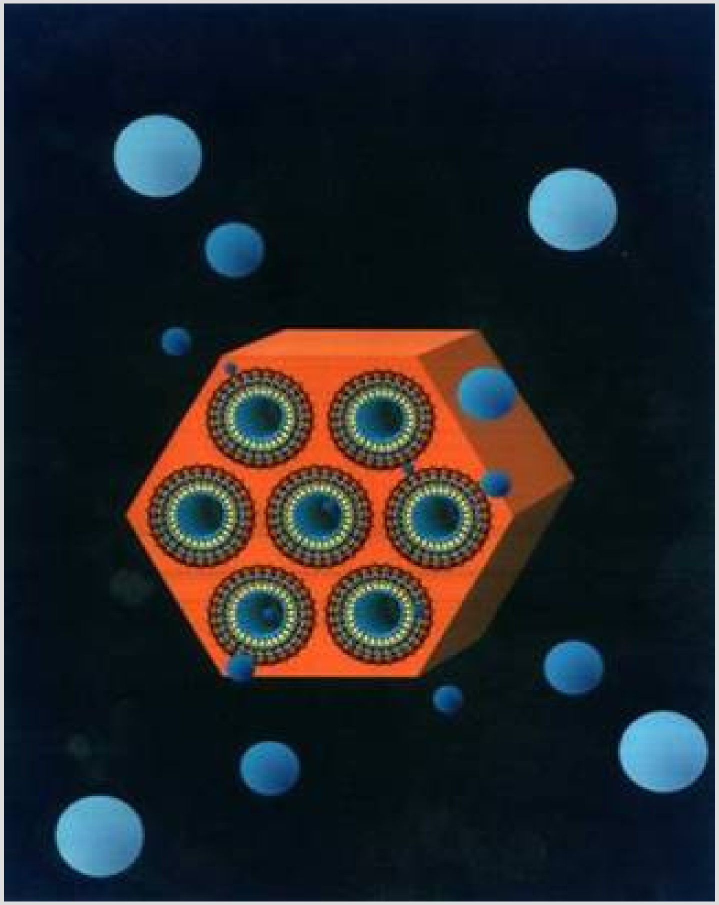
Nanomaterials for Enhanced Environmental Measurements



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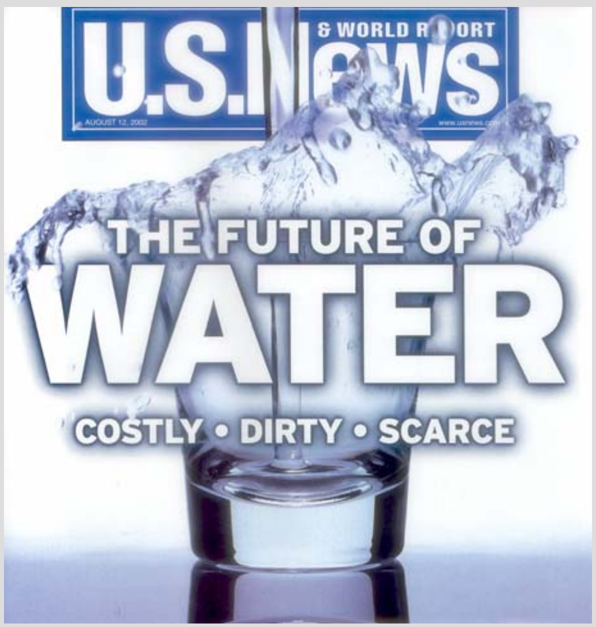
Richland Washington

Do environmental scientist, materials experts, and analytical scientists have any thing to say to each another?

Yes—especially if they speak of small things.
(very very small things)

Information is the Pivot Point

- Environmental Remediation and Monitoring
- Homeland Security
- Improved Medical Measurements
- Industrial Efficiency
- Consumer/Personal



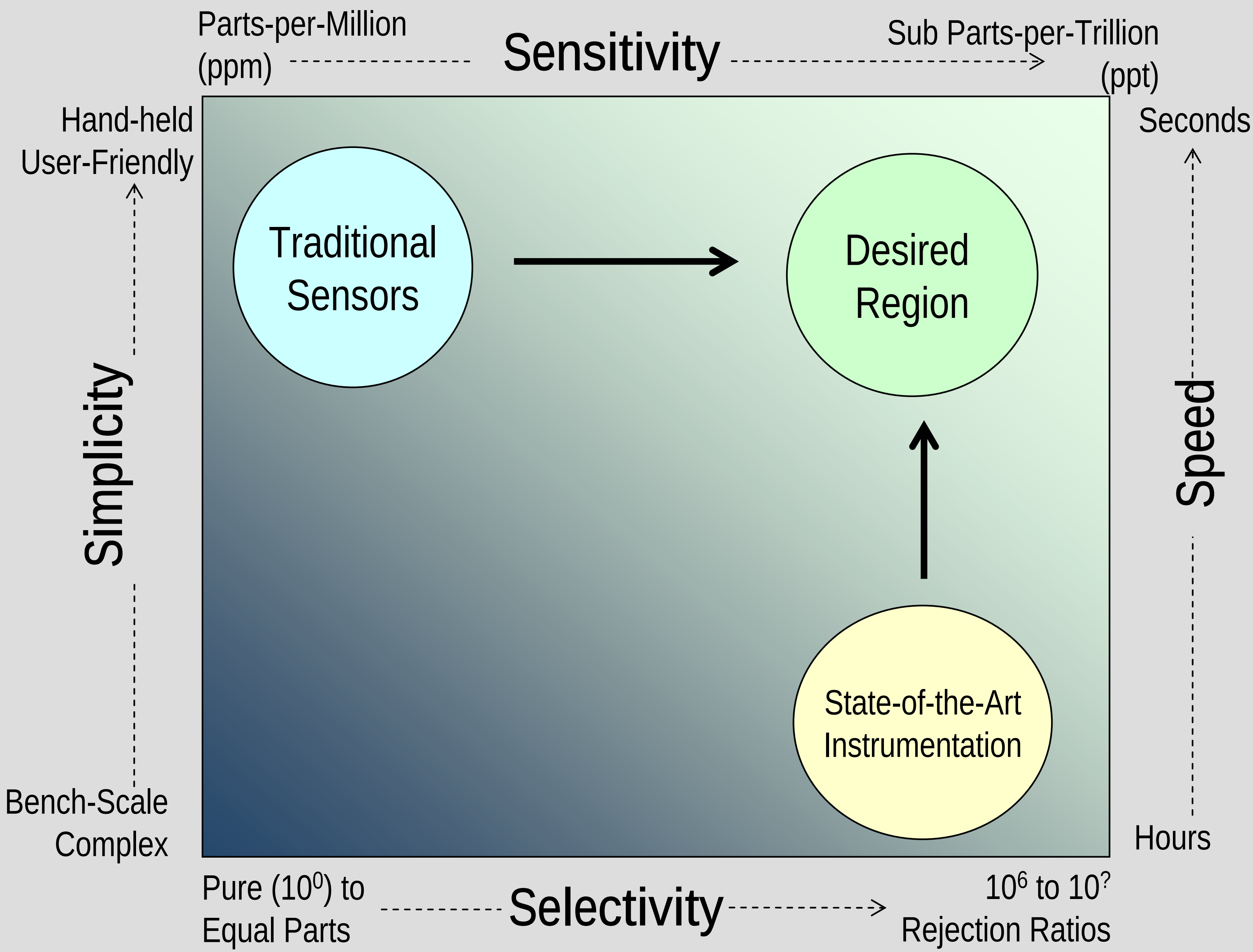
"Technology gives power to the skeptical public" ***--USA Today headline***

