SENSITIVE AND SELECTIVE HEAVY METAL AND RADIONUCLIDE ANALYIS USING THE "LABORATORY-ON-A-CHIP"

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Outline

I. Specific Nature of DOE Problem

II. Site Needs

III. Research Objectives

IV. Background on Laboratory-on-a-Chip

V. Research Results

VI. Research Status

VII. R&D Transition Strategy

Specific Nature of DOE Problem

- **Decontamination and Decommissioning and Subsurface Contamination/Vadose Zone Issues**

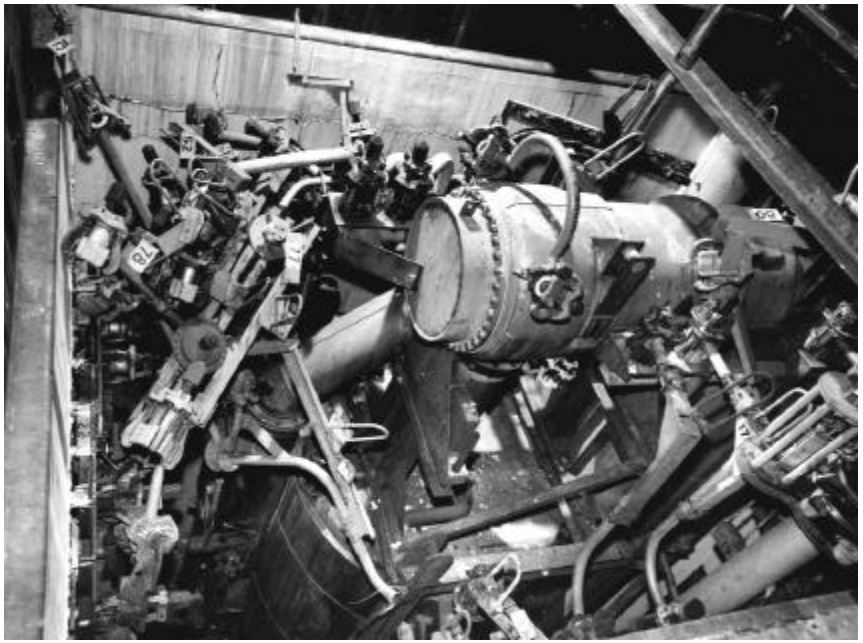
  -Tasked to deactivate and/or decommission nearly 10,000 buildings at 3314 EM release sites.

  -Must decontaminate and dispose of all metal and concrete within these buildings (~180,000 metric tons of scrap metal), all of which may or may not be contaminated with various radionuclides and heavy metals.

  -More than 5700 groundwater plumes from DOE sites have contaminated nearly 600 billion gallons of water and 50 million cubic meters of soil.

  -Current characterization techniques for radionuclides typically require lengthy analysis times at external laboratories, causing costly delays from a health and fiscal standpoint.

Decontamination and Decommissioning Characterization Needs



Demolition, decontamination and decomissioning of debris at a Hanford Site- analytical characterization challenges

(source: www.fetc.doe.gov/dd)

Example Linkages to Site Needs

- **Improved measurement techniques for free release of property and salvageable equipment contaminated with radionuclides, Need ID: RF-DD04**

- **Improved, real-time field screening during excavation for radionuclides with emphasis on the following: uranium, plutonium, strontium-90, and technetium-99**
  Need ID: RL-SS14

- **Long-term monitoring sensor technology**
  Need ID:AL-09-01-27-SC-S

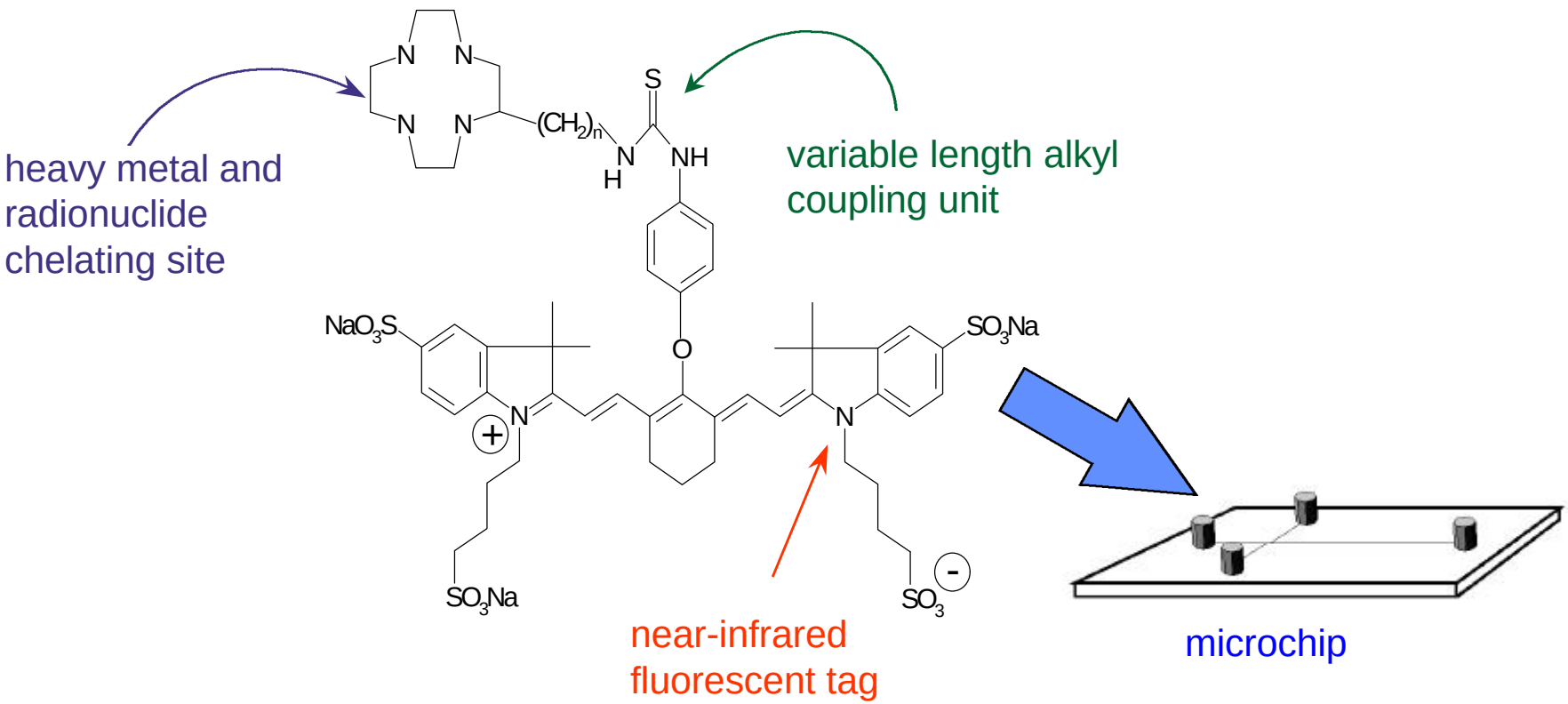
- **Real-time field instumentation for characterization and monitoring soils and groundwater, Need ID: ID-S.1.04**

Transition Benefit of Implementing a Field Portable Laboratory-on-a-Chip for Heavy Metal and Radionuclide Characterization

- real-time segregation of contaminated and non-contaminated scrap metal and concrete materials.
- identification of type and extent of radionuclide and heavy metal contamination apparent on building materials.
- the microchip's compact instrumentation lends itself well to portability, and its affordability will permit sensors to be employed in the field at a multitude of remediation sites.
- more rapid characterization times in the field will help reduce life cycle costs, mortgages, and health risks, while enabling big savings for the DOE.

