Automated Radiochemical Separation, Analysis, and Sensing*

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*[a]Automation of Radiochemical Analysis by Flow Injection and Sequential Injection Methods
OBER - Wolf-Broido Initiative for ER/EM Collaboration

*[b]Radionuclide Sensors for Water Monitoring
EMSP - Subsurface Contamination and Vadose Zone Issues

Papers and Awards

O. B. Egorov, S. K. Fiskum, M. J. O'Hara, and J. W. Grate,
"Radionuclide Sensors based on Chemically Selective Scintillating Microspheres: Renewable Column Sensor for Analysis of 99Tc in Water",
Anal. Chem., 71, 5420-5429, 1999.

Jay W. Grate, Sandra K. Fadeff and Oleg Egorov,
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Oleg B. Egorov, Matthew J. O'Hara, Jaromir Ruzicka, and Jay W. Grate,
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Oleg B. Egorov, Matthew J. O'Hara, Jay W. Grate and Jaromir Ruzicka,
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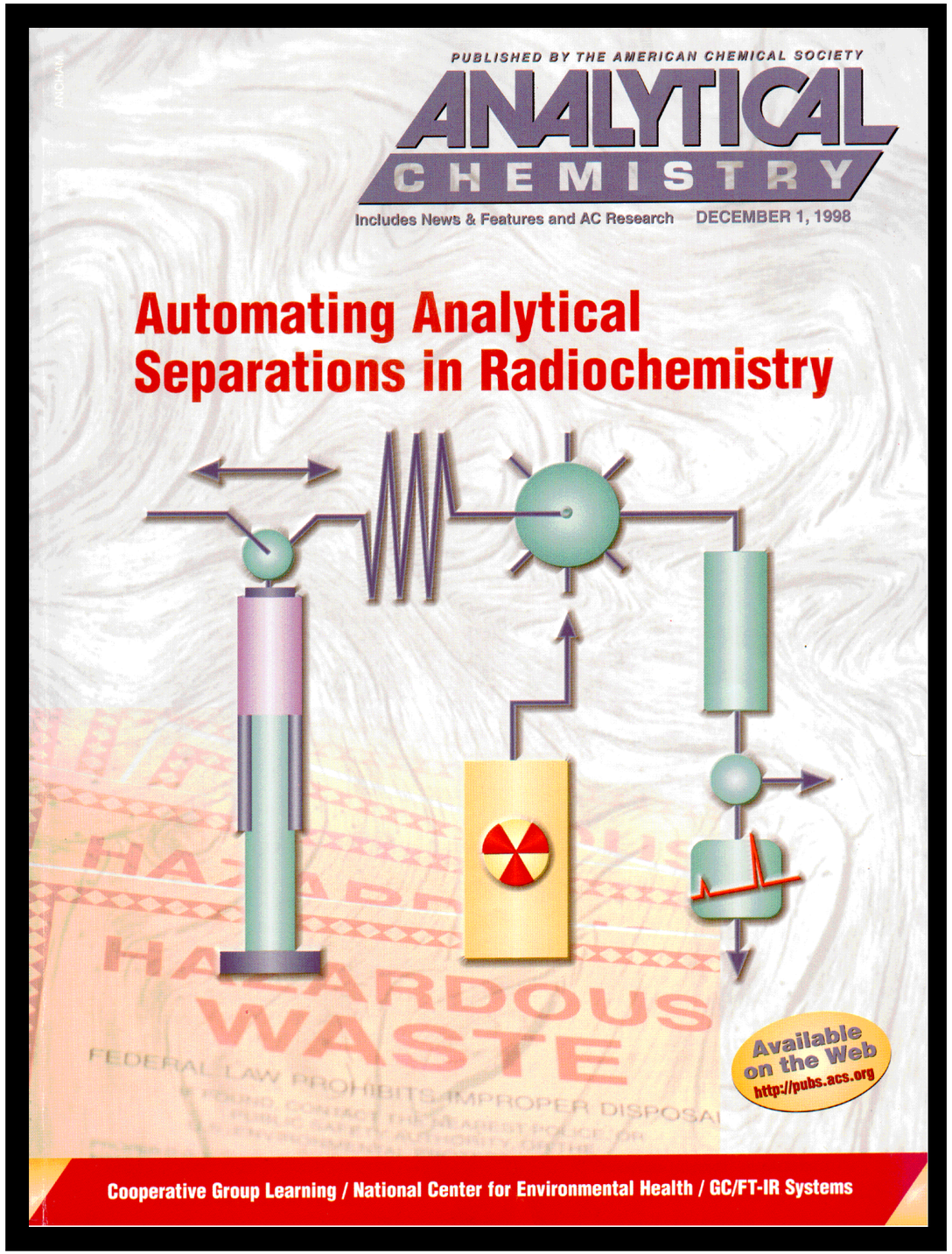
ALARA Award, PNNL, Oleg B. Egorov, 1998.



Problem

Radiochemical analyses are required throughout the nuclear waste characterization, processing, and environmental remediation effort

Chemical separations are required to remove matrix components and interferences prior to determination of many radionuclides

Conventional manual radiochemical analysis procedures involving sparation methods such as precipitations, extractions, and ion exchange are tedious, labor intensive, and costly

Manual batch procedures still predominate at DOE analytical laboratories. Analysts are exposed to radioactive samples and hazardous chemicals

Advantages of Automation

- ***reduced cost***
- ***consistent analytical protocols***
- ***improved precision***
- ***greater sample throughput***
- ***reduced secondary waste***
- ***reduced worker exposure***
- ***increased safety***

Approach

Use flow injection (FI) and sequential injection (SI) methods as a versatile fluid handling approach to automate radiochemical separations, taking advantage of sorbent extraction separation materials

Integrate detection with automated fluid handling to study separations and develop complete analytical procedures

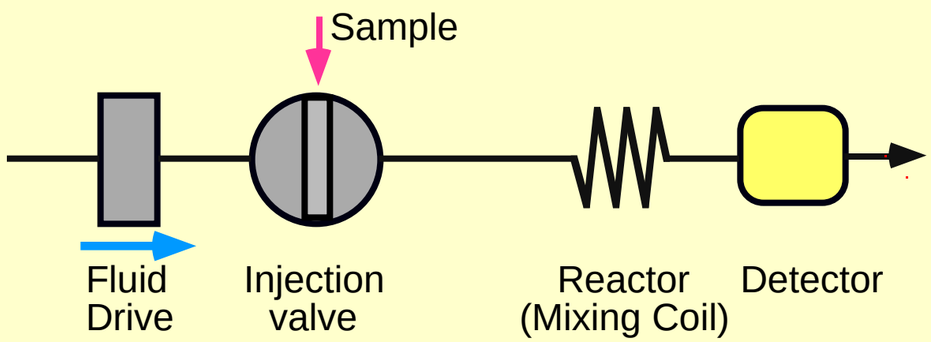
Develop new automated techniques for radiochemical separation and analysis

