Project 86759: Radionuclide Sensors For Water Monitoring

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(renewal)

Radionuclides Sensors for Water Monitoring

• Continuation of the research program directed at the development of novel radiometric sensor concepts and materials for sensitive and selective determination of beta and alpha emitting contaminants in water

•The expected outcome is knowledge necessary to develop reagentless sensors suitable for in situ long-term monitoring applications

Project Goals

•Extend previous work on preconcentrating radionuclide sensors to **reagentless sensors** for ***in situ*** measurements and **long term** monitoring

•Develop a fundamental understanding of reagentless sensor operation and the effects of sample matrix components

•Investigate separation chemistries that will enable reproducible and reversible analyte binding in chemically untreated groundwater

•Develop an understanding of the sensor fouling issues in chemically untreated groundwater

•Investigate and compare various sensor geometries for integrating chemistry, transduction, and signal collection

•Develop simulation approaches that can be used for sensor geometry optimization

•Investigate and develop improved methodologies for scintillation detection of β-emitters for reliable, low power operation

•Perform rigorous analytical characterization of ^{99}Tc sensor prototype

•Define the limitations and the potential of the proposed in situ sensing approach.

•Educate students in modern radiochemistry and DOE waste cleanup challenges.

Approach

Need for Tc, U and Sr-90 sensors

•Long term in-situ monitoring in groundwater

Technical Gap

•Lack of analytical methodologies capable of detecting beta and alpha emitters in water at required levels

Scientific Challenge

•Ultra low mass concentrations

•Short ranges of beta &alpha radiation in matter

•Sample matrix

Overall Sensor Approach

•Radiometric detection (scintillation & solid state) with analyte spatially localized & preconcentrated within the detector

•Reagentless sensing based on sensor equilibration

Separation Chemistry

•Selective, reversible, robust high affinity sorbents for selective capture of analytes in chemically untreated groundwater

Radiometric Detection Methodologies

•Optimization of radiation detection for optimal sensitivity, minimal size and power consumption

•New solid state scintillation light detection methodologies

Sensor Geometry

•Optimal coupling of preconcentration & radiometric detection components for maximum sensitivity and minimal size

Integration and Analytical Testing

•Integration of preconcentration and detection into a single functional unit

•Long term testing in chemically untreated Hanford groundwater

Outcome

•Knowledge to design efficient in situ probes for radioactive contaminants in groundwater

Radionuclide Sensors for Groundwater Monitoring: Challenges

Analyte	Radioactivity,Bq/mL	Mass Conc., 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-2
$^{239}Pu^{a}$	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/year
b-drinking water standard

- Radiometric detection is a detection method of choice for a sensor device
- Compared to γ-emitting radionuclides, β and α-emitters represent substantial challenges for environmental sensing due to:
  - Short radiation ranges and rapid energy dispersion
  - Energy overlap problems (limited energy resolution)
  - Low-level detection requirements
- ***Analyzed in laboratories using wet radiochemical methods***

Radionuclide Sensors : Requirements and Definition

Radionuclide sensors: radiation detectors with chemically selective preconcentrating layers for analyte capture and localization

- Must provide selective preconcentration and separation from interferences & matrix
- Must localize radionuclide species in the close proximity to the radiation transducer
- Must retain analyte for counting
- Must be reversible, regenerable or renewable for reuse
- *For long-term field operation ideally must be reagentless*
- *Small instrumentation size, compatible with down-well installation, long-term operation in the field*

General sensor configurations:

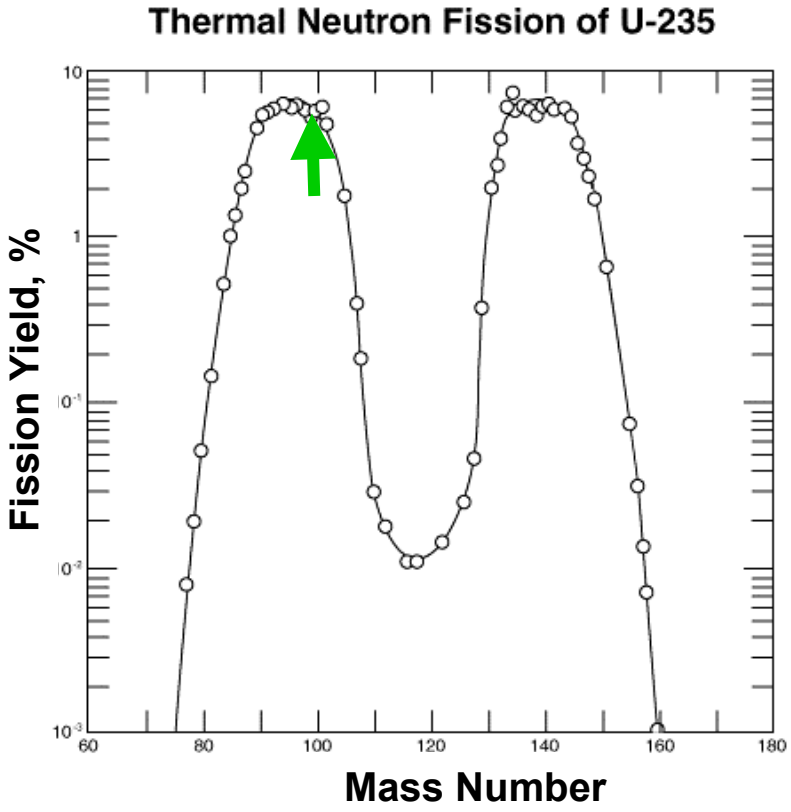
- ***Preconcentrating column sensors using scintillation detection***
  - ***Chemically modified PIPS diode detectors***