The "Macro" Perspective on Measurement Challenges

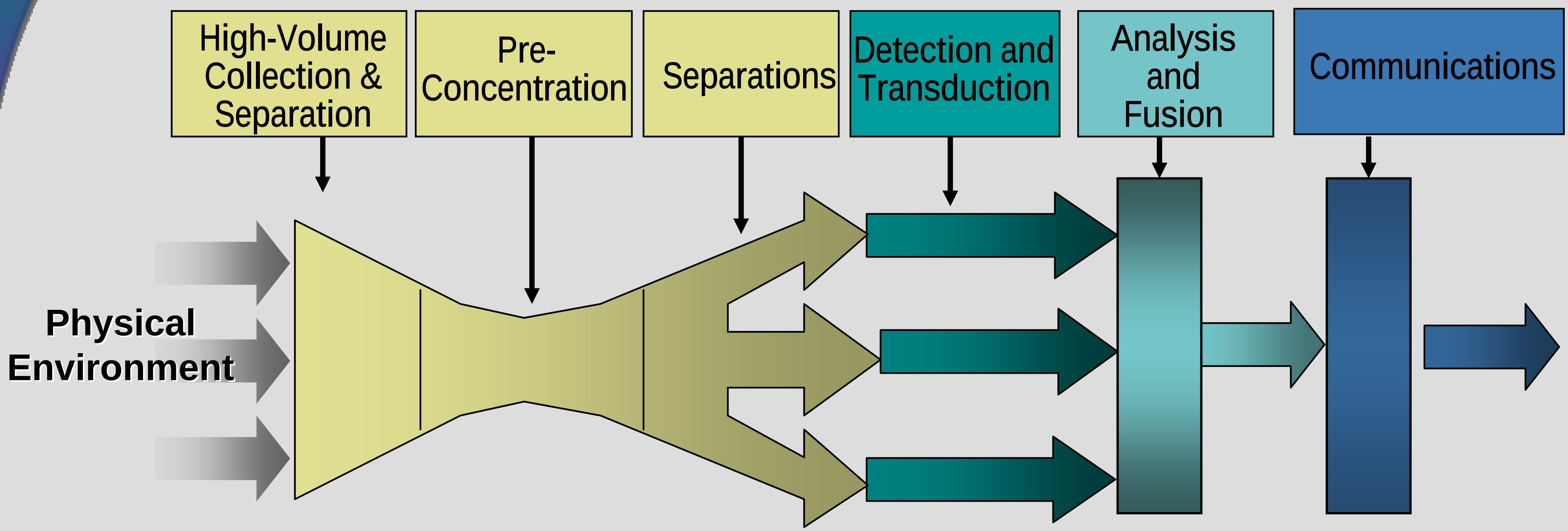
- part-per-trillion sensitivity (a needle-in-a haystack)
  - Assuming nothing else looks like a needle (i.e. low background)
  - If a needle is 116 mg then the haystack is
    - *20' wide x 15' high x ~11.2 miles long*

- 10^6 error rate (1 in a million)
  - Assuming 2 car trips/day then
    - 1 accident/mistake/ticket/wrong turn every ~1370 years

The Analytical Challenge



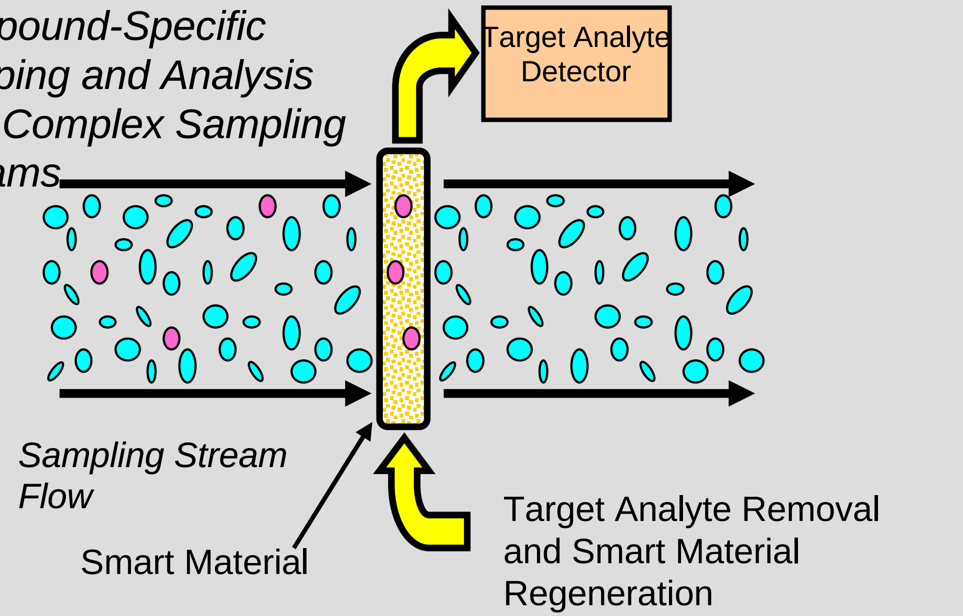
The Integrated Analytical Approach
"Remedial Tricorder Prototyping"



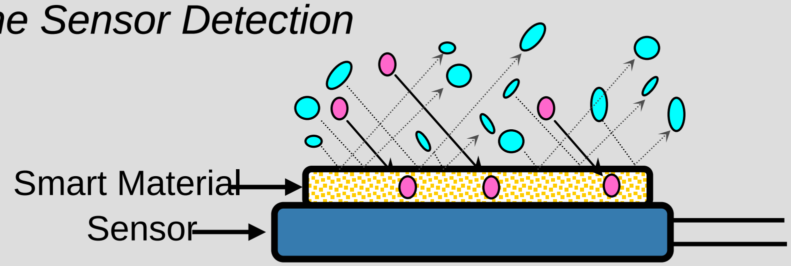
Advanced Materials (can) Enable Improved Sampling and Assay

- "Smart" materials enable
  - Collection
    - Preconcentration
    - Selective Separation
  - Detection
    - Selective transduction
    - Multivector information
      - Spectral/electronic
      - Spatial
  - Miniaturization
- "Orthogonal" Enhancement
  - Sensitivity, Selectivity
  - Simplicity, Speed

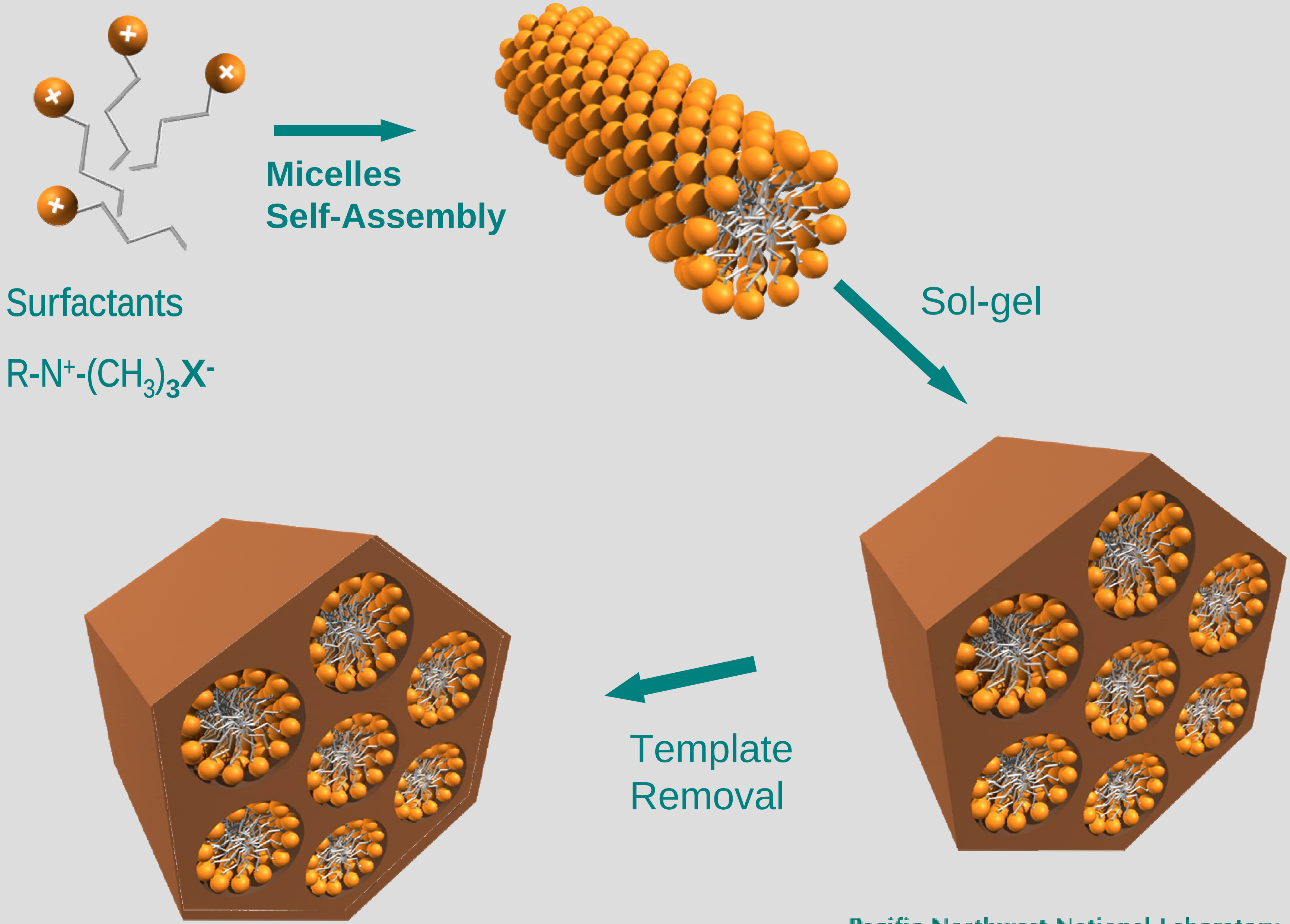
Compound-Specific Trapping and Analysis from Complex Sampling Streams



Compound-Specific Trapping and Real-Time Sensor Detection



Practical Example
Nanoporous Ceramic Substrates



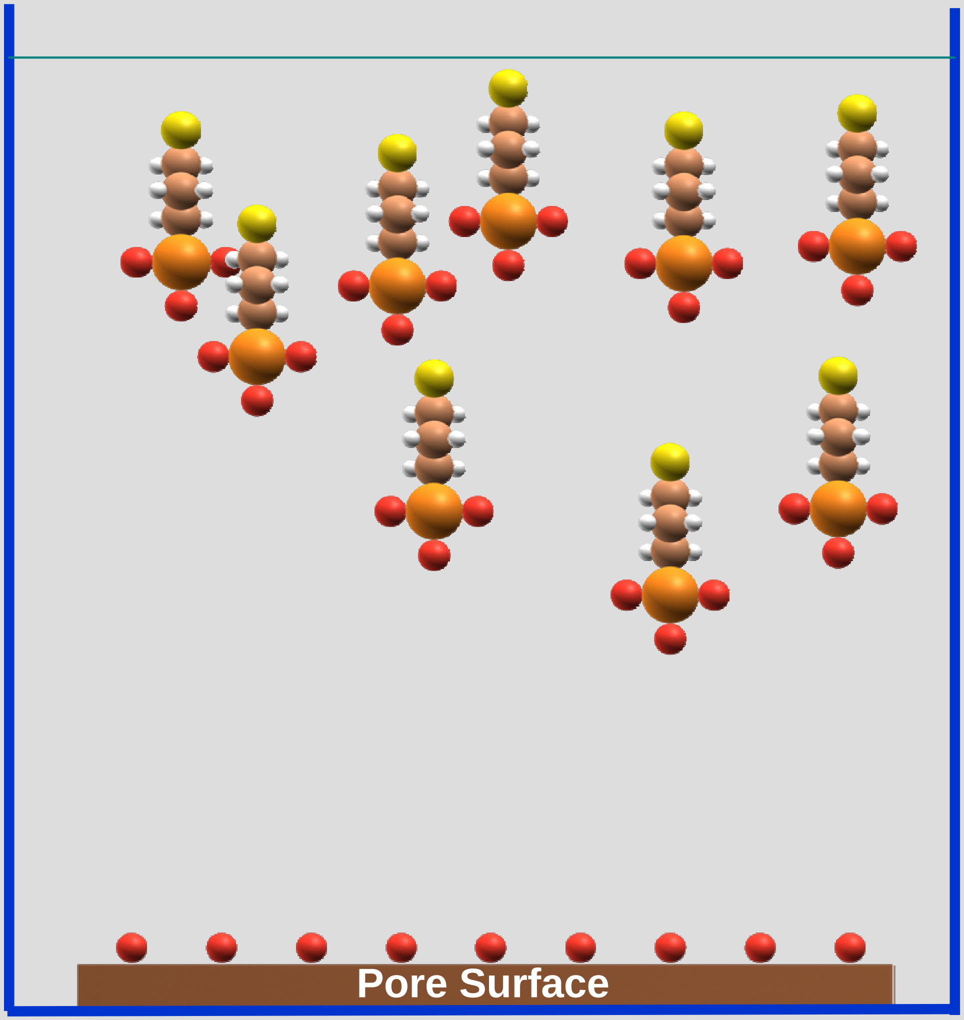
So the way that we get the surface chemistry we need is….

Molecular self-assembly

Self-assembly driven by van der Waals interactions between chains, as well as the interaction between the headgroup and the surface.

Monolayer Advantages

- Well-established silanation chemistry
- Stabilized surface
- High ligand density
- Easily tunable chemistry

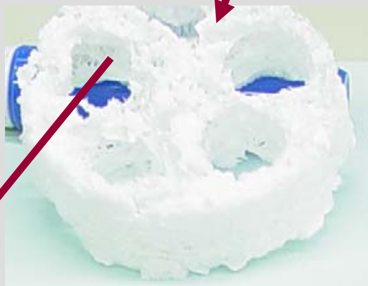


"Designing Surface Chemistry in Mesoporous Silica" in "Adsorption on Silica Surfaces"; pp. 665-687, Marcel-Dekker, **2000**.

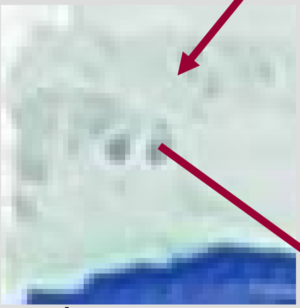
Structures—3D Macroforms

- Three Dimensional Cellulose Templated Mesoporous Silica Macrostructures
  - Various filter papers
    - Thin planar, Thick planar, Tubular
  - Natural filters structures.
  - Carbon foams
    - Structural stability a function of foam
  - Corrugated cardboard
  - Cellulose sponge
  - Polyurethane foam

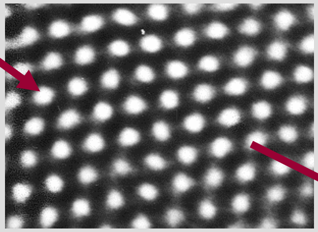
Loofa Bath Sponge



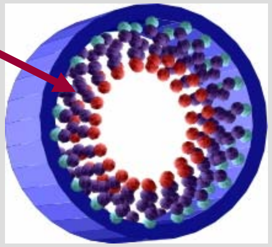
Mesoporous Silica Loofa (calcined)



Fibrous Substructure of Mesoporous Silica Loofa (calcined)



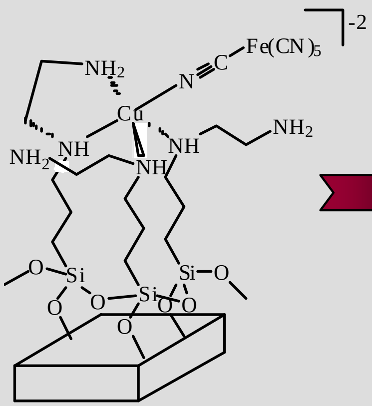
Mesoporous Silica Structure



Monolayer Modified Nanopore

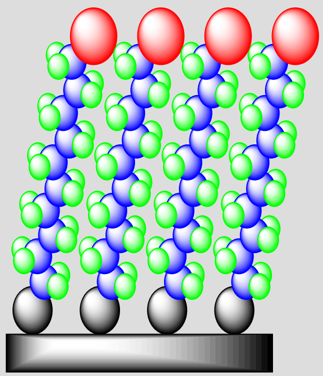
Mesoporous Silica Sensing and Separation
Tailored Structure from the Molecular to Macroscale

Complexation Site ⇨



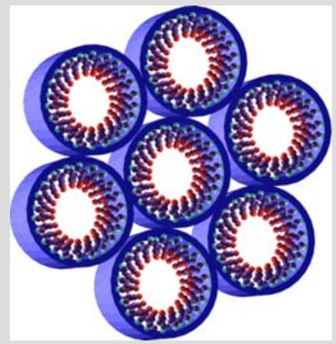
High affinity ligands
•Inorganic
•Organic
•Nuclear
•Biological

Surface Monolayer ⇨



~1-6 binding sites/ nm^2
•High capacity
•Chemically selective
•Shape selective
•Signal Transduction

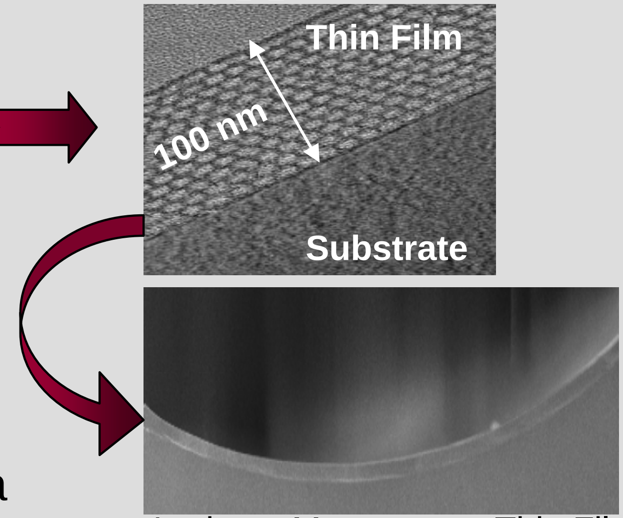
Ordered Porosity ⇨



High surface area
(500-1000 m^2/g)
- Sensitivity
- Capacity

Nondendritic porosity
- rapid response
- size selective

Macroscopic Support

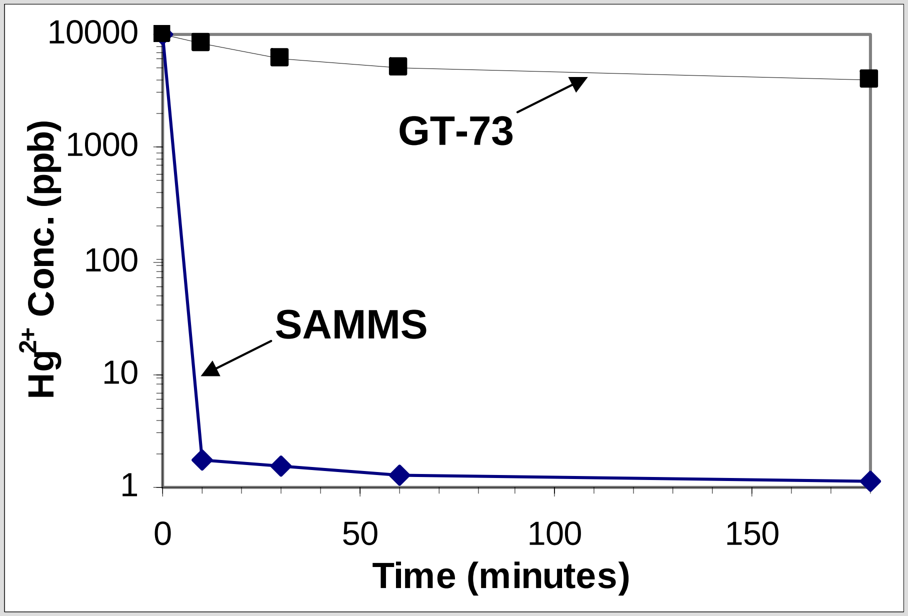


1 micron Mesoporous Thin Film within a 75 micron Capillary

•Capillaries
•Planar Thin films
•Particles
•Monoliths

Comparative Performance of SAMMS*
(Thiol material for capture of heavy metals)

- Thiols SAMMS
  - High surface area (500-1000 m^2/g)
  - High site density (4-6 thiol groups/nm2)
  - High affinity (K_d's > 10^6)
  - Open porosity (fast response)
- High Capacity (over 50% wt/wt)
  - Uptake linear over very large range
    - Volume
    - Concentration
  - 10^6 selective preconcentration demonstrated
- Efficiency depends upon
  - Capture/material configuration
  - Binding affinity
  - Sample matrix
  - pH
- Material can be directly assayed



* **Self Assembled Monolayers on Mesoporous Supports**

Separation Science and Technology, 1999, *34*, 2329-2345.
Adv. Mater. 1998, *10*, 161-165.
ES&T, submitted

X-ray Fluorescence

- Fast, portable
- Simultaneous multimetal assay
- Limited sensitivity (ppm)
- Matrix sensitive

Heavy Metal Capture with SAMMS Direct XRF analysis

Experiment

- 2 ppb metals in Columbia River water
- 15 mg microcolumn
- Direct XRF assay of SAMMS Sorbent

Metal	SAMMS Monolayer Composition	EPA DWS[a] (ppb)	SAMMS Conc. (ppm) 500 mL	XRF LOD[b] (ppm) 60 sec	SAMMS Conc. (ppm) 100 mL	XRF LOD[b] (ppm) 60 min
Hg	Thiol	2	46.7	15	9.3	1.9
Pb	Thiol	15	35	12	7	1.5
Ag	Thiol	100	40.7	30	8.1	3.9
Cd	Thiol	5	46.7	35	9.3	4.5
Cr	Cu(II) EDA	100	44.5	115	8.9	14.8
As	Cu(II) EDA	100	31	10	6.2	1.3

a) EPA Drinking water standards (DWS), from www.epa.gov/safewater/mcl.html
b) limit of detection (LOD) for field portable XRF system,
40mCi ^{109}Cd source (14mCi ^{241}Am source for Cd)

Conclusions

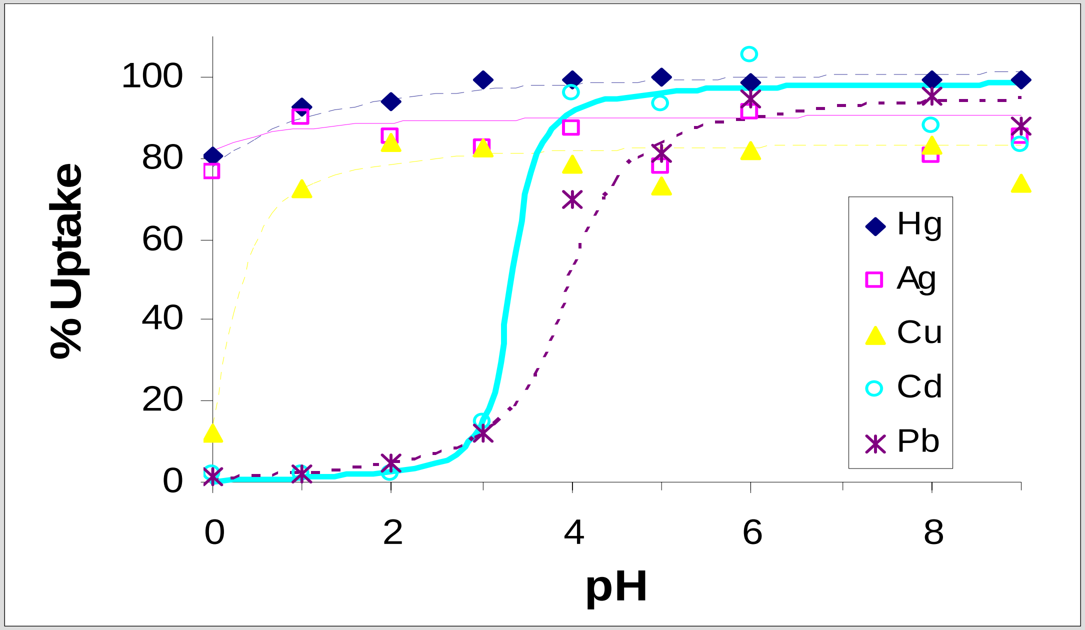
- 60 min assay on 100mL sufficient for DWS (except Cr)
- 60 sec assay on 500mL sufficient for DWS (except Cr)
- 60 min assay on 500mL for Cr DWS (can be improved)
- XRF Instrumentation Improving
- Collection configuration limiting factor

Environmental Matrix Effects

Heavy Metal Uptake with Thiol SAMMS

Matrix	pH	% Uptake				
		Hg	Cu	Pb	Ag	Cd
DI Water, Acidified	1.9	99	64	0	104	0
Ground Water	8.2	77	37	49	30	94
Ground Water, Acidified	1.9	101	68	0	90	1
River Water	8.5	68	35	42	56	69
Sea Water	7.2	98	52	75	103	72

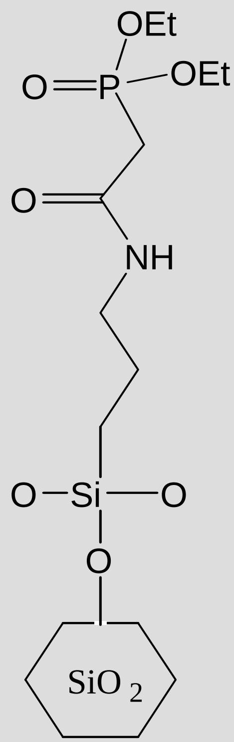
200ml of water spiked with 1 ppm of heavy metals, 1 mL/min, 15 mg of SAMMS in microcolumn. Acidification with HNO_3, Replicate analysis +/- 5%.

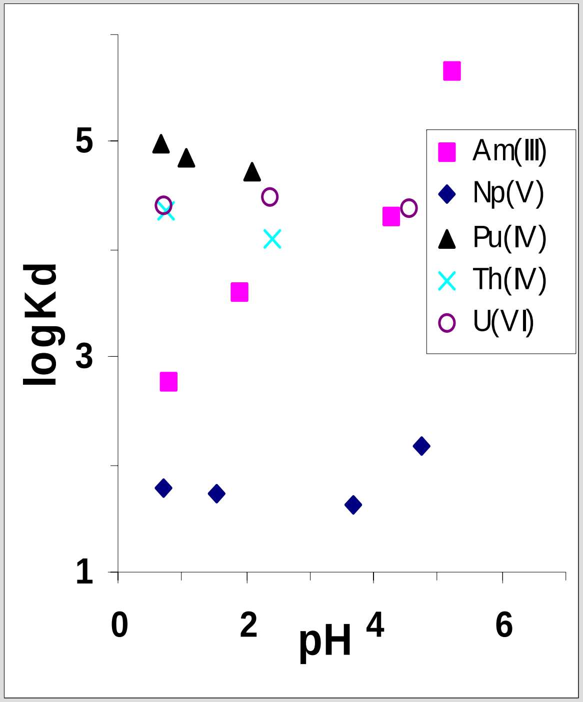


Radionuclide Preconcentration and Measurement with SAMMS

- Need a sorbent with high selectivity AND affinity
  - Preconcentration 10^4- 10^7
- Need material to support sampling AND assay
  - Particles
  - Thin films
- Actinide Select Silane
  - Variants of CMPO† ligands
  - Molecule has both desired protic and synergistic ligands in a geometry suitable for chelation
  - Other systems available/in development

† Carbamoylphosphonate oxide





Ac-Phos* SAMMS

* acetamide diethylphosphonate moiety with 3-aminopropylsilane linkage

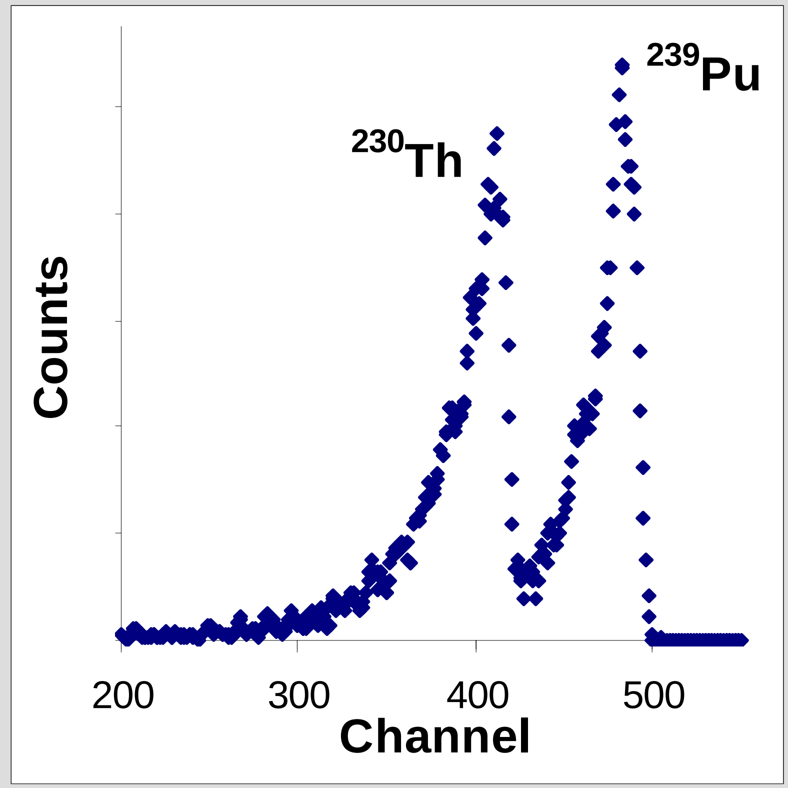
Chemical Communications, 2002, 1374-1375.

Measurement of Radionuclides

Simple Field Assay

Detector ~ 20% Efficiency
SAMMS ~ 10000X preconcentration.
2000X increase in sensitivity
Selectivity provided by sorbent

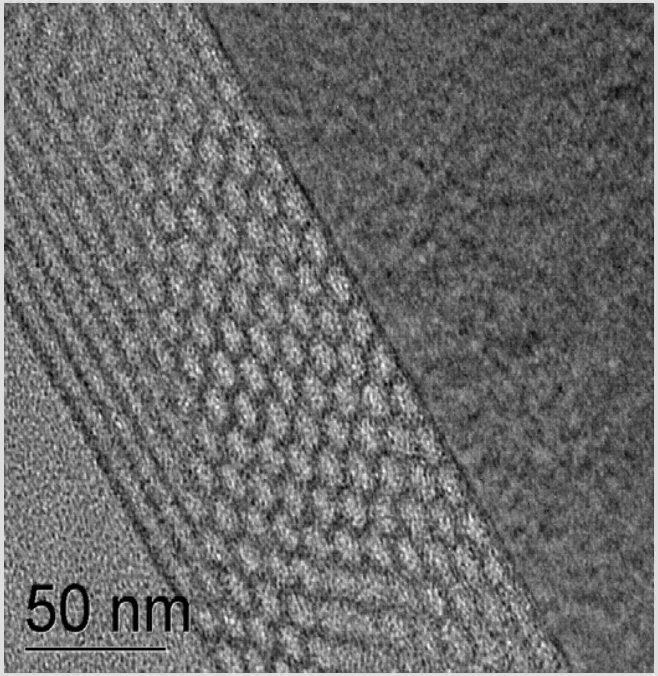
Laboratory Assay



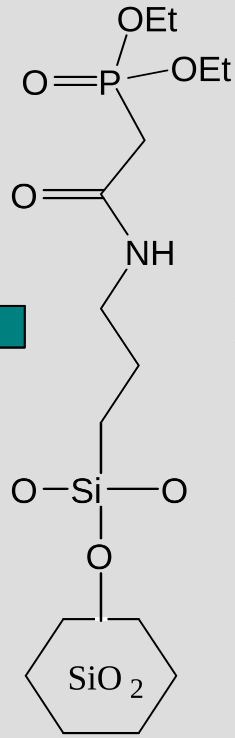
Alpha energy spectrum of Ac-Phos SAMMS after exposure to a solution of ^{230}Th and ^{239}Pu.

SAMMS Thin Films

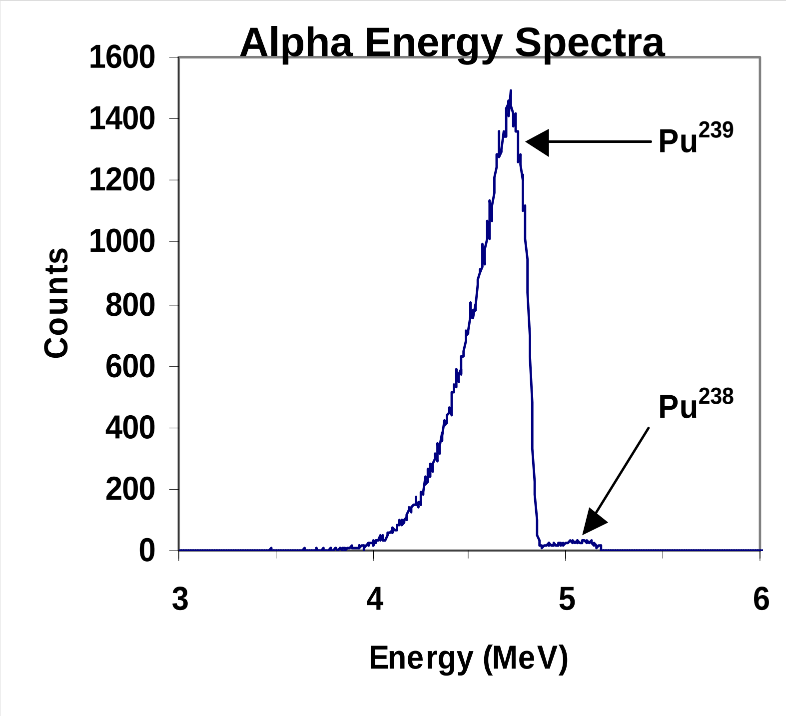
- Water stable, rapid, selective preconcentration
- Relative surface area increased 100 - 10,000X



0.1- 3 μm thick, 1-10 nm pores, 600-900 m^2/g

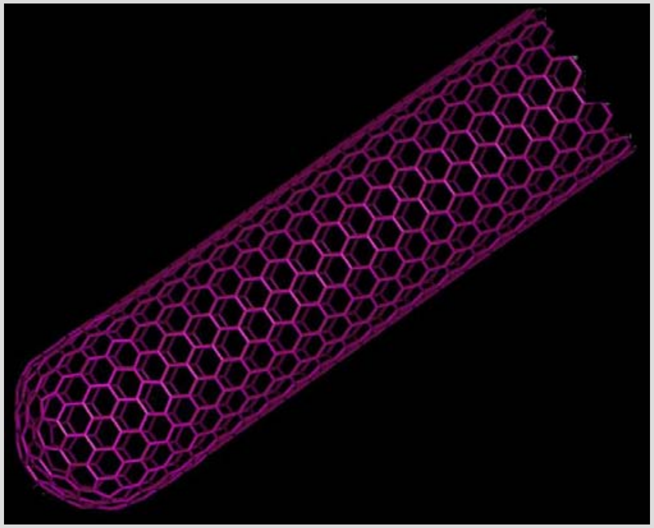


acetamide diethylphosphonate moiety with 3-aminopropylsilane linkage

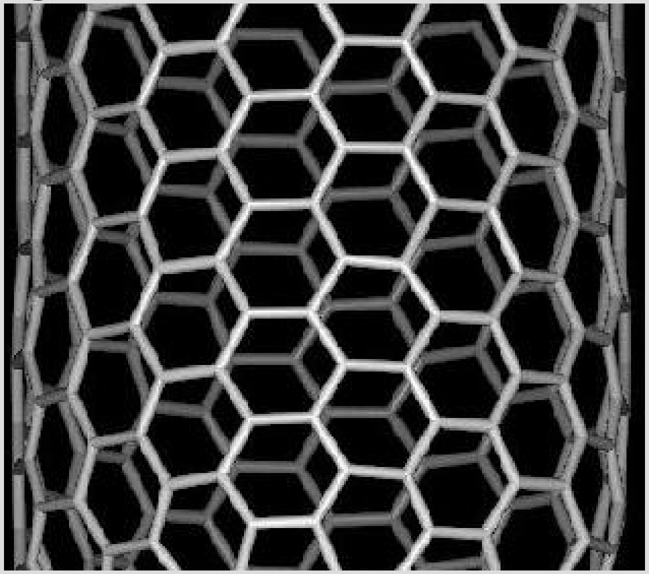


1.8 μm thick, 8 nm pores, 620 m^2/gm,

Carbon Nanotubes (CNTs)

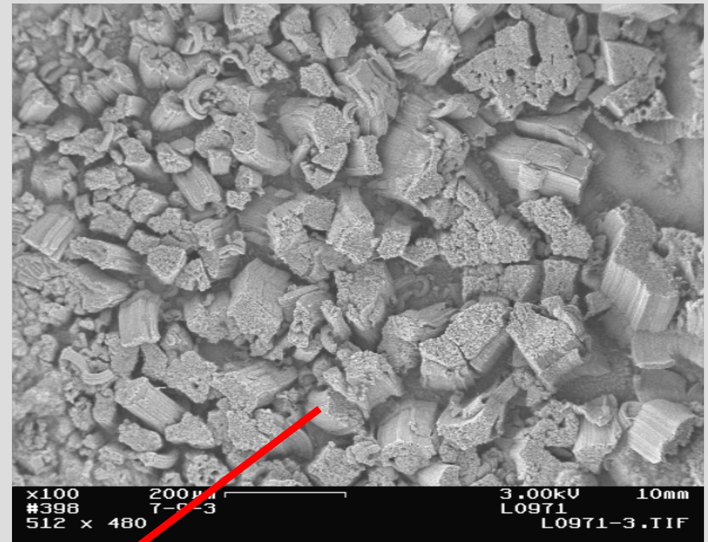


- High surface area
- High electrical conductivity
- High thermal conductivity
- High mechanical strength
  - Reinforce soft materials
  - Particulate form…..
- Excellent chemical/physical stability
  - Allow use in harsh/corrosive environments
  - Not reactive……