Generic Issues in Automating Separations

- analyte recoveries and reproducibility
- separation from interferences
- rigorous control of speciation
- kinetics of on-line reaction chemistry
- effects of complex sample matrices
- column reuse or renewal
- flow rate effects
- eluent compatibility with on-line detectors or off line analysis

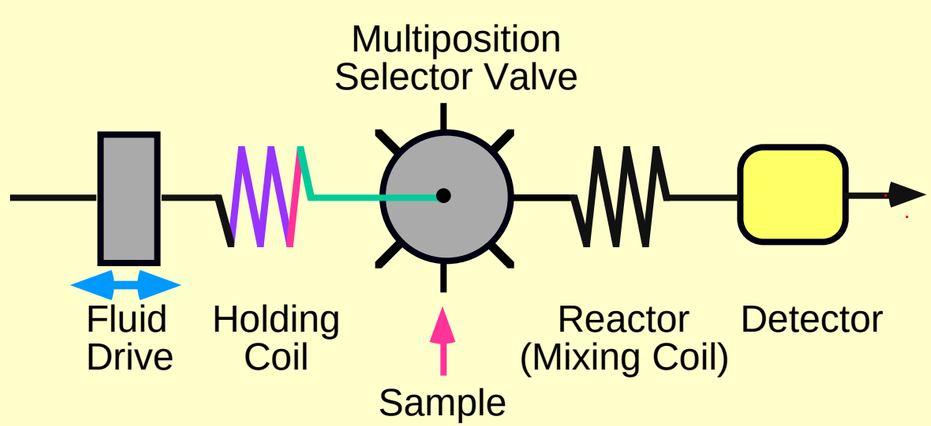
Flow Injection Analysis

- continuous forward flow
- widely used to automate serial assays



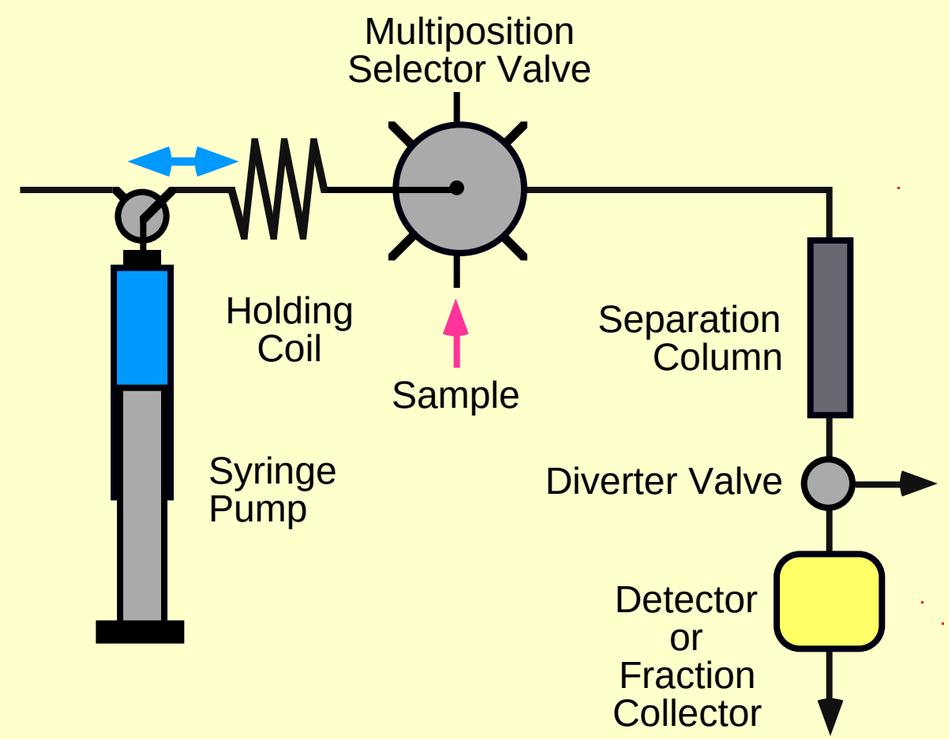
Sequential Injection Analysis

- programmed flow reversals and stacked zones
- sample and reagent volumes keyboard selectable
- very flexible technique for manipulating fluids and suspended solids



Sequential Injection Separation

- automated fluid handling by SI methods optimized for manipulations of corrosive or radioactive solutions
- method handles solutions from microliter to milliliter volumes
- separations in a column format
- eluted species may be detected on-line or collected for off-line analysis
- detection on-line by radiometric methods or by inductively coupled plasma mass spectrometry (ICP-MS)



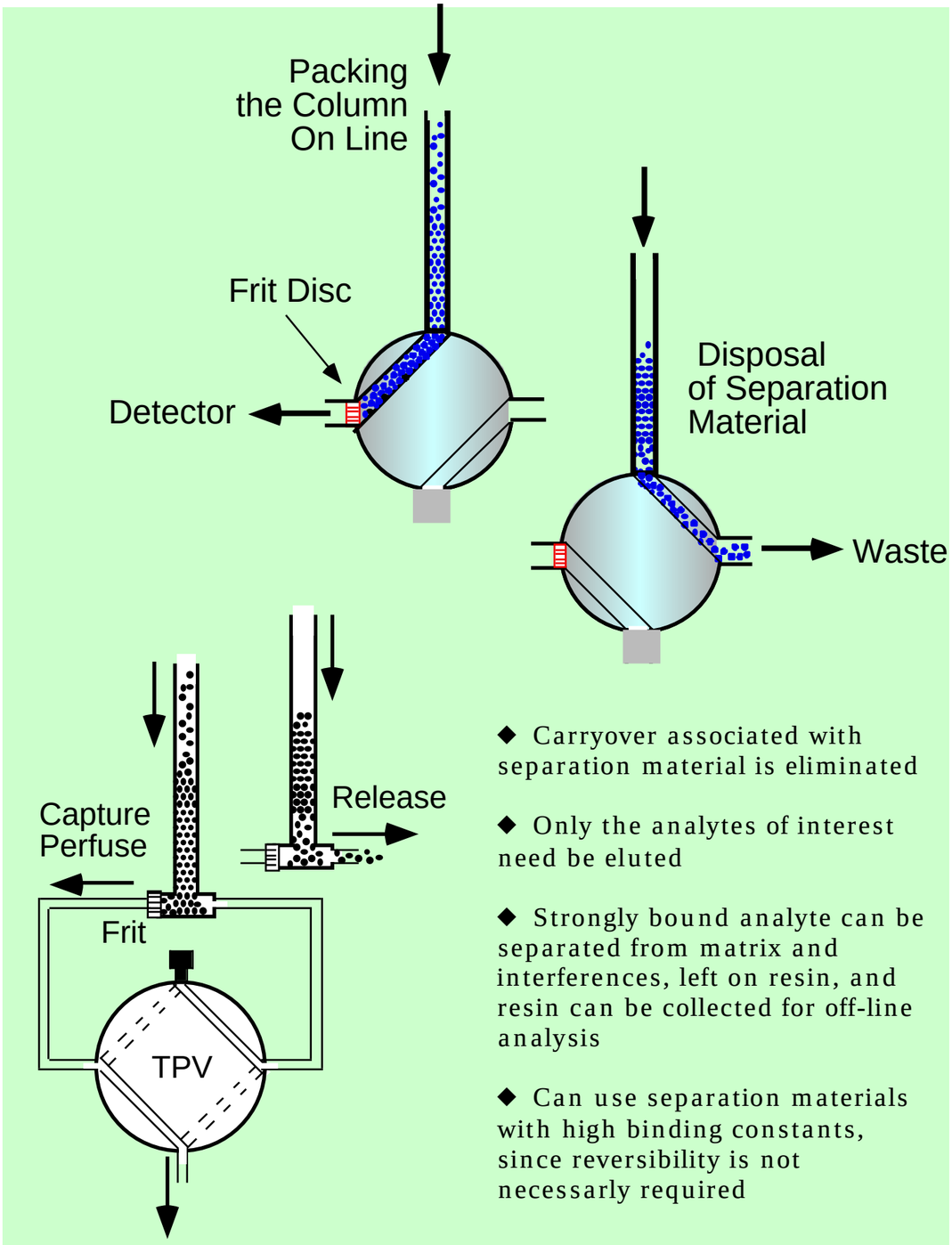
SI Renewable Separation Column Technique (SI-RSC)