Tc Groundwater Monitoring Needs at Hanford

$^{99}Tc \xrightarrow{2.13 \times 10^5 \text{ years}} {}^{99}Ru$

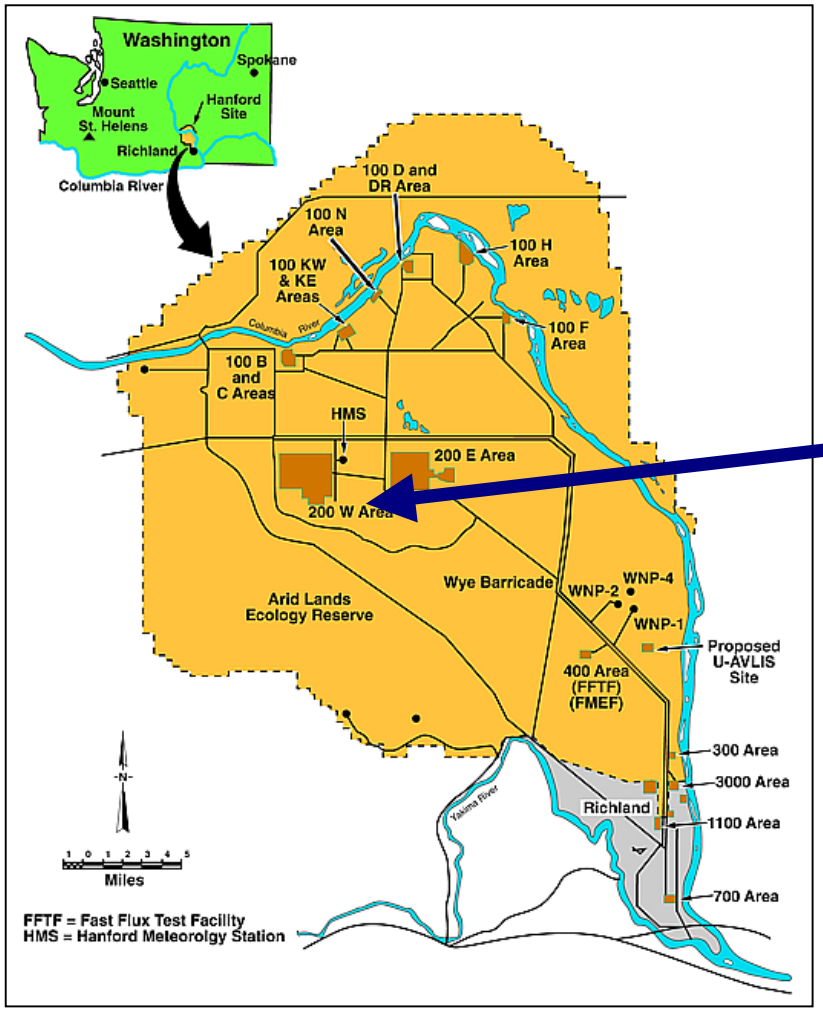
E_β=294 keV

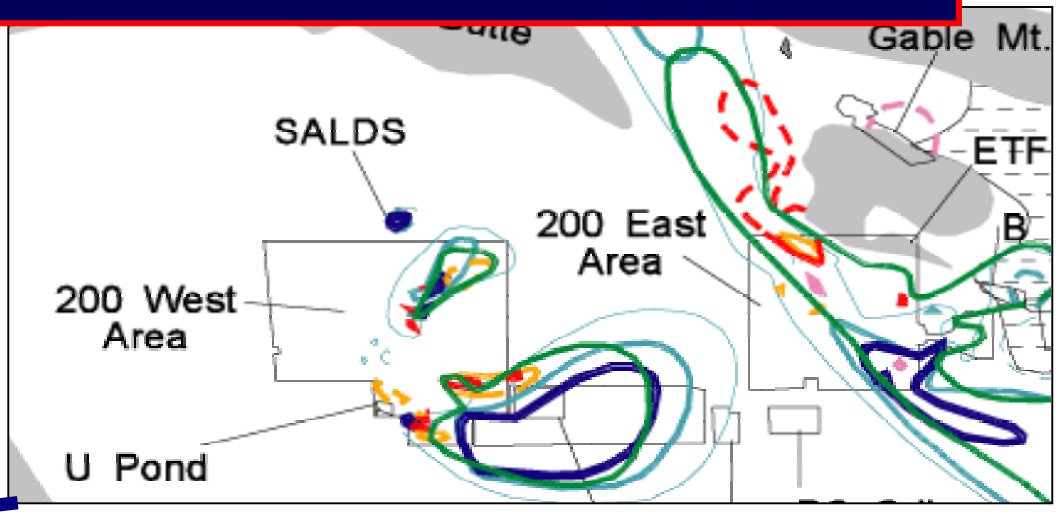
- high mass abundance in nuclear waste (1 ton (20 kCi) is present at Hanford)

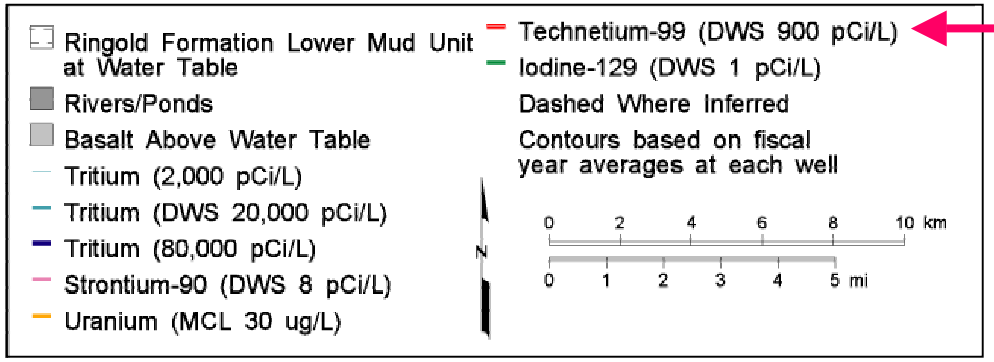


- Long radioactive half life and high abundance in nuclear waste
- High mobility in environment
- Detected in groundwater at elevated levels
- Difficult to detect and analyze (pure beta-emitter)
- Considered one of the primary risk drivers at Hanford

