date, the preconcentrating minicolumn sensor represents the best available sensing approach for meeting the daunting detection limit requirements for α- or β-emitting radionuclides in groundwater.

5. Acknowledgment

We gratefully acknowledge sustained funding from U.S. DOE Office of Science Environmental Management Science Program and the Environmental Remediation Science Program. Funding for the development of the engineered sensor probe was provided by the DOE Environmental Management Advanced Monitoring Systems Initiative. We thank Dr. John Hartman at the Pacific Northwest National Laboratory (PNNL) for leading efforts in the development of this prototype. J.W.G. acknowledges the William R. Wiley Environmental Molecular Sciences Laboratory, a U.S. DOE scientific user facility operated for the DOE by PNNL. The Pacific Northwest National Laboratory is a multiprogram national laboratory operated for the U.S. Department of Energy by Battelle Memorial Institute.

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CR068115U