Using advanced SI techniques with bead suspensions, preconcentration and separation columns can be packed on-line and disposed of after each separation.

Used in automated radiochemical separations and sensors.

Novel approach generally applicable to sorbent extractions, solid-phase extraction, affinity capture, and chromatographic methods in environmental and bioanalytical applications.

A versatile method with many advantages!

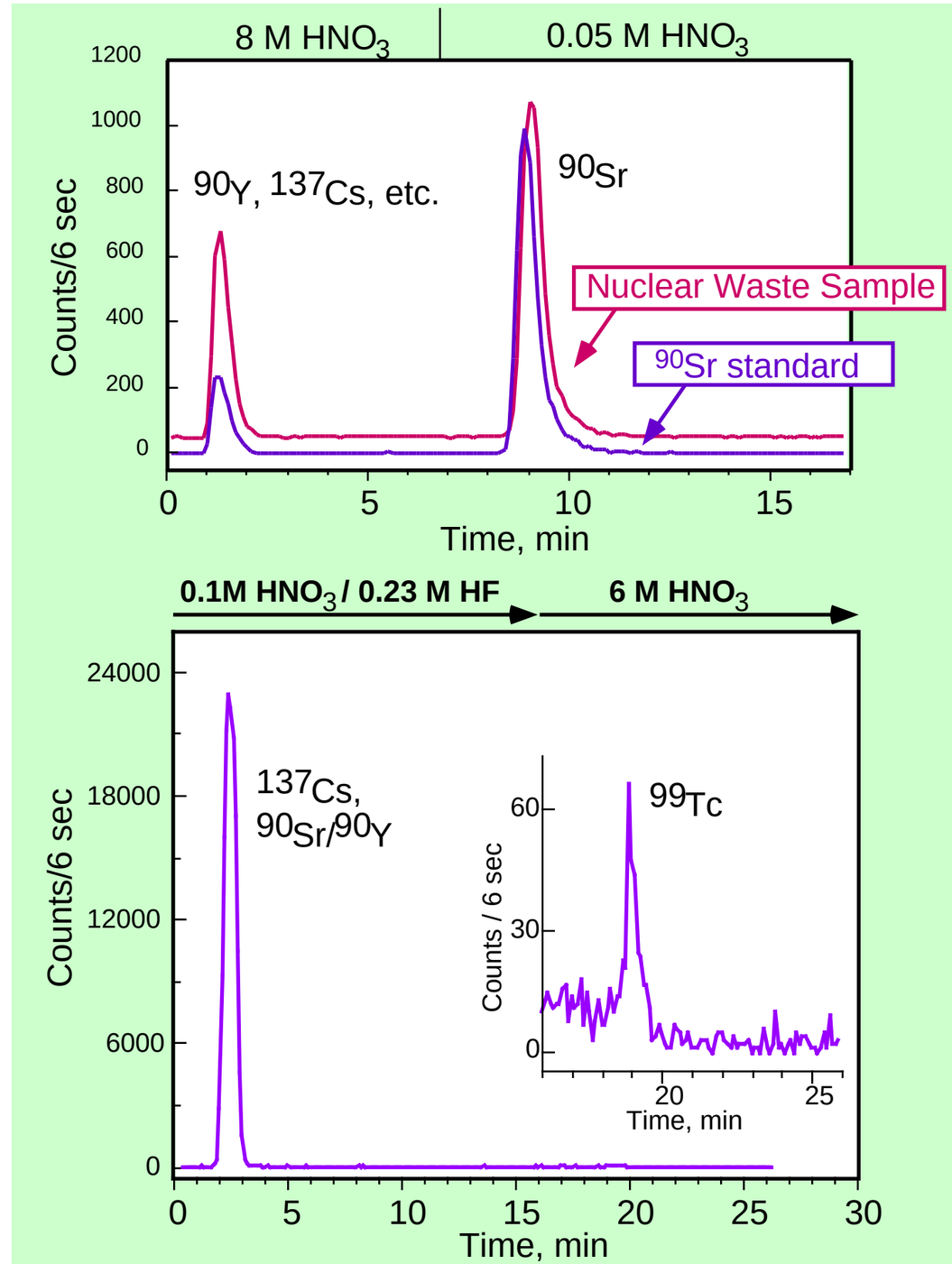


SI Separations for ^{90}Sr and $^{99}Tc(VII)$

Load, wash, and elute separation methods using Sr-resin (crown ether in 1-octanol supported on polymer resin) and TEVA-resin (immobilized Aliquat 336 liquid anion exchanger) for selective retention of Sr and Tc(VII) respectively

These procedures provided high and reproducible separation recoveries, and immediate on-line detection