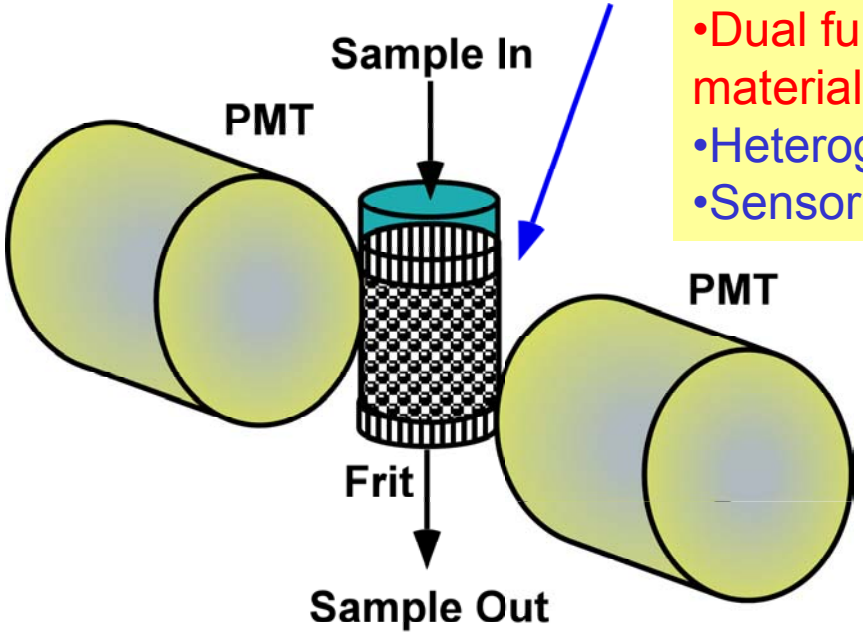
Tc Groundwater Contamination at Hanford



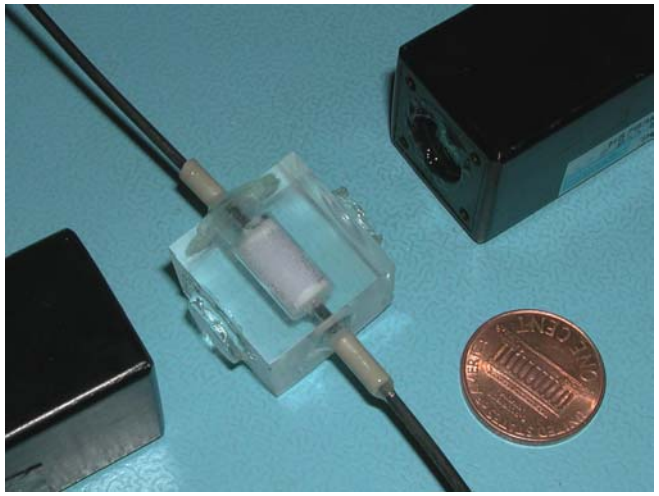


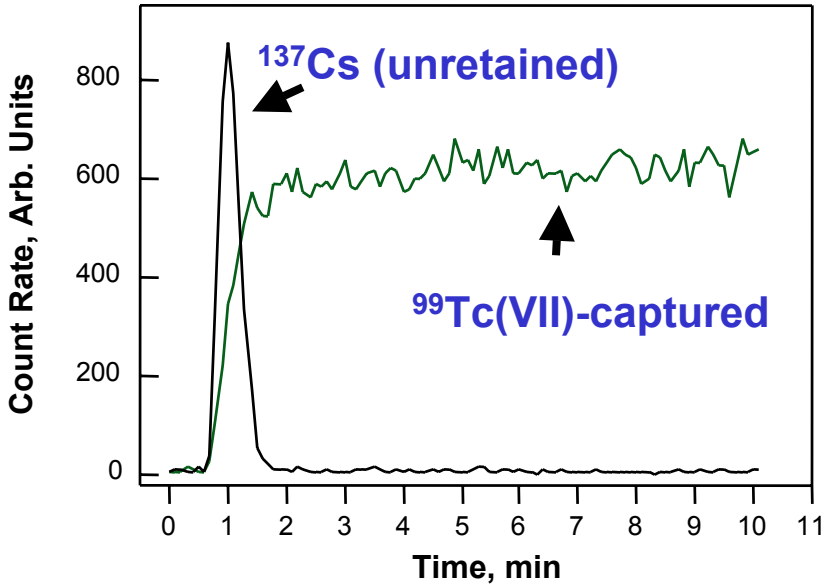


Preconcentrating Column Sensor Concept



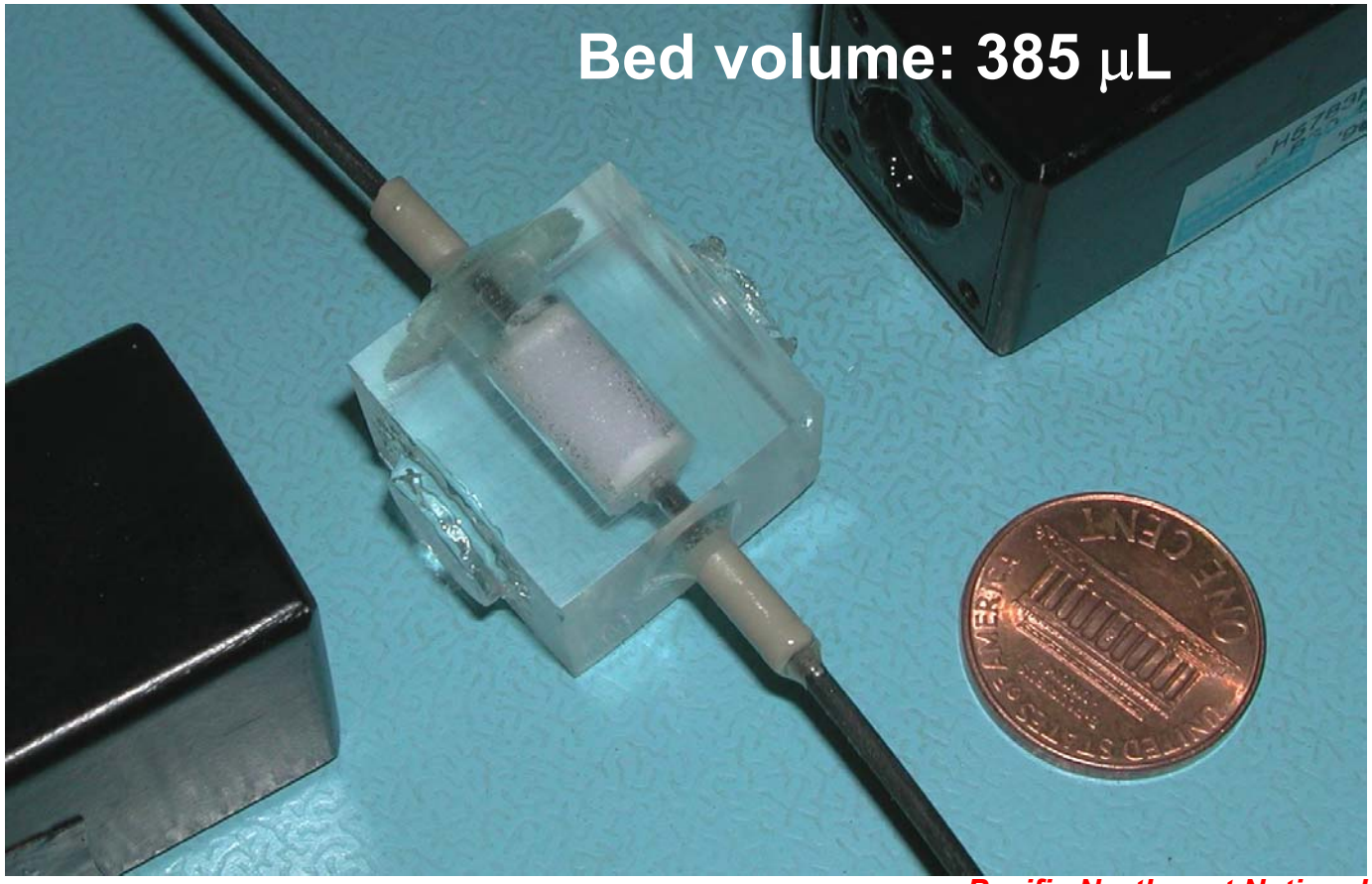
- Dual function scintillating/sorbent sensor materials
- Heterogeneous composite column bed
- Sensor bed volume 0.02-3 mL