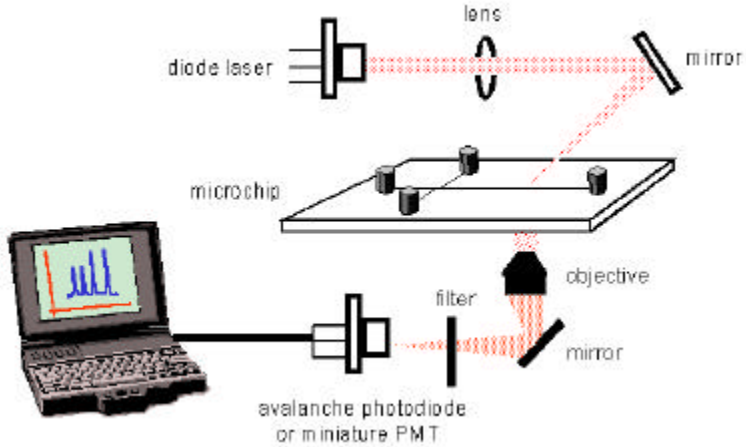
Research Objectives

- To synthetically couple red or near-infrared fluorophores to selective, heavy metal and radionuclide complexation agents.
- Determine optimal length of the alkyl coupling unit- themodynamic formation constants, selectivity coefficients, kinetics.
- To utilize these new fluorophores on a microchip for the selective quantitation of target pollutants of concern at DOE cleanup sites.



Why Use “Laboratory-on-a-Chip”

Instrumentation



Advantages of a Microchip Analysis Platform

-Ability to separate and quantitate heavy metal and radionuclide ions on microchip.

-Portable instrumentation will permit real-time analysis of target metal ions in the field, saving time and money.

-Rapid separation times (sec).

-No mechanical pump required to transport liquid or separate ions.

-Low volume injections (pL) allow very little waste to be generated.

-Inexpensive instrumentation.

-Disposable microchips add to practicality for radionuclide analysis.