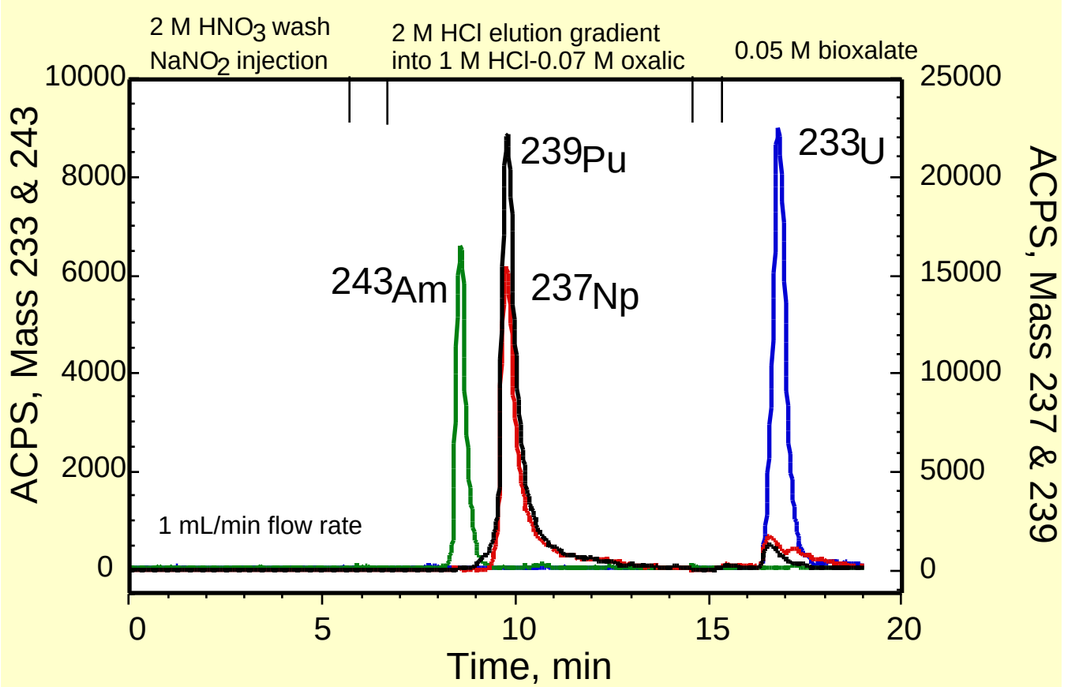
This automated method is being adapted for on-line process monitoring of Tc removal from the aqueous fraction of the Hanford high level tank waste. (work supported by BNFL, Inc.)

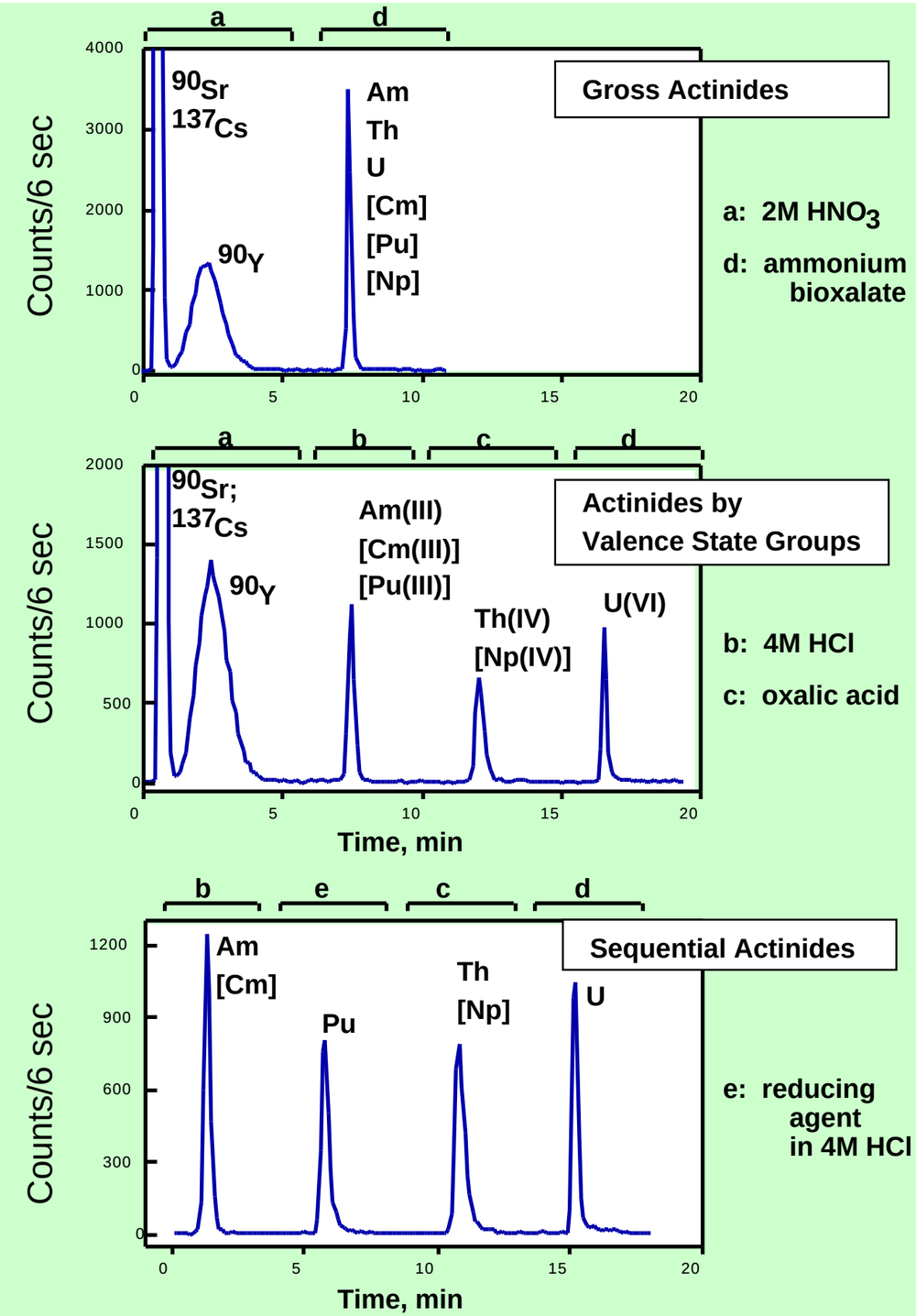


Group and Individual Actinide Separations

Actinides selectively retained on TRU-resin were eluted individuallyor as groups through control of speciation

Examples are shown using on-line radiometric (right) and ICP-MS (below) detection methods





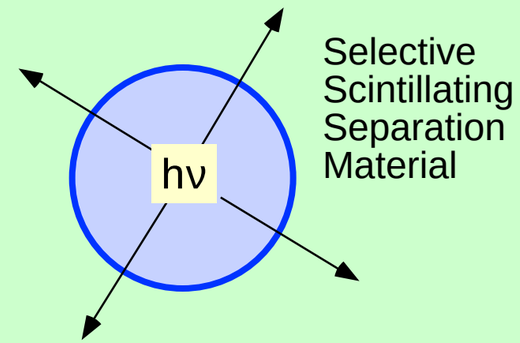
Radionuclide Sensor Concept

Dual functionality material -
- Selective radionuclide uptake
- Scintillates to transduce radionuclide activity into luminescent signal