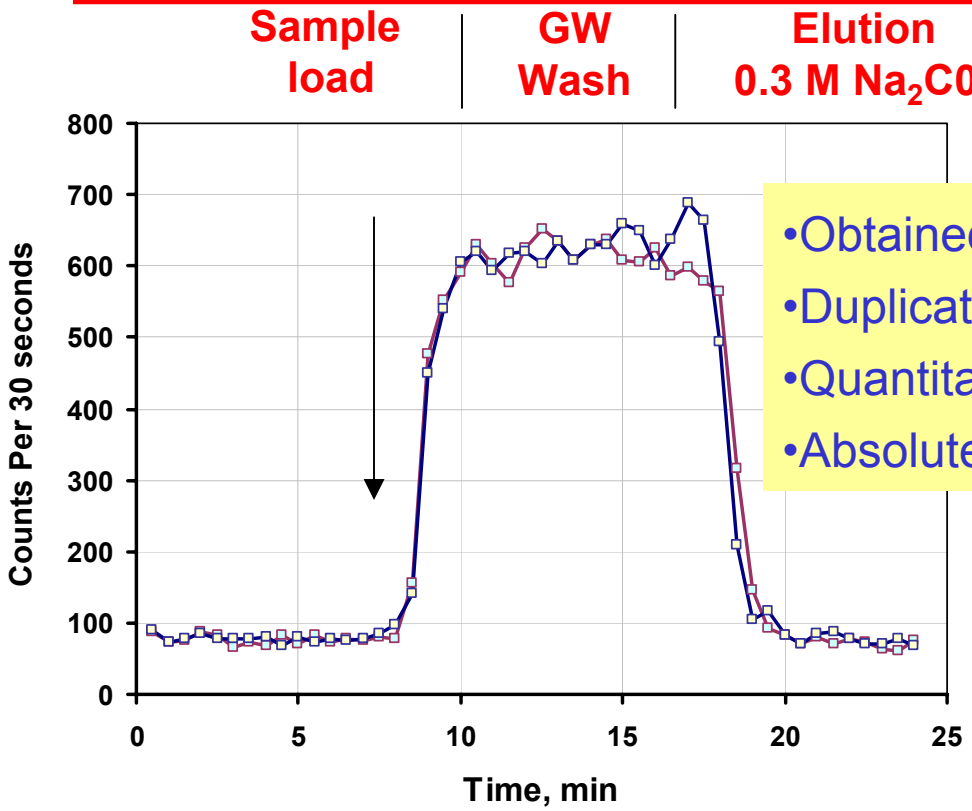


Pertechnetate-Selective Composite Bed Sensor

- Composite cell: uniform mixture of weak anion exchange sorbent and polymer scintillator (2:1 ratio)
- Weak anion exchanger selective for ^{99}Tc; (D~270 mL/g in Hanford groundwater)
  - *resistant to irreversible fouling by NOM*



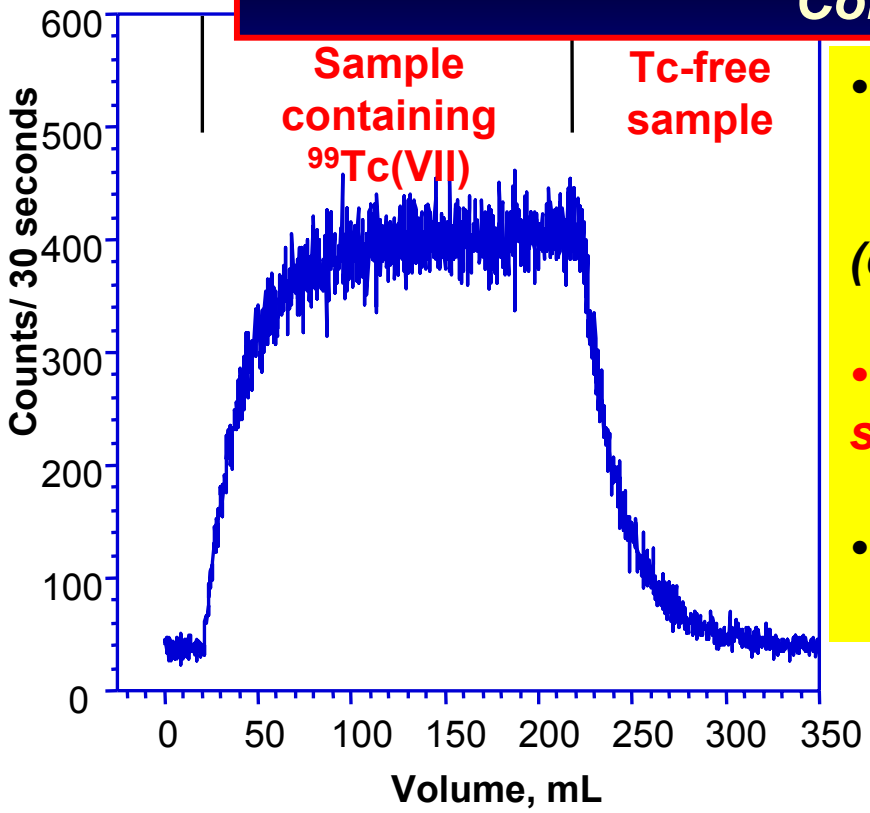
Tc-selective Sensor: Detection Efficiency and Sensor Regeneration



- Obtained using Packard Radiomatic 515A
- Duplicate 0.6 mL Tc(VII) sample injection
- Quantitative analyte capture on the sensor
- Absolute detection efficiency 22±2%

- Composite sensor bed provides efficient analyte capture
- Detection efficiency is adequate for practical applications
- Weak anion exchange sorbent functionality enables regeneration using environmentally benign reagents

Equilibration Sensing Approach Using Preconcentrating Column Sensors



- ***Sample solution is delivered through the sensor until chromatographic equilibrium is attained throughout the sensor column (column breakthrough occurs)***
- ***Equilibrium response is proportional to the sample activity***
- ***Sensitivity is determined by the uptake affinity***