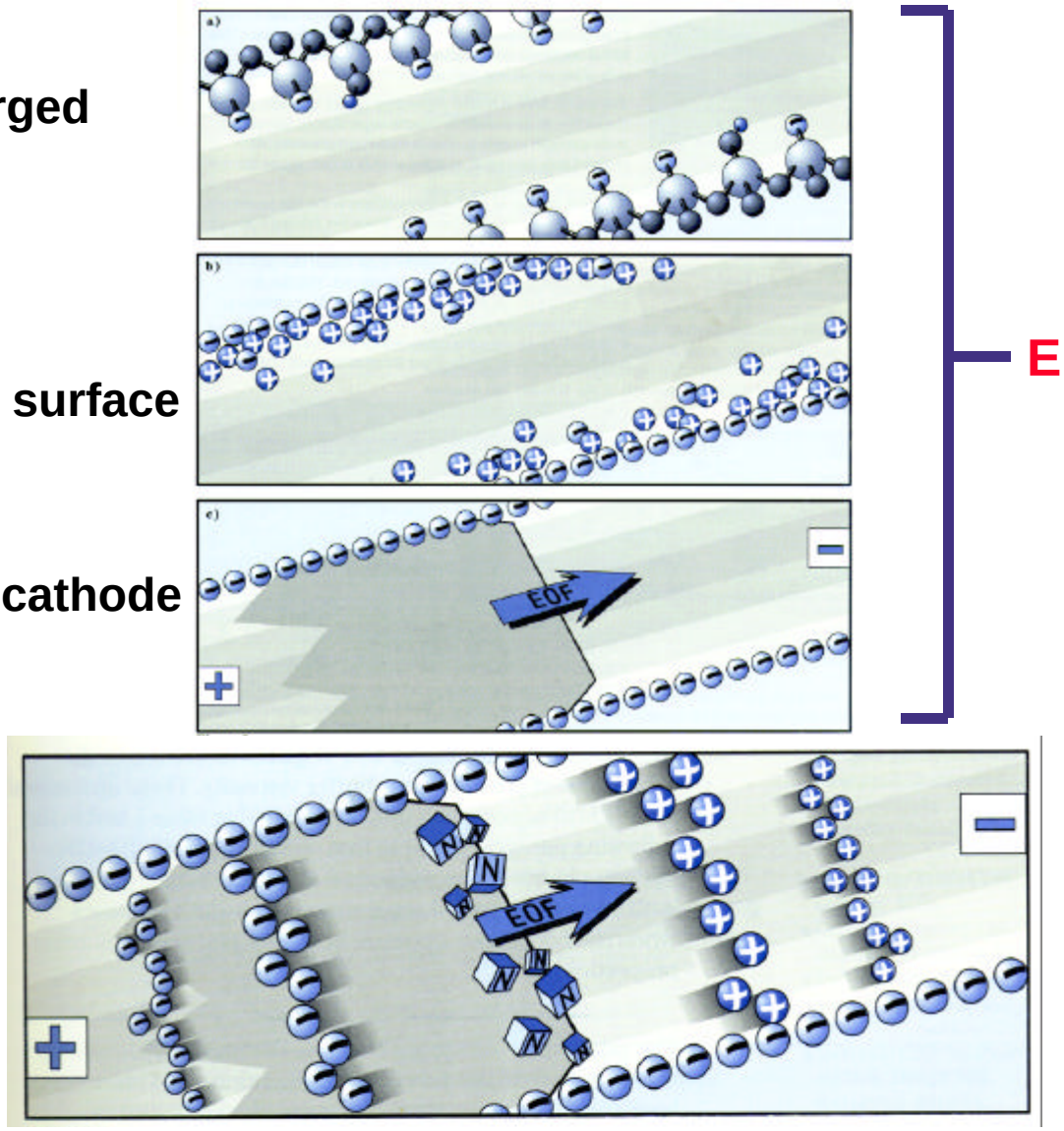
Capillary Zone Electrophoresis

Negatively charged silica suface

Hydrated cations accumulating near surface

Bulk flow toward cathode with flat profile

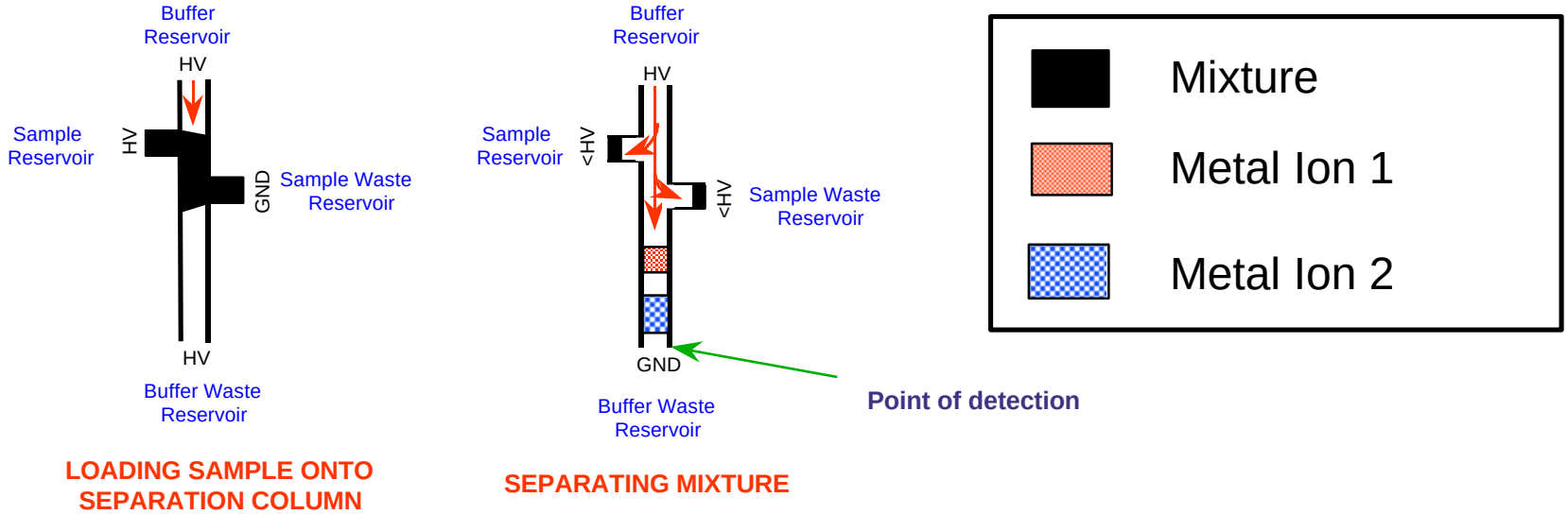
Differential solute migration



Electroosmosis

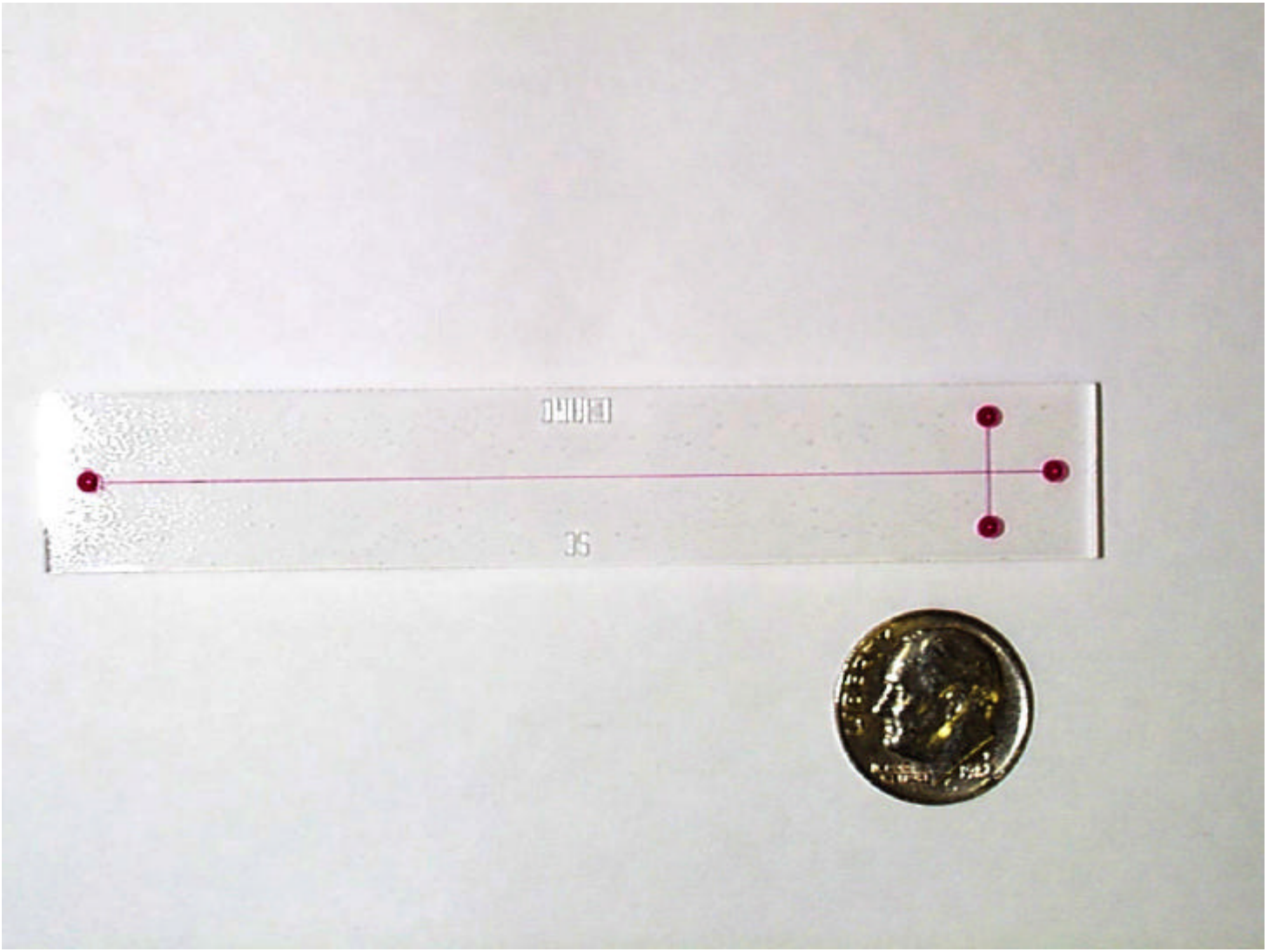
Heiger, D.N., ***High Performance Capillary Electrophoresis- An Introduction***, Hewlett Packard Company: France, **1997**, pp. 17; 19.

Sample Introduction and Separation Procedure

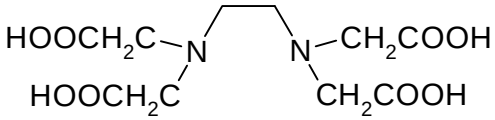


- **Electroosmosis is utilized to transport ions and liquid down microchannels.**
- **Sample loading is achieved through the careful selection of applied voltages to the four reservoirs.**
- **Separations of metal ion complexes are achieved via their differences in migration in an applied field.**

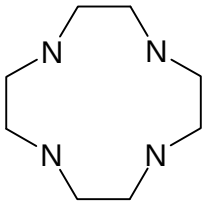
Laboratory-on-a-Chip Layout



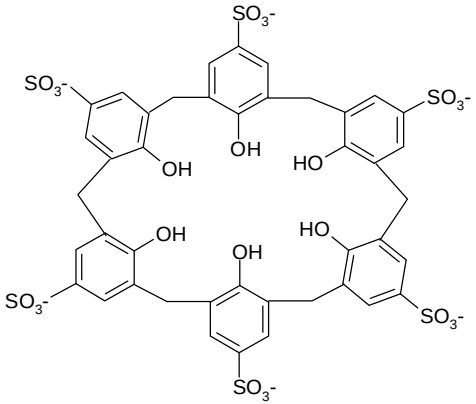
Metal Complexing Ligands of Interest



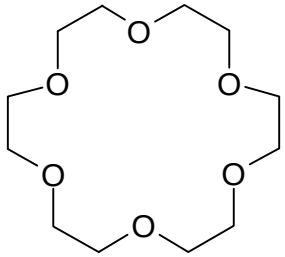
EDTA



Cylcen



Calixarene



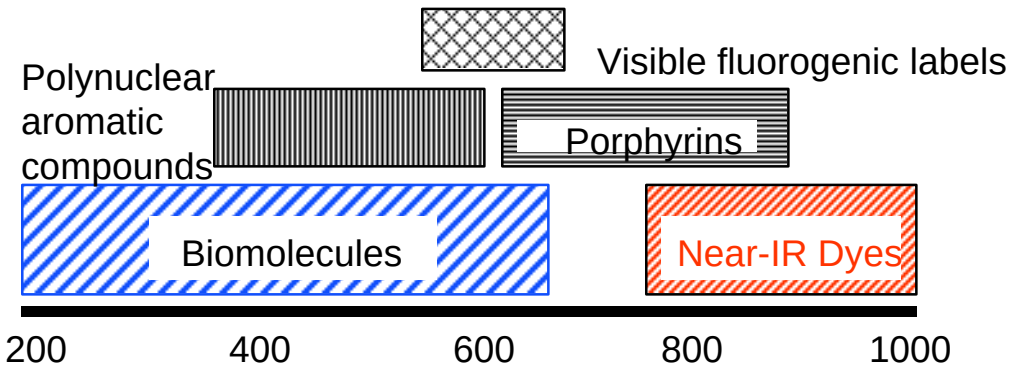
Crown ether

Thermodynamic Stability Constants

Metal	EDTA	Cyclen	Calix-arene	Crown Ether
UO_2^{2+}	25.8		19.2	3.9
Pu^{4+}	25.7			
Cs^{+}				0.96
Sr^{2+}	8.74			2.76
Hg^{2+}	21.5	25.5		2.42
Pb^{2+}	18.1	15.9		4.27