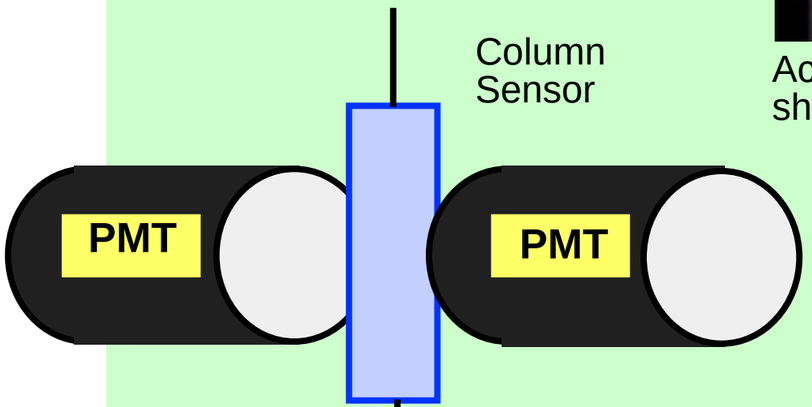
Packed column with regeneration or renewable column format

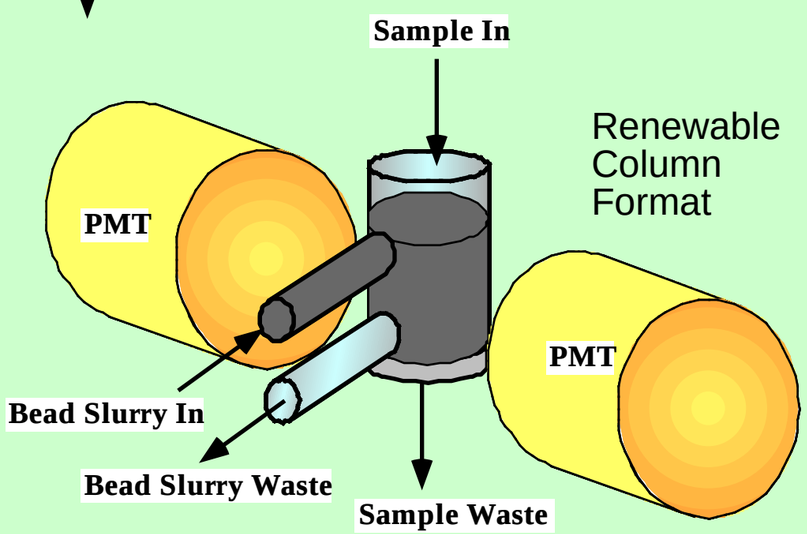
This concept meets the following requirements

- Spatial localization of α- and β-emitting radionuclides
- Radioactivity detection
- Selectivity
- Preconcentration
- Retains radionuclides for counting
- Regeneration or renewal



Actual column sensor shown under UV lamp



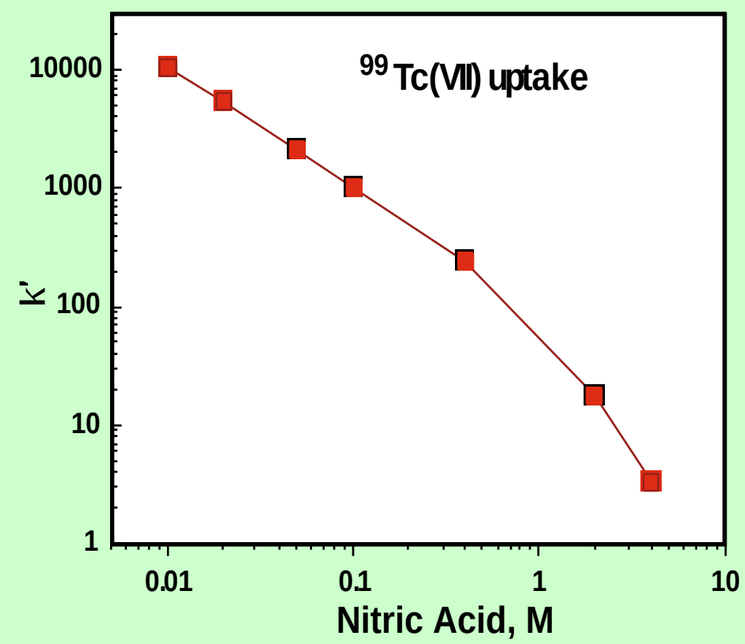


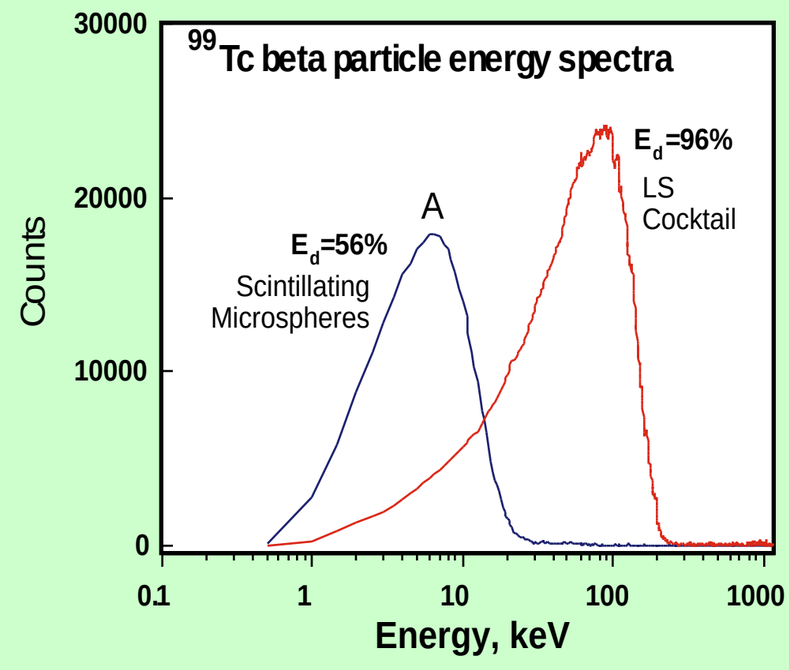
Dual Functionality Microspheres

Microspheres are prepared that are scintillating and have selective radionuclide uptake properties.

Porous polymer beads can be modified with scintillating fluors and impregnated with extractants for radionuclides. PNNL prepared scintillating resins for Tc extraction and obtained the results shown at the right.

A series of resins called ScintEx (Eichrom) resins have been developed that are similar to the Eichrom extraction chromatographic resins, but are also scintillating.