Response: $A_e = E \bullet D \bullet V_{st} \bullet A_{sm}$

A_e -equilibrium response

D - distribution coefficient

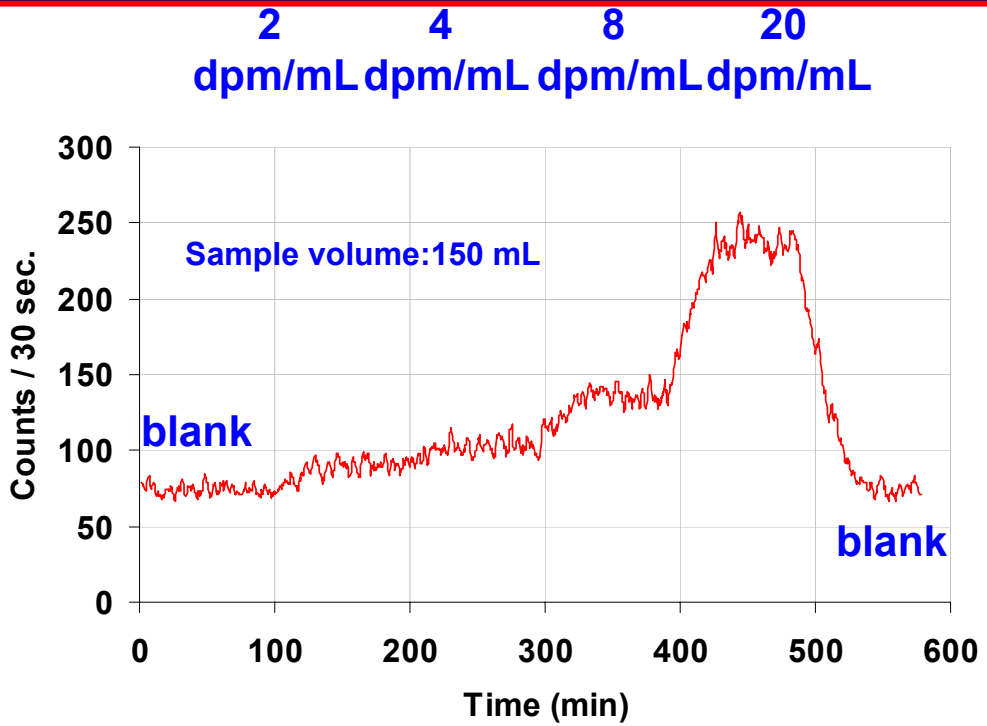
V_{st} -volume of the stationary phase

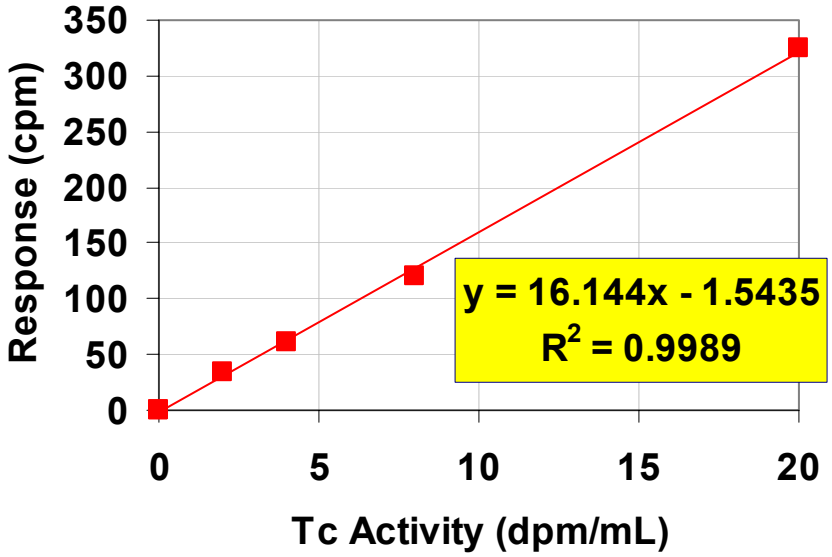
A_{sm}- sample activity

Sample volume to attain equilibrium:

$$V \geq k' V_m \left[1 + 3\sqrt{\frac{H}{L}} \right]$$

Feasibility of Equilibration Sensing Using Spiked Hanford Groundwater



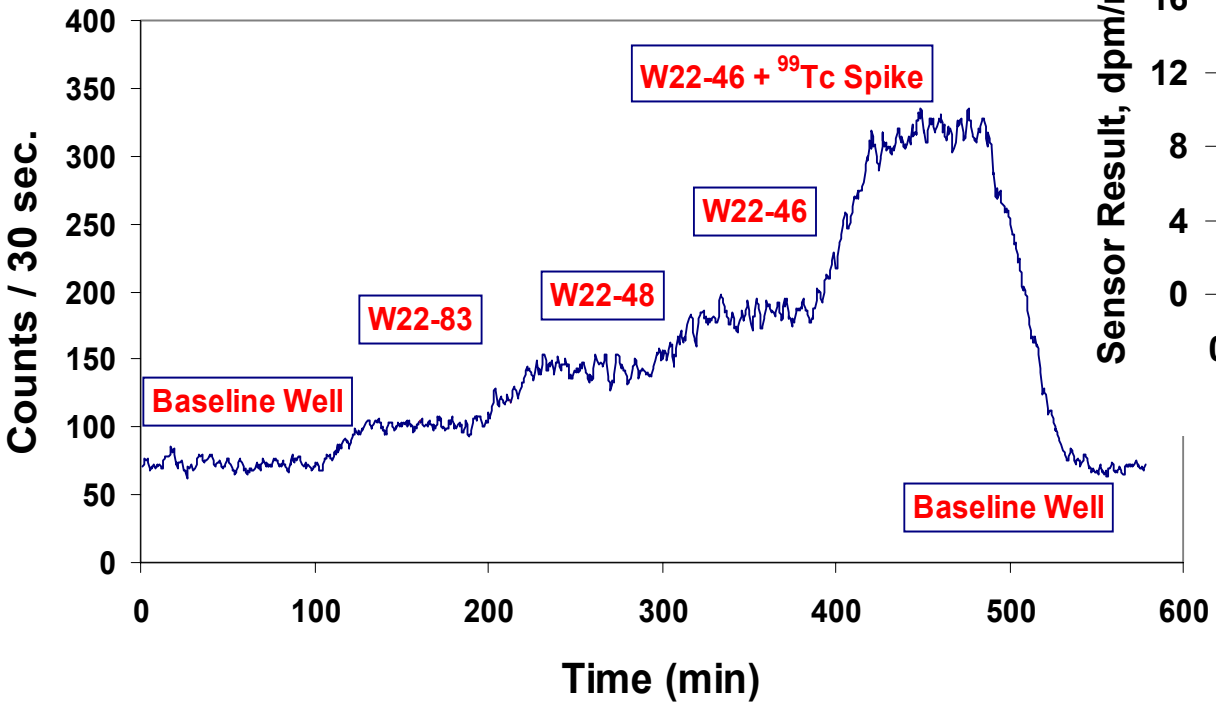


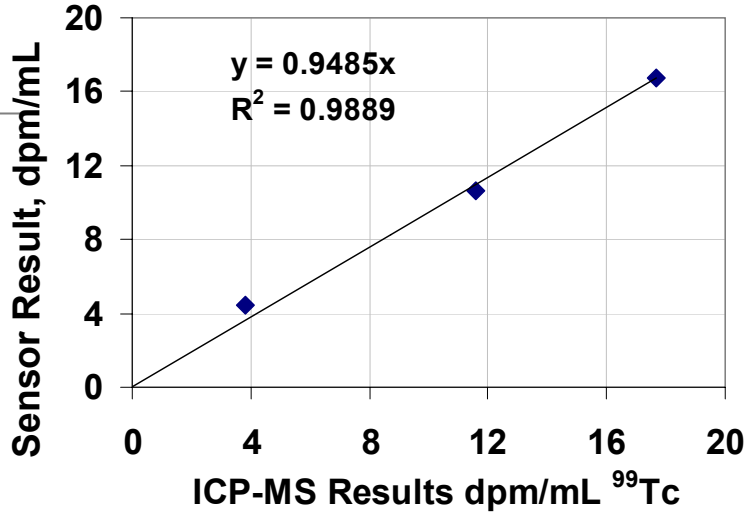
Laboratory data using Packard Radiomatic 515A detector

- equilibrium sensor response is proportional to the analyte activity
- no reagents are necessary for sensor regeneration or renewal
- no frequent calibration if fouling/degradation occurs

Groundwater Analysis Using Equilibration Sensing Approach

Laboratory data using Packard Radiomatic 515A detector

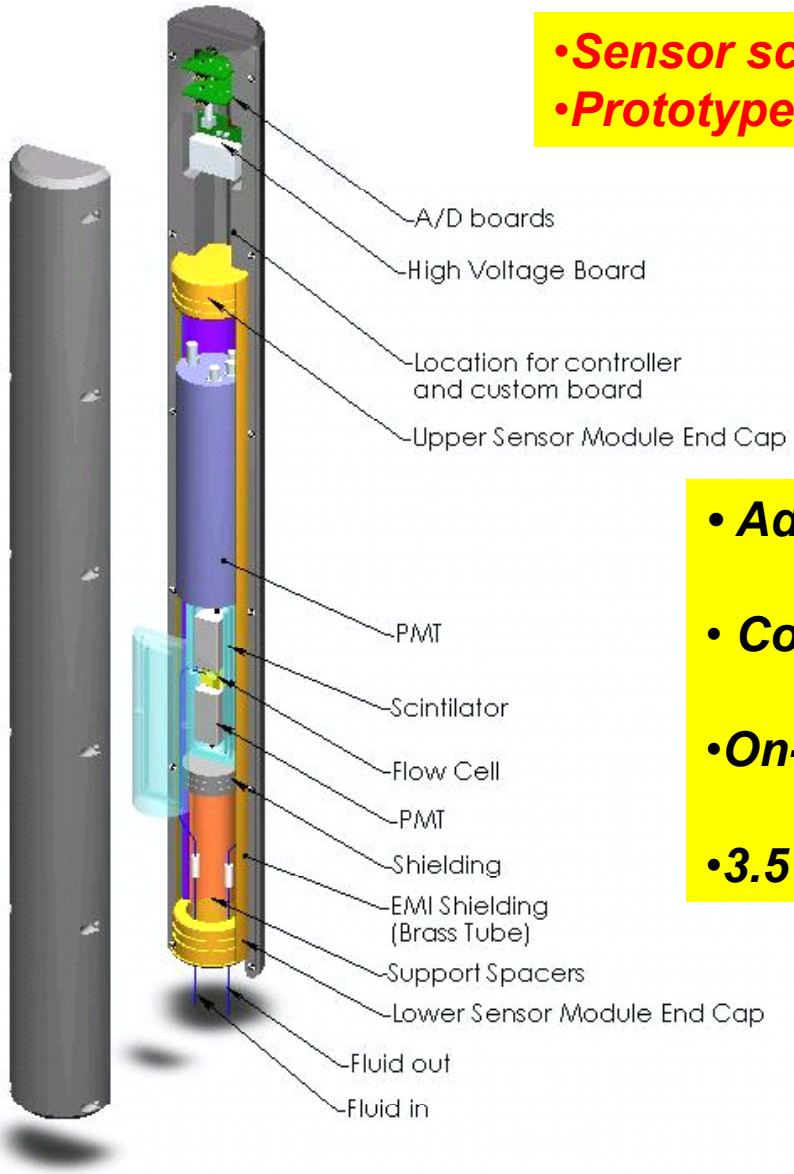




- standard addition was used for sensor response calibration
- accurate analysis of actual groundwater is possible

Design of the In-situ Sensor Probe Prototype:

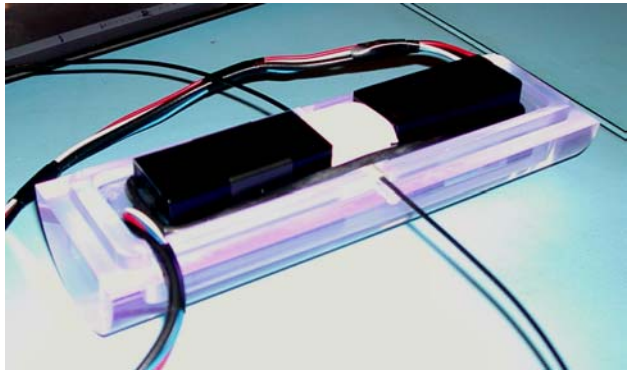
- *Sensor science is being developed under EMSP*
- *Prototype engineering is supported by AMSI (EM)*