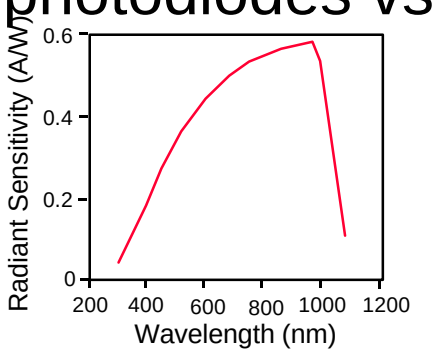
Advantages of Detection in the Red to Near-IR

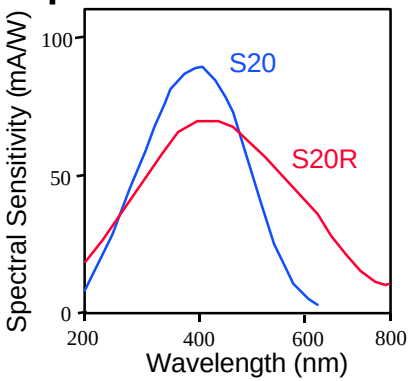
- Near infrared region is red-shifted away from the blue fluorescence of impurities



G. Patonay and M.D. Antoine, Anal. Chem., 63, 321A (1991).

- Silicon photodiodes vs. Photomultiplier Tubes

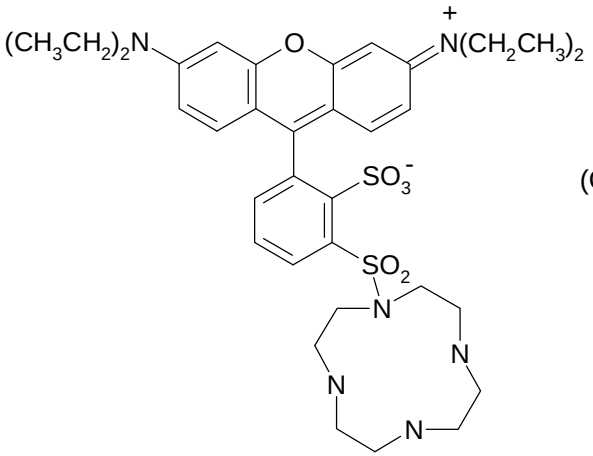




Photodiode lasers vs. Ar ion laser

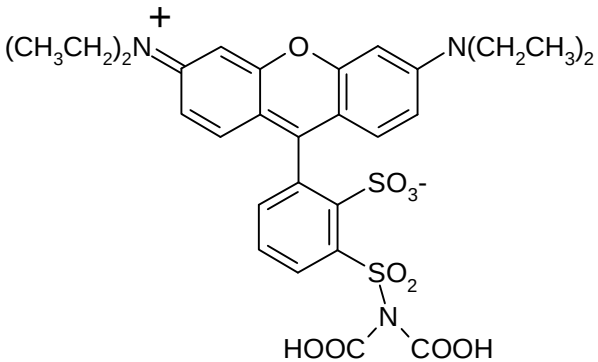
- lower cost
- smaller size

Molecules Synthesized and Purified to Date



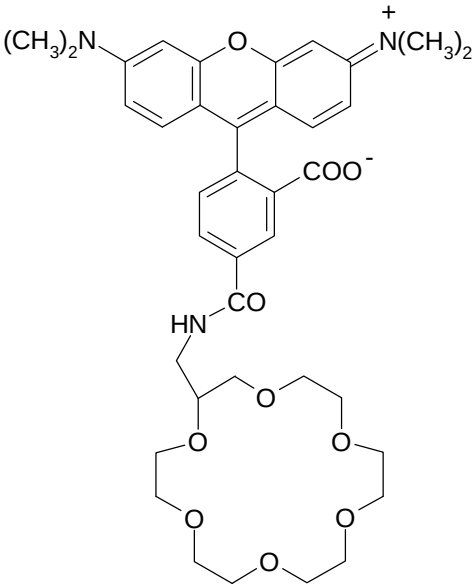
Rhodamine-cyclen

Target Ions: Hg^{2+}, Pb^{2+}



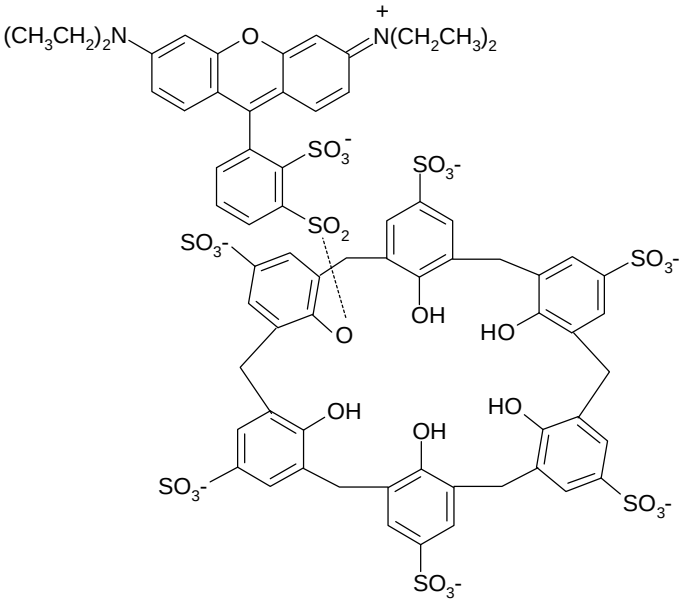
Rhodamine-IDA

Target Ions: Hg^{2+}, Pb^{2+}



Rhodamine-18-Crown-6

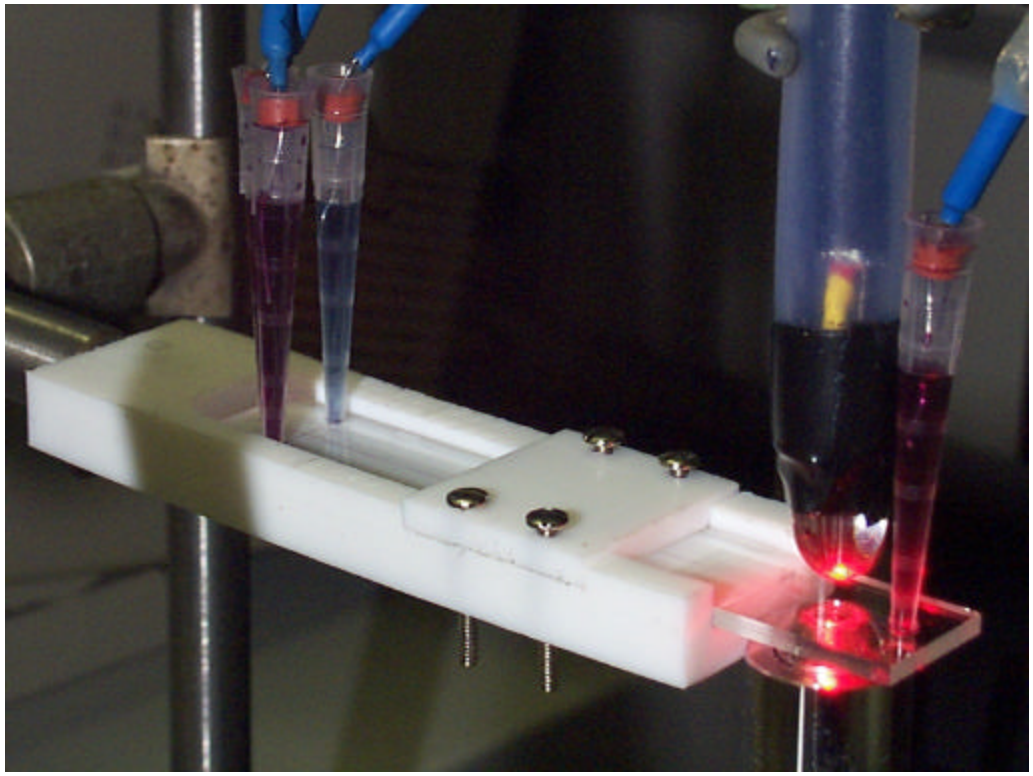
Target Ions: Cs^{+}, Sr^{2+}

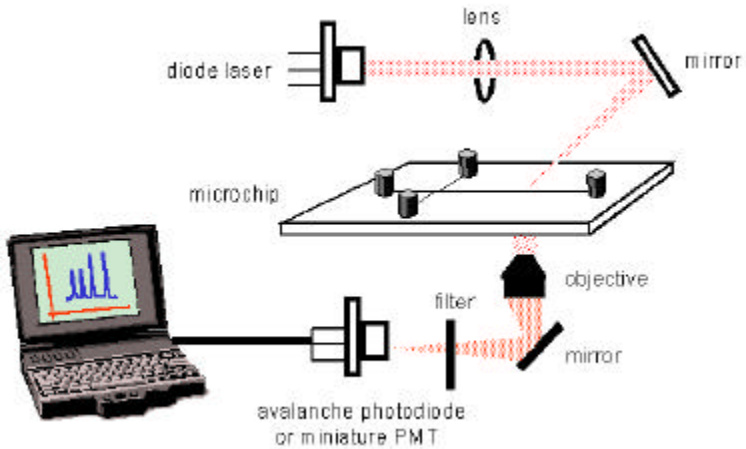


Rhodamine-Calix[6]arene

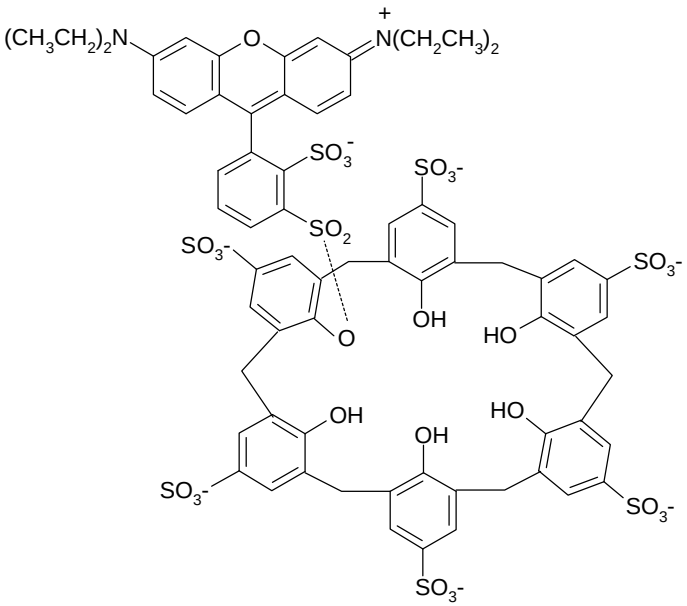
Target Ion: UO_2^{2+}

Microchip Instrumentation

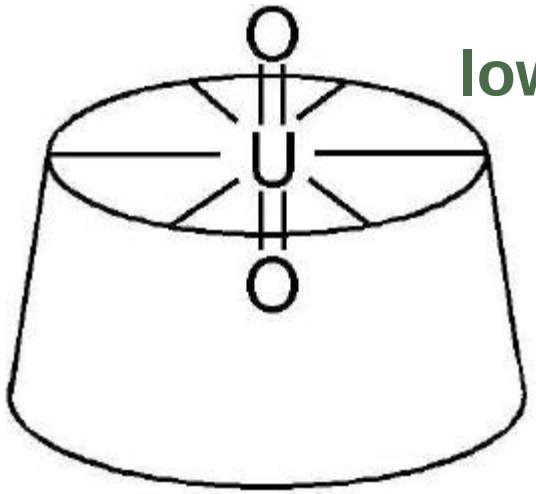




Geometric Selectivity of Calixarenes for Uranium- "Super-Uranophiles"



Rhodamine-calix[6]arene

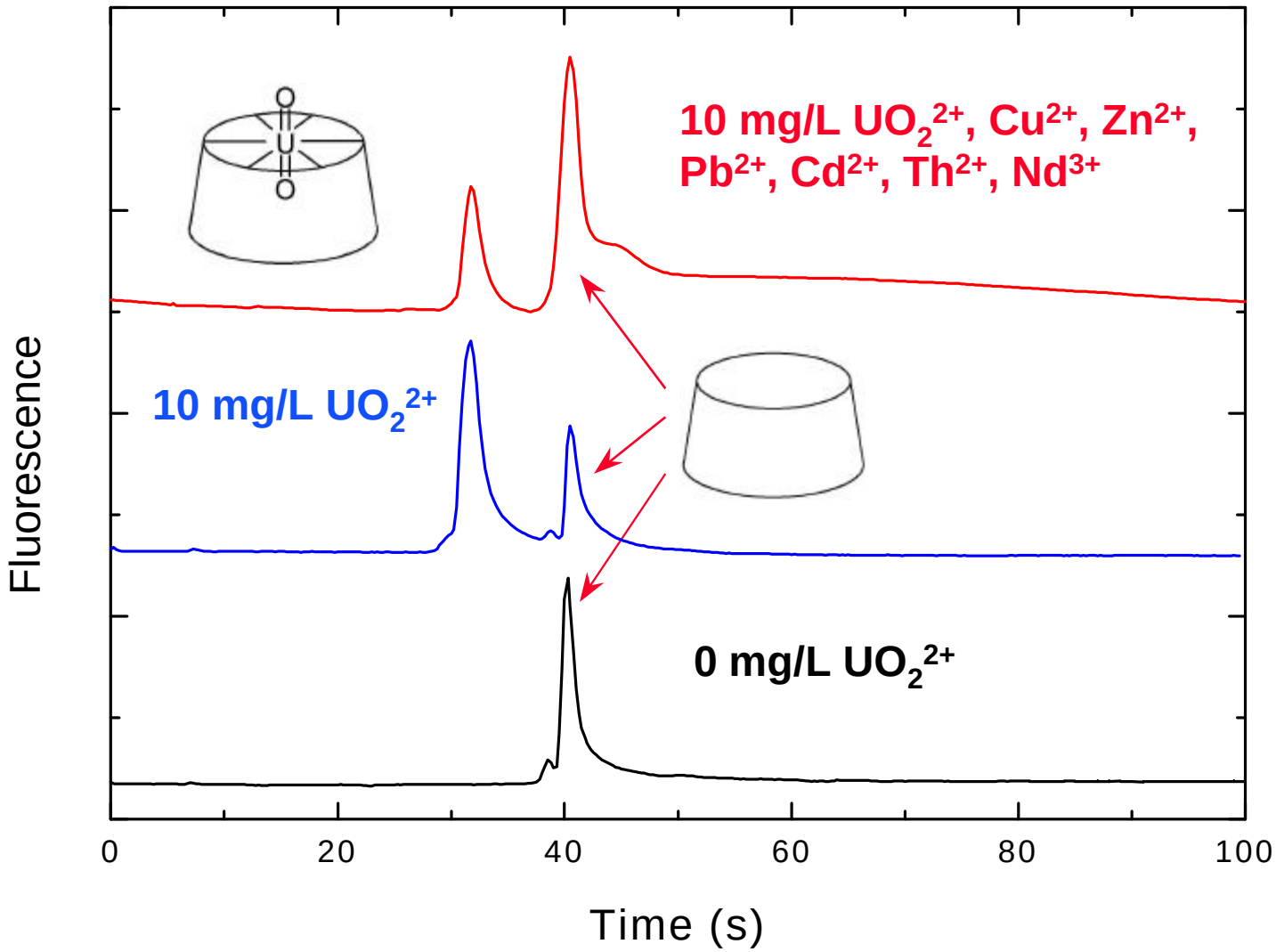


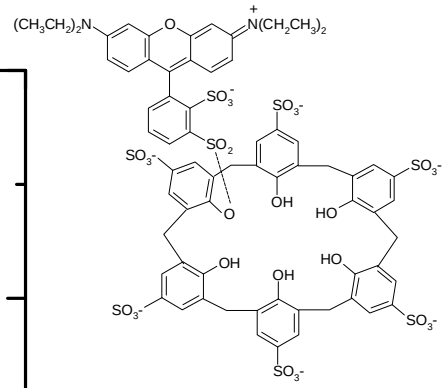
lower rim

upper rim

- Calixarenes form a barrel-shaped geometry which is well-suited for uranyl ion metal complexation.
- The UO_2^{2+} ion likely adopts a pseudoplanar penta- or hexa-coordinate structure.
- The selectivity factors of calix[6]arene for UO_2^{2+} over other metal ions are greater than 10^{12}, making this ligand a "super-uranophile."

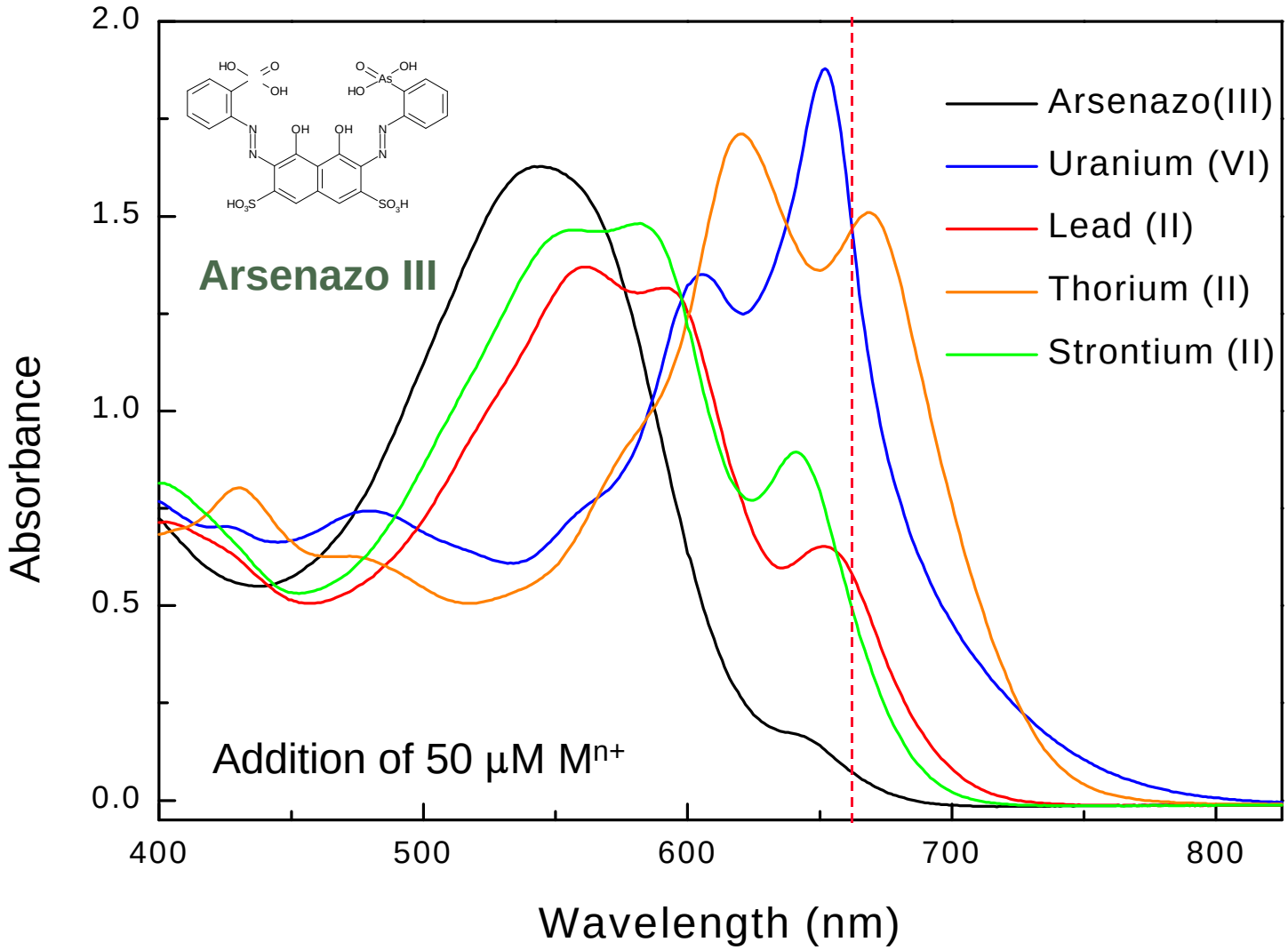
Microchip Separation of Uranium Using Rhodamine-Calix[6]arene and Fluorescence Detection





Rhodamine-Calix[6]arene

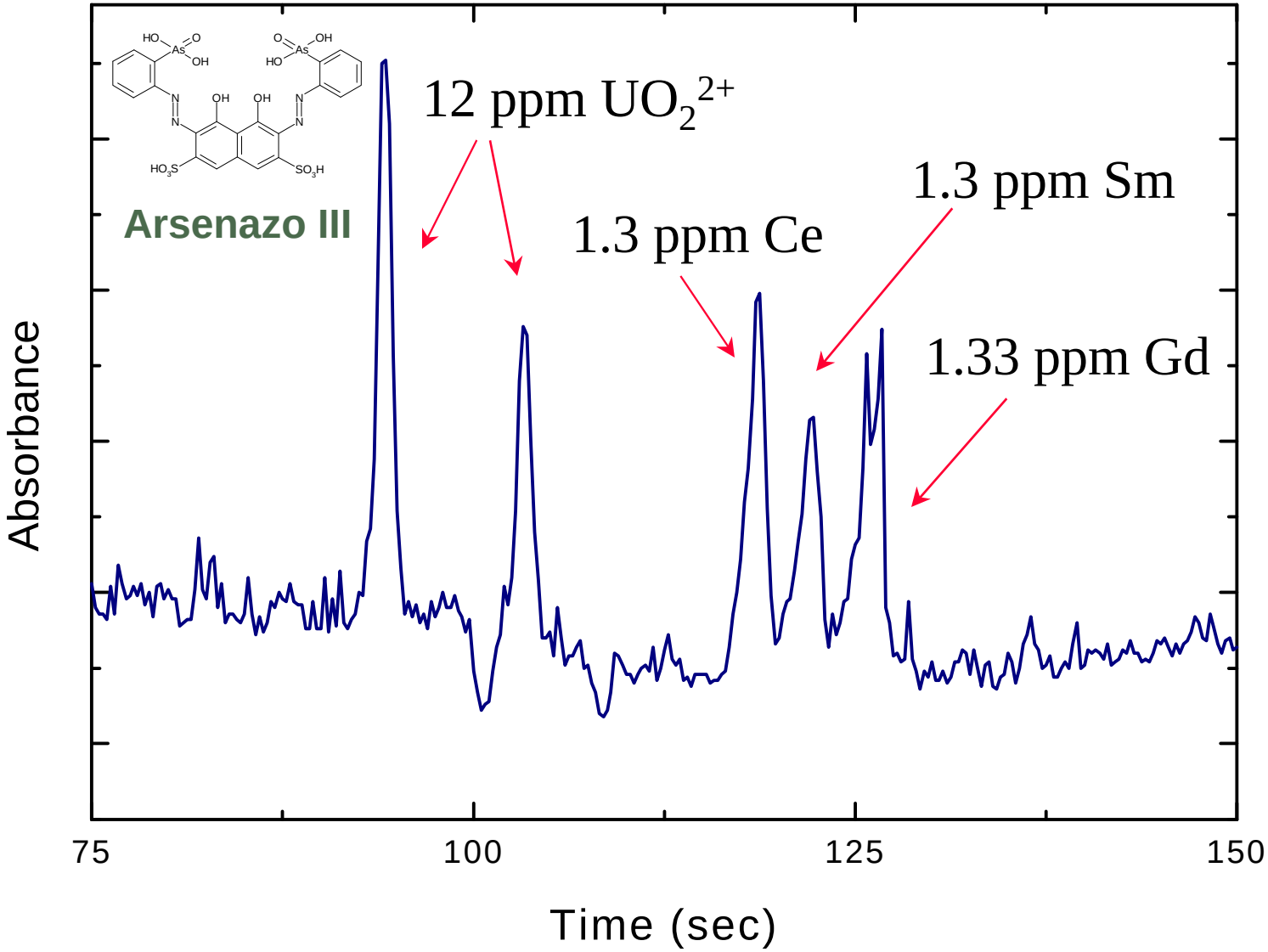
Arsenazo III: Metallochromic Dye Colorimetrically Bound to Uranium (VI) and other Metal Ions



Arsenazo III: Survey of Colorimetric Sensitivity at 660 nm

Metal Ion	($LM^{-1}cm^{-1}$)	Detection Limit
Gd>Eu>Nd>Ce>La>Tb>Sm>Pr>Dy>Ho>Er>U>Tm>Y>Th>Yb>Lu	$1.9\text{-}4.2 \times 10^{4}$	$1.9 - 3.1 \times 10^{-7}$ M or 23-54 ppb
Ca>Pb>Sr>Ba	$6.72\text{-}10.7 \times 10^{3}$	$5.6 - 8.9 \times 10^{-7}$ M or 23-122 ppb
Cu, Fe, Mg, Ni, Cs, Nb, Rb, Cr, V, Mn, Co, Ta, Mo, Ru, Hg, Zn, Cd, Se, Ga, Al	0.0-400	$>1.5 \times 10^{-5}$ M or >1 ppm

Microchip Separation of Uranium and Several Lanthanides using Arsenazo III Absorbance Detection



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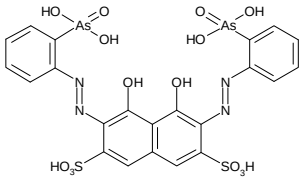
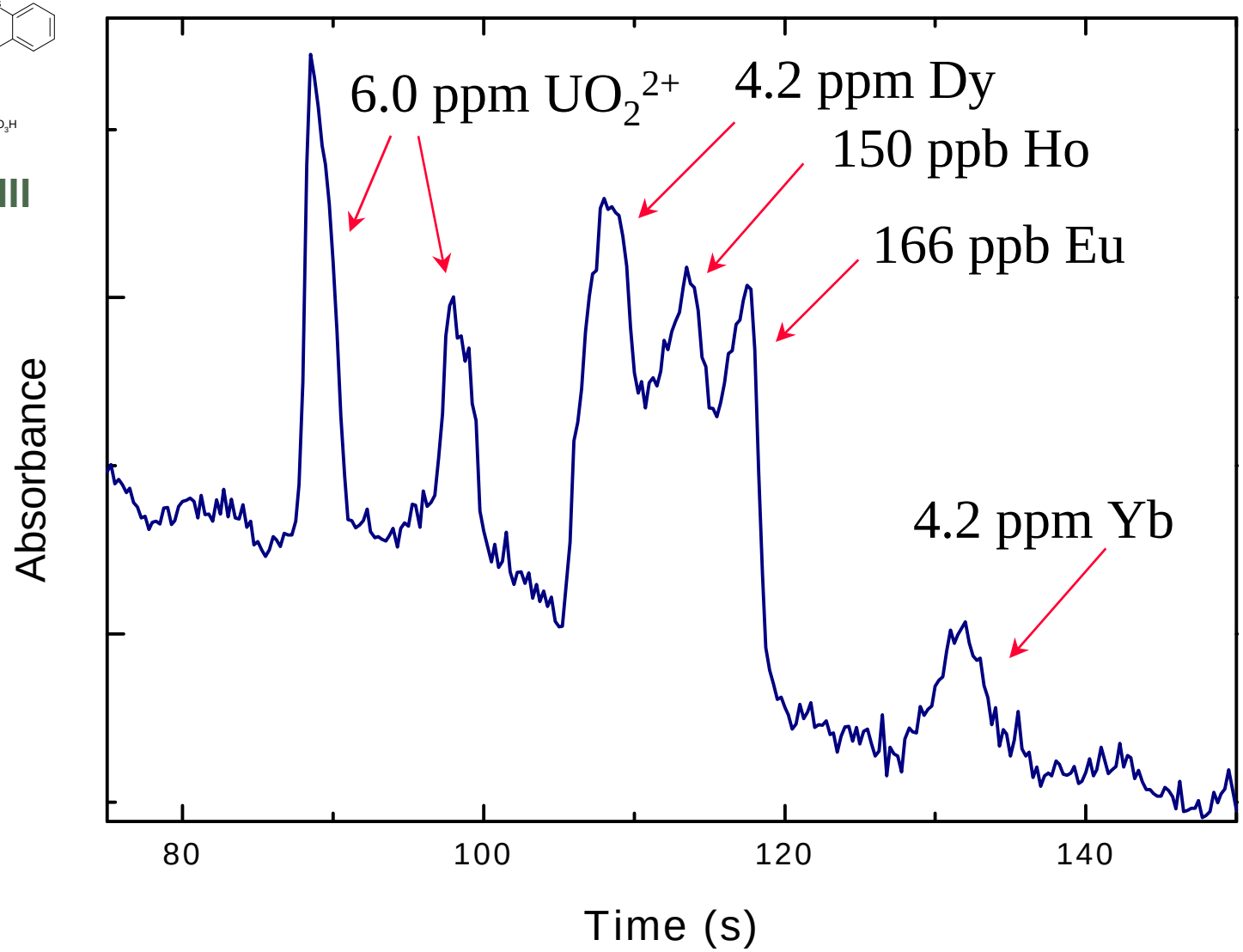


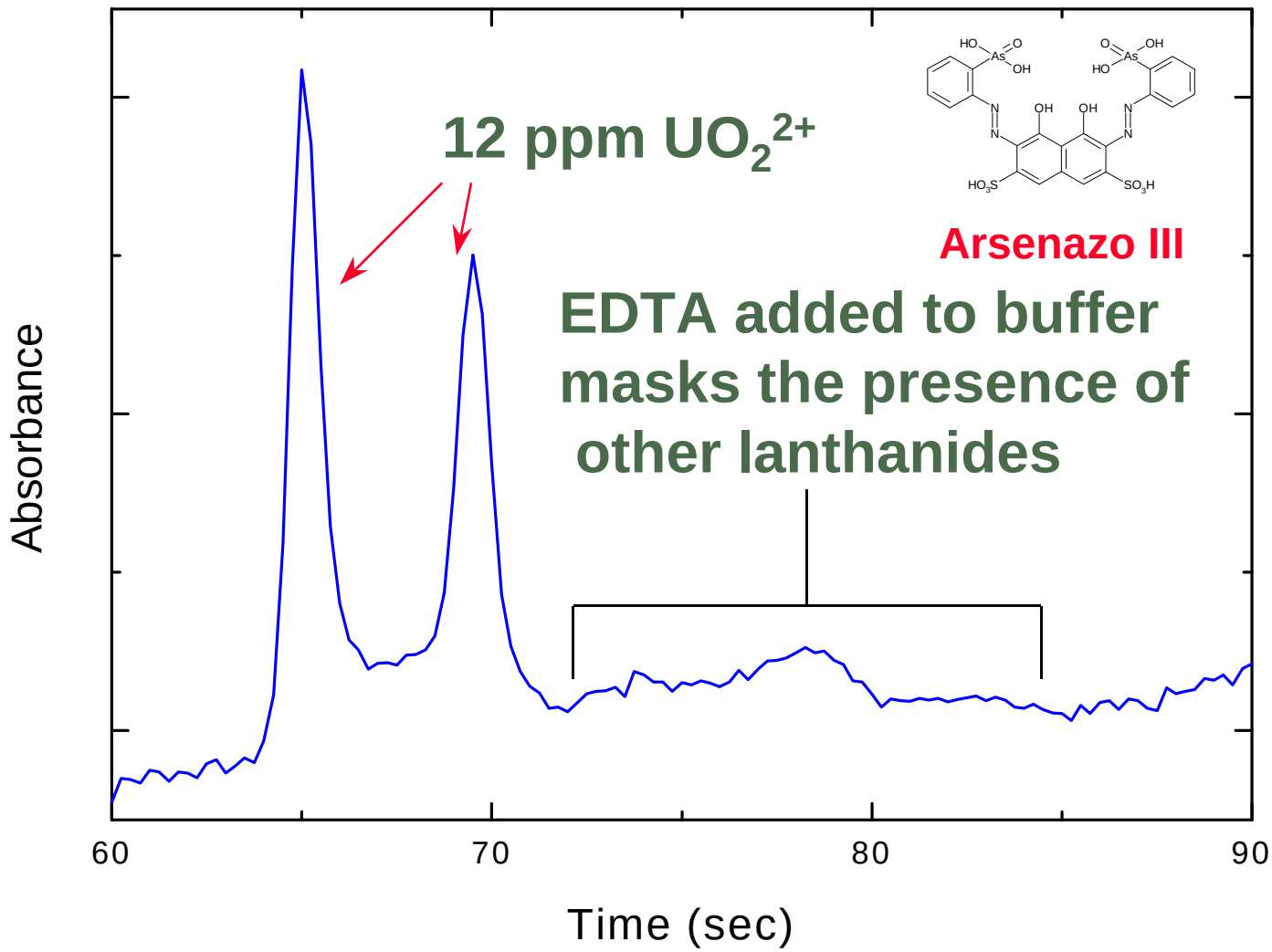
Arsenazo III



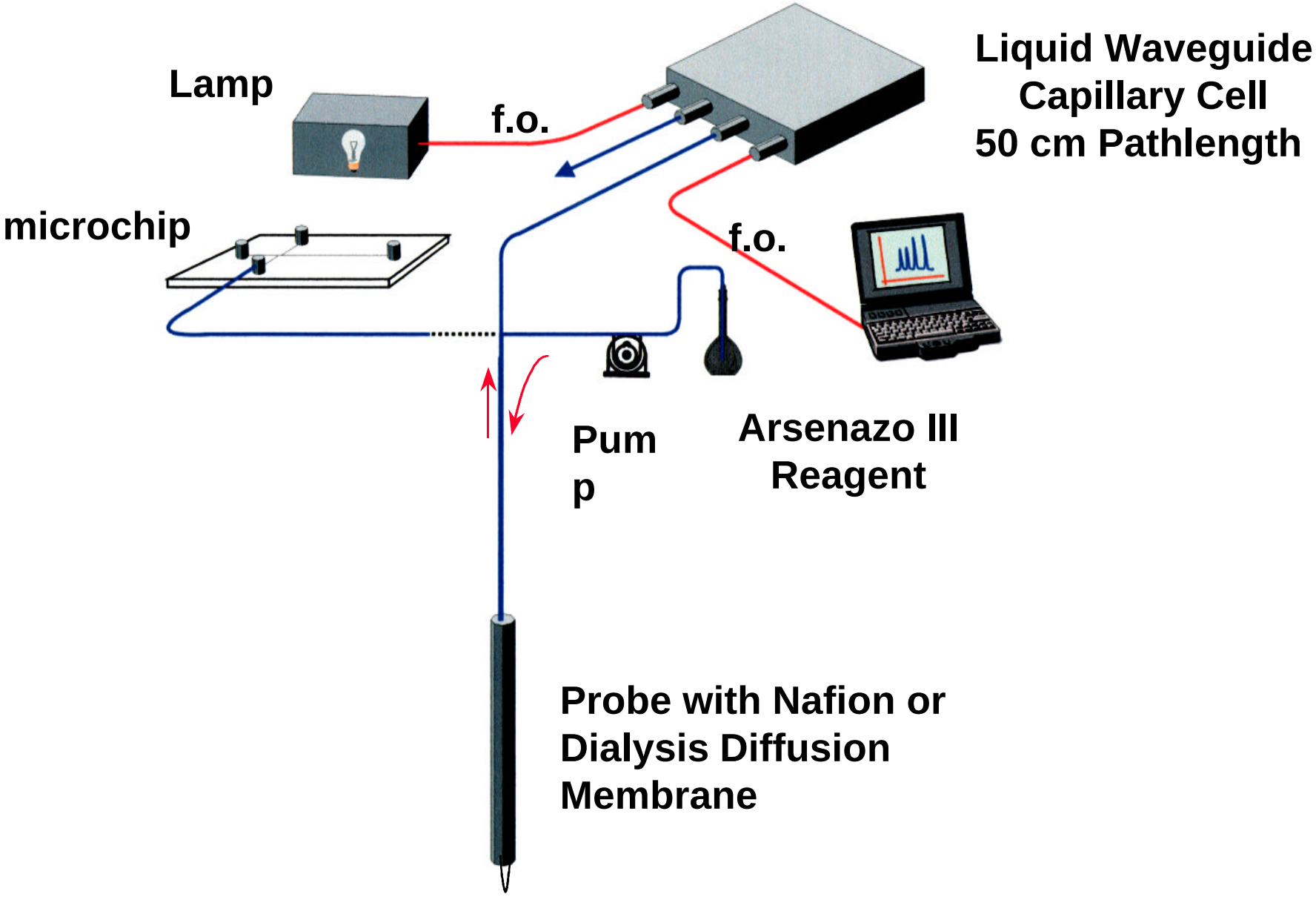
Separation and Detection Capabilities of Microchip Using Arsenazo III

Metal Ion	t_R (s)	t_R (s)	FWHM (s)	Detection Limit μM	Detection Limit ppb
U	90.0	0.0	2.0	1.3	305
U	100.3	10.3	2.0	-----	---
Ce	110.3	20.3	2.3	0.69	96
Pr	112.3	22.3	3.5	0.45	63
Yb	113.3	23.3	4.8	-----	---
La	115.3	25.3	2.5	0.41	57
Ho	117.0	27.0			
Y	120.5	30.5	3.5	0.26	23
Eu	121.5	31.5			
Er	123.0	33.0	5.0	0.14	23
Tm	130.5	40.5	4.8	0.14	23
Yb	135.0	45.0	5.8	9.8	1692

Selective Microchip Detection of Uranium using an EDTA Masking Agent and Arsenazo III Absorbance Detection



Membrane Diffusion Probe for Remote Sampling Linked to Microchip or Fiber Optic



Research Status

- **Synthesis and purification of four, new fluorophore-tagged metal complexation ligands- cyclen, crown ether, iminodiacetic acid, and calix[6]arene.**

- **Demonstrated separation and quantitation of uranium on a microchip in less than a minute.**

- **Highly selective ligands or matrix components have been established for the detection of uranium.**

- **Both absorbance and fluorescence modes of detection have been demonstrated as sensitive modes of operation (ppb level detection limits) for detecting uranium on a microchip.**

R&D Transition Strategy

- **Selective, Portable Uranium Sensor**
  -fiber optic dipping probe- in-situ, remote sensing
  -microchip with red LED and photodiode detector

- **Transition from breadboard to field deployable instrument**

- **Work more closely with field managers to enable field studies**
  Dick Meservey, INEEL
  Brad Frazee, INEEL