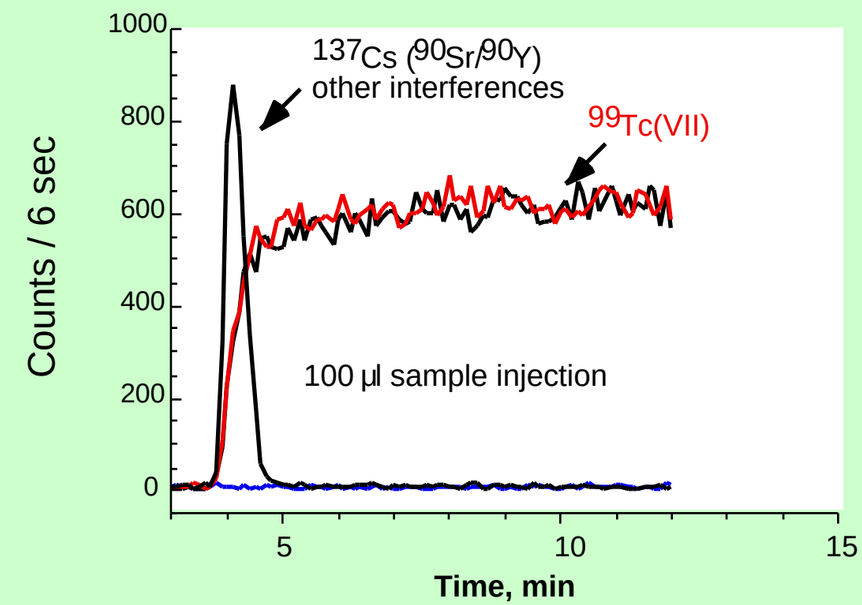


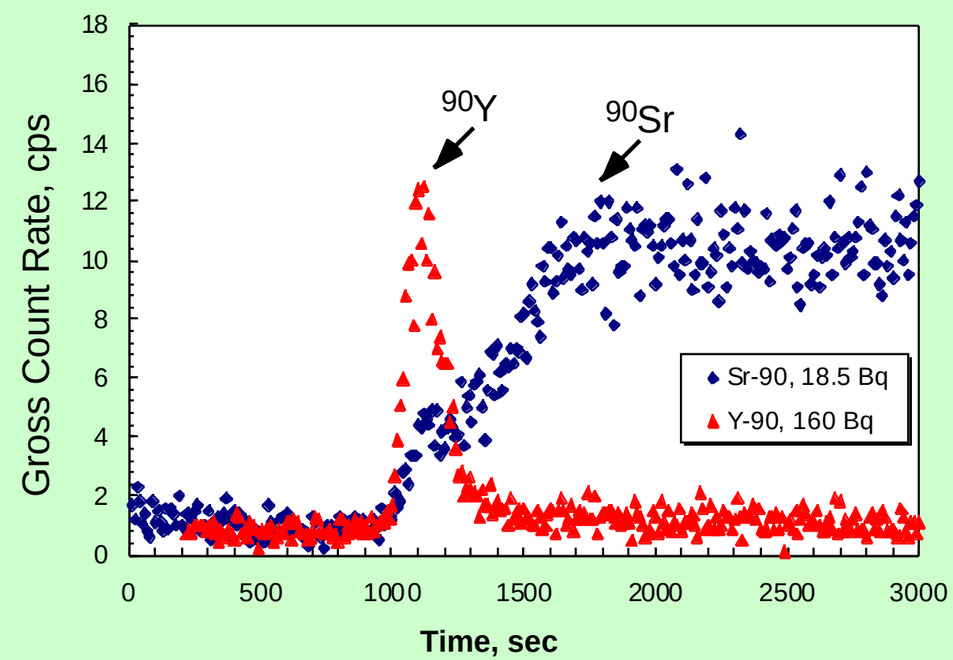
Sensing Approach: Selective Retention

The upper plot shows the selective retention of ^{99}Tc on scintillating beads impregnated with Aliquat 336.

The lower plot shows selective retention of ^{90}Sr on Sr-ScintEx resin.

In this approach, total counts due to selectively retained analyte are accumulated for the time period necessary to achieve the required the detection limits.



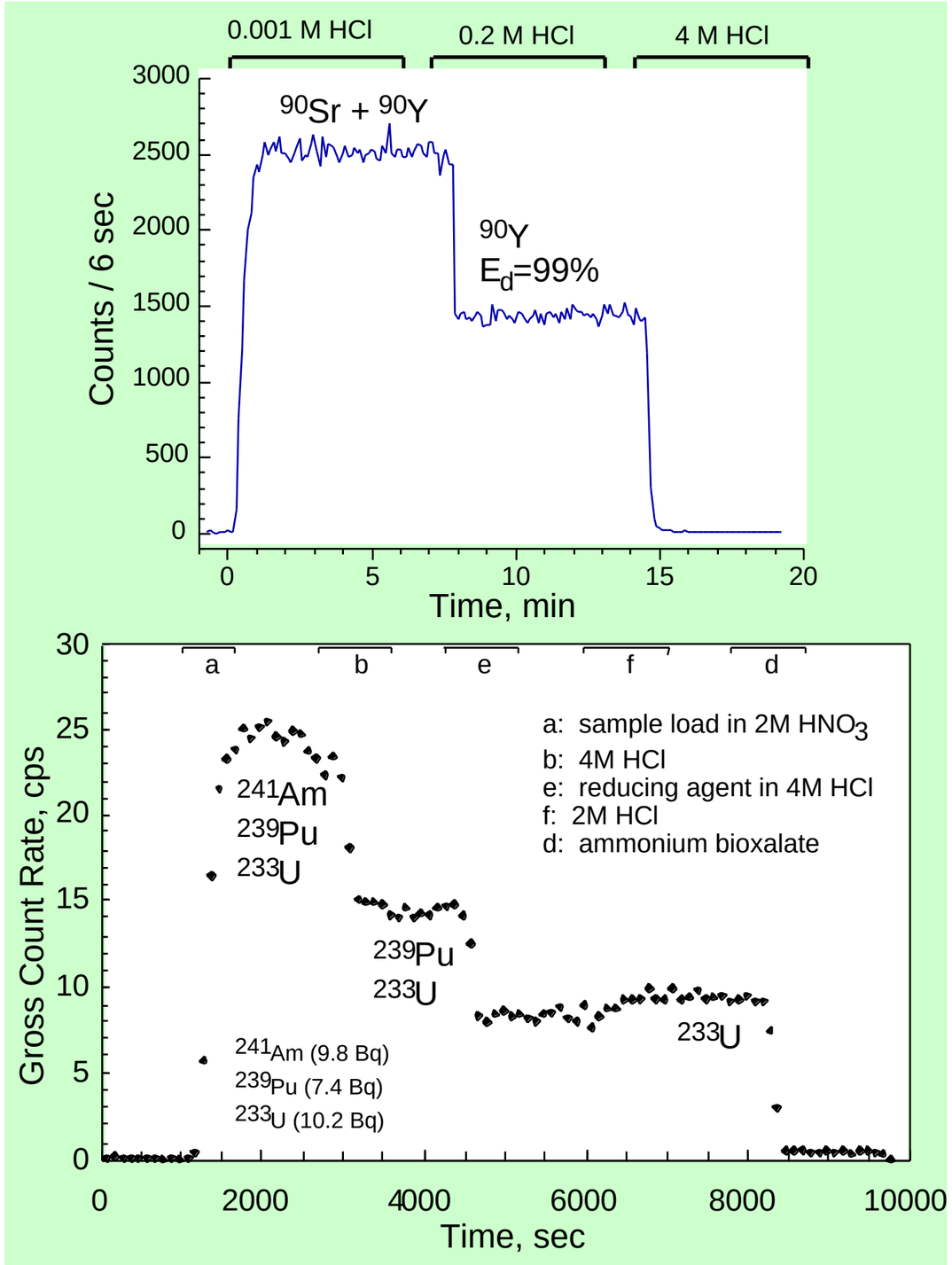


Sensing Approach: Selective Elution of Co-Retained Analytes

The upper plot shows co-retained ^{90}Sr and ^{90}Y collected on HDEHP-impregnated scintillating beads.