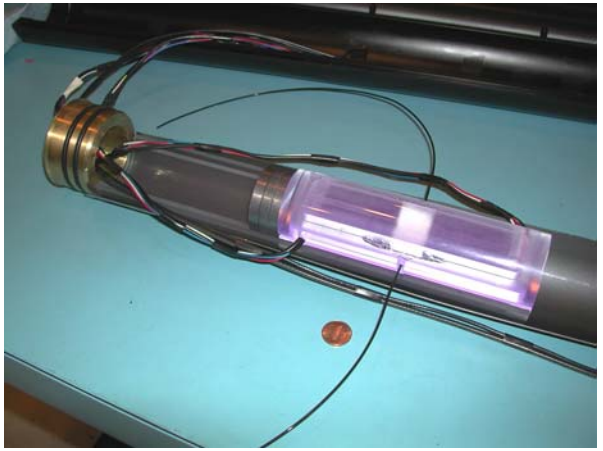


- ***Advanced scintillation detector for field use***
- ***Coincidence-anticoincidense logic***
- ***On-board computer for remote control***
- ***3.5 inches OD compatible with well casing***

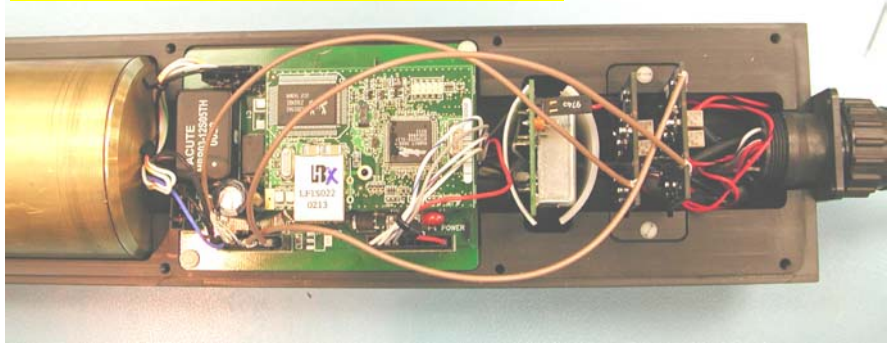
Prototype Sensor Probe Assembly

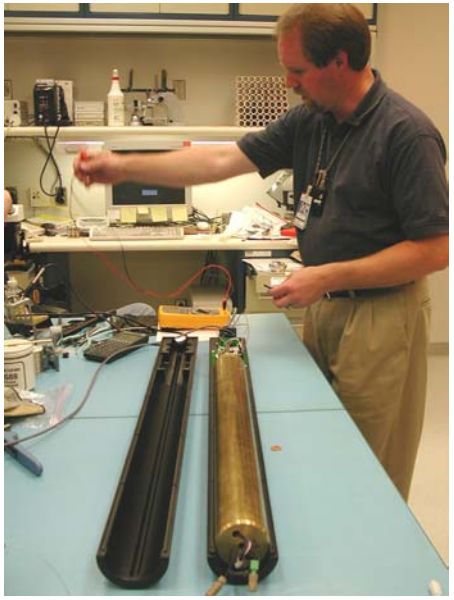
Scintillation detection & anticoincidence shielding





Electronics/ Computer

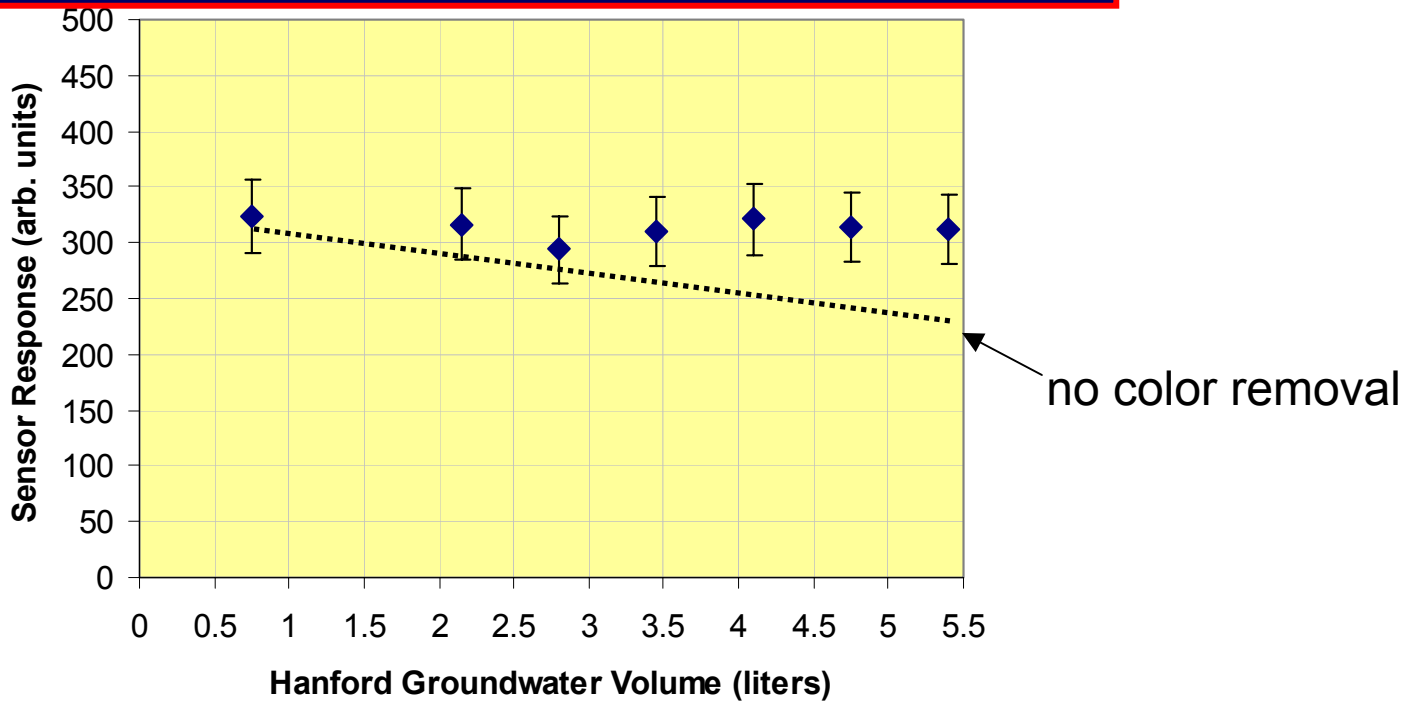




In-situ Sensor Probe Prototype Testing under AMSI Program

- *Initial demonstration in the field*
- *LOD ~100 pCi/L using 10 min count*
- *BKG ~ 2 cpm, 10% detection efficiency*
- *At least 5 fold improvement in FOM*

Long Term Sensor Stability Issue



- sensor fouling & color quench are generic issues
- NOM removal is required for in situ sensing
- use of hydroxylapatite for NOM removal is effective and is being characterized in detail

Reality of Groundwater Sensing

- Novel reagentless equilibration approach is well suited for in-situ sensing and its scientific basis is being developed under EMSP program

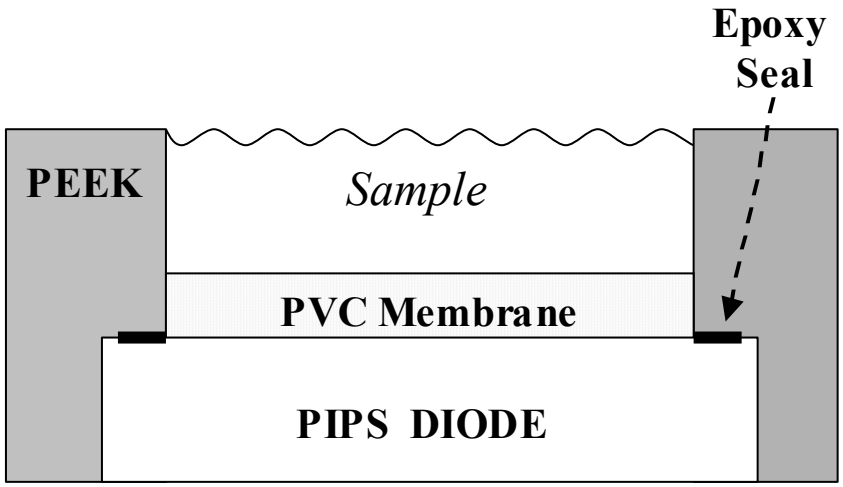
Generic issues affecting sensor design strategy:

- baseline determination
- fouling and long term material stability
- periodic regeneration may be desirable desirable
- periodic calibration is desirable for accurate measurements

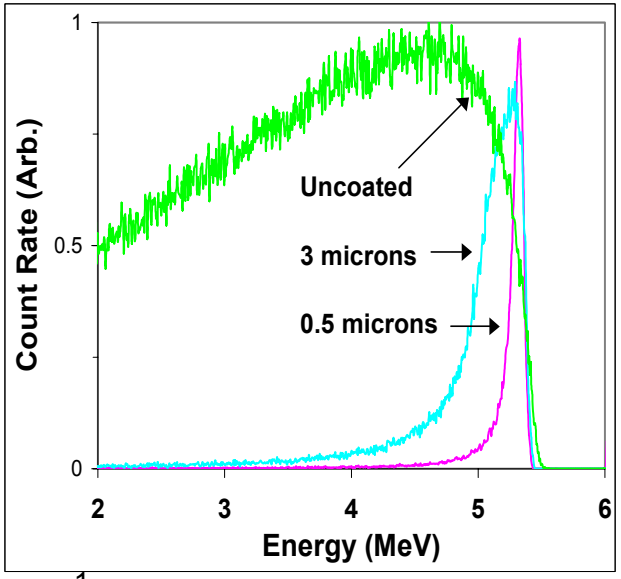
- in-situ sensing vs. in-situ sampling with external sensor placement
- external deployment facilitates maintenance, calibration, addition of sensor probes. Sensor size is less critical.
- external deployment is preferable from the stand point of analytical chemistry

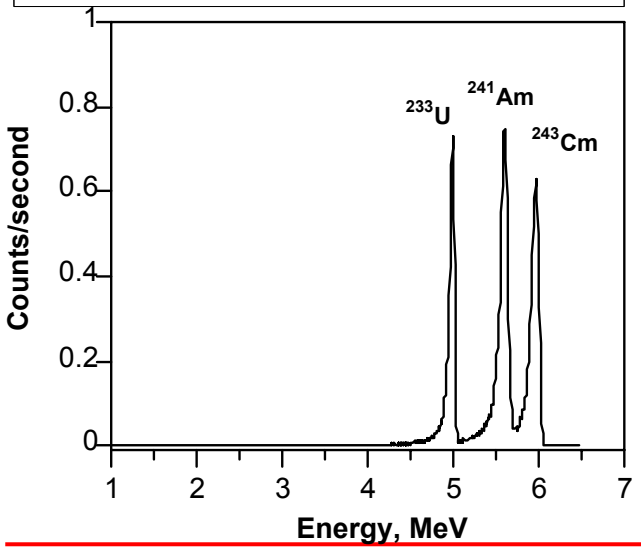
Preconcentrating Diode Sensors for Alpha Emitters

- **Exclude interfering species**
- **Well defined sample**
  - **Geometry**
  - **Matrix**
- **Semi-permeable membrane allows flexible chemistry**

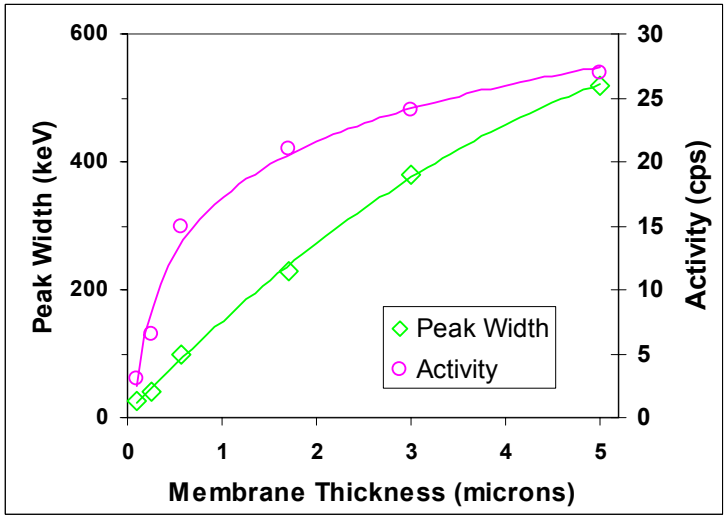


In situ Alpha Spectroscopy Using Chemically Modified Diodes





pH 2 solutions with ^{241}Am.
Membranes are PVC / HDEHP (60/40 wt/wt)



Current Status and Future

- Introduced radionuclide selective sensor principle based on radiometric detection combined with selective separation chemistries
- Demonstrated initial feasibility of reagentless operation based on equilibration sensing
- Developed and tested initial prototype of an in-situ sensor probe
- Developing a general platform for field detection of non-gamma emitters in water

- Continue research and development of radionuclide selective sensor platform
  - separation chemistries
  - groundwater and fouling chemistries
  - alternative sensor geometries (planar and fiber)
  - Sr-90 and U sensing
- Work under AMSI to develop & deploy next generation of an in-situ sensor probe

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