The lower plot shows selective elution of actinides co-retained on TRU-ScintEx.

Selective elution of co-retained radionuclides allows quantification of each radionuclide individually.



Detection Limit Requirements

Radioactivity detection is the method of choice for achieving the required detection limits.

In addition, radiometric detection, as opposed to chemical analysis, is required to distinguish among isotopes, for example, radiostrontium from natural stable strontium.

Required detection limits for selected radionuclide contaminants:

Analyte	Radioactivity, Bq/mL	Mass concentration, µg/mL
^{90}Sr[a]	2.96E-04	5.74E-11
^{99}Tc[a]	3.00E-02	4.77E-05
^{238}U[b]	2.00E-04	2.00E-02
^{239}Pu[a]	4.00E-05	1.93E-08
^{241}Am[a]	4.00E-05	3.15E-10

a- maximum contaminant level standards to yield an annual dose equivalent of 4 mrem/yr
b-drinking water standard

The Requirement for Preconcentration

Calculations were made to determine the sample volumes required to obtain sufficient activity for particular radionuclides to reach regulatory detection limits

These calculations demonstrate that a successful sensor must localize the radionuclides in significant sample volumes for counting

The calculations below assume detection by scintillation methods with a detection efficiency of 100% and a background level of 50 cpm, and quantitative analyte capture.

Required sample volumes in mL to achieve the required detection limits

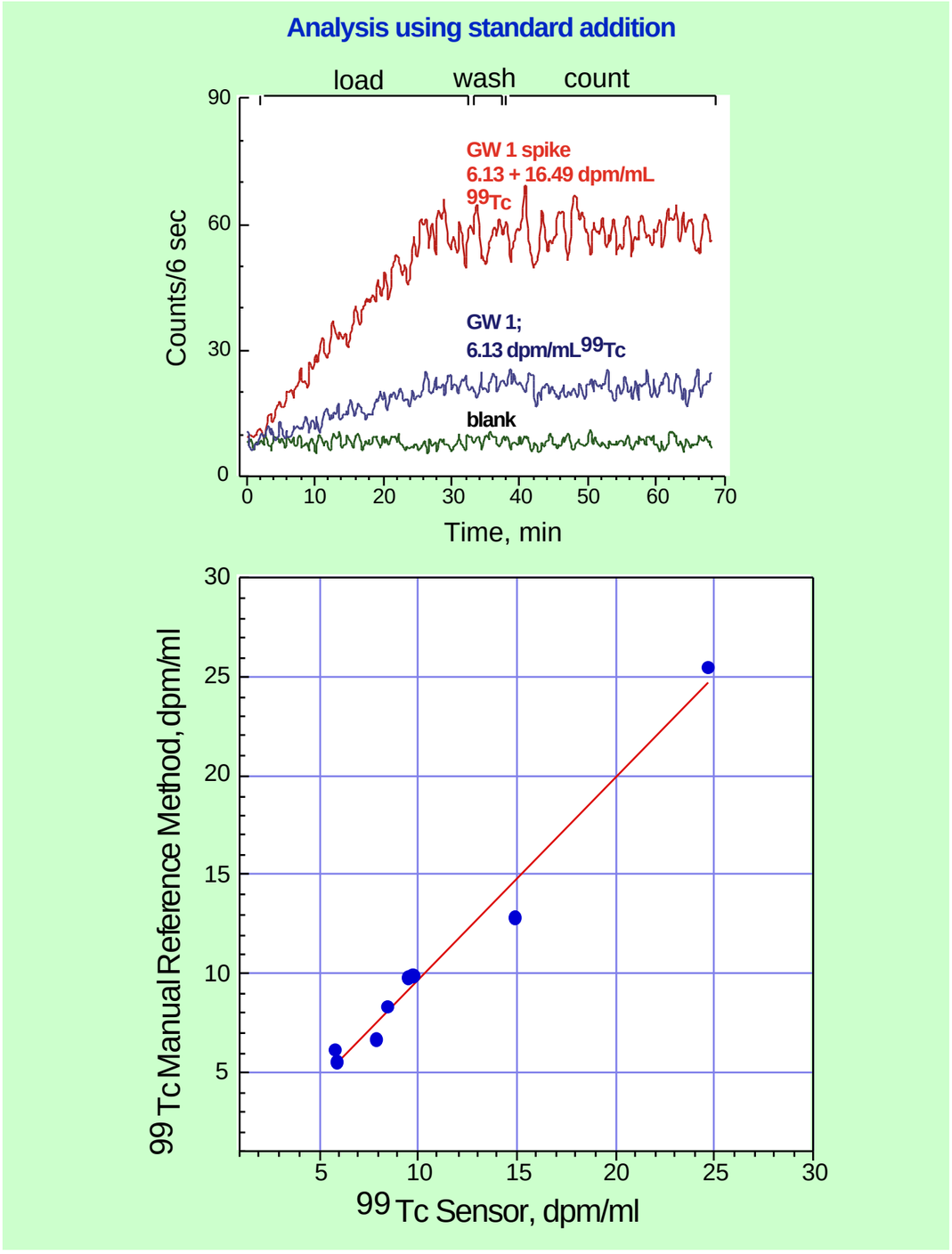
	Counting Times	
Analyte	30 minutes	12 hours,
^{90}Sr	338	67
^{99}Tc	3	.7
^{238}U	500	100
^{239}Pu	2500	500
^{241}Am	2500	500

Analysis of Hanford Site Groundwater

Hanford well water samples were analyzed by the preconcentrating column sensor using the method of standard addition to calibrate the measurement and address any matrix effects on analyte capture and/or detection efficiency.

As shown, analyses using the sensor are in good agreement with analyses by the standard manual laboratory method.

The detection limit was 167 pCi/L or 9.8 parts per trillion using 50 mL samples and 30 minute counting times.



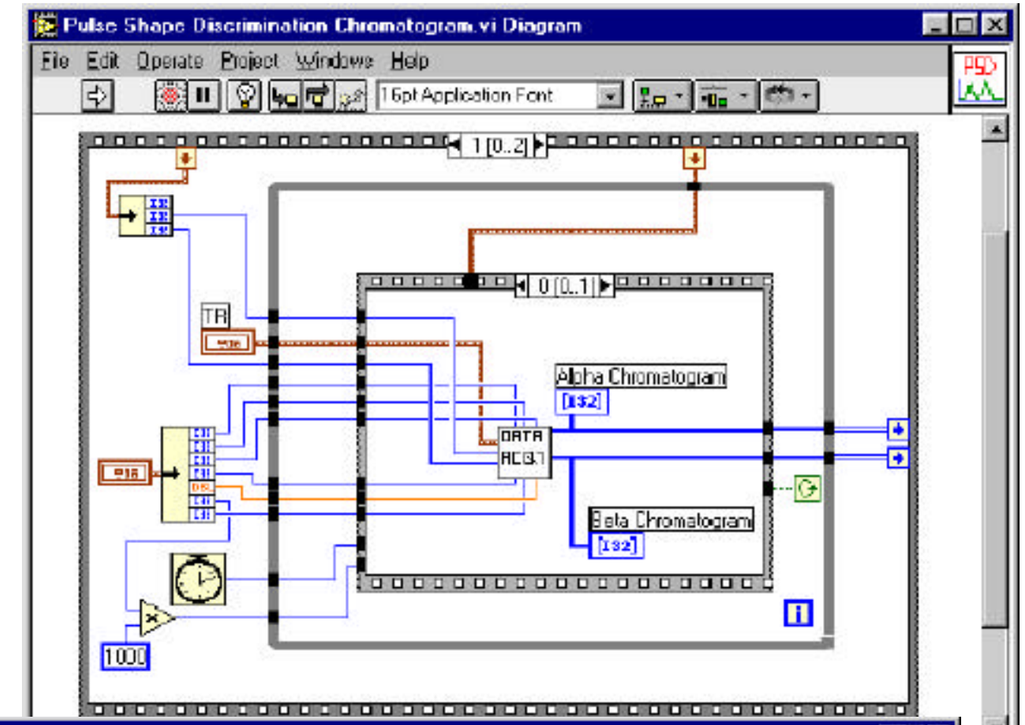
Digital Data Acquisition

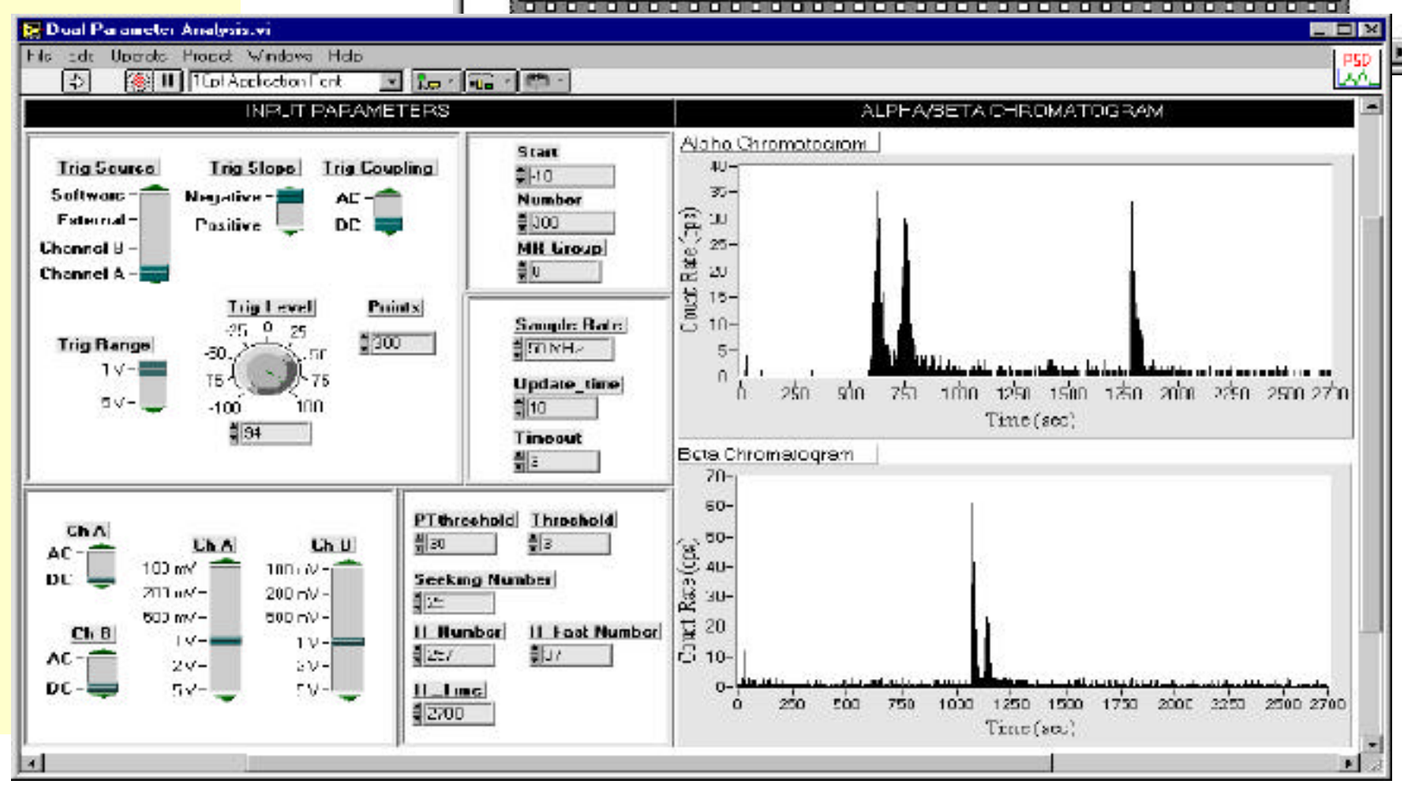
Signals from the flow cell radiation detector are directly digitized by the computer-based digital oscilloscope card and processedby the LABVIEW Virtual Instrument.

Digital data acquisition rather than conventional analog data acquisition simplifies the instrumentation.

- less hardware
- less expensive
- more compact
- reduced power requirements
- more versatile
- potentially better information

Digital data are processed for pulse shape and pulse height analysis.





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Tan, H., Fjeld, R.A., and DeVol, T.A.,
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Education and Training

Most universities in the United States offer very little training in radiochemical analysis.

As part of these programs, we have trained a PhD student at PNNL, whose thesis was completed in March 1998, and one Bachelor's Degree student. Both were hired by PNNL.

The Environmental Engineering and Science program at Clemson University has nuclear facilities in the L.G. Rich Environmental Research Laboratory that include a teaching laboratory, radiation detection instrumentation, a low level counting laboratory for environmental samples, a radiation detection and measurement laboratory, and a radiochemical separation laboratory. Almost all radioisotopes, including actinides, can be handled in these facilities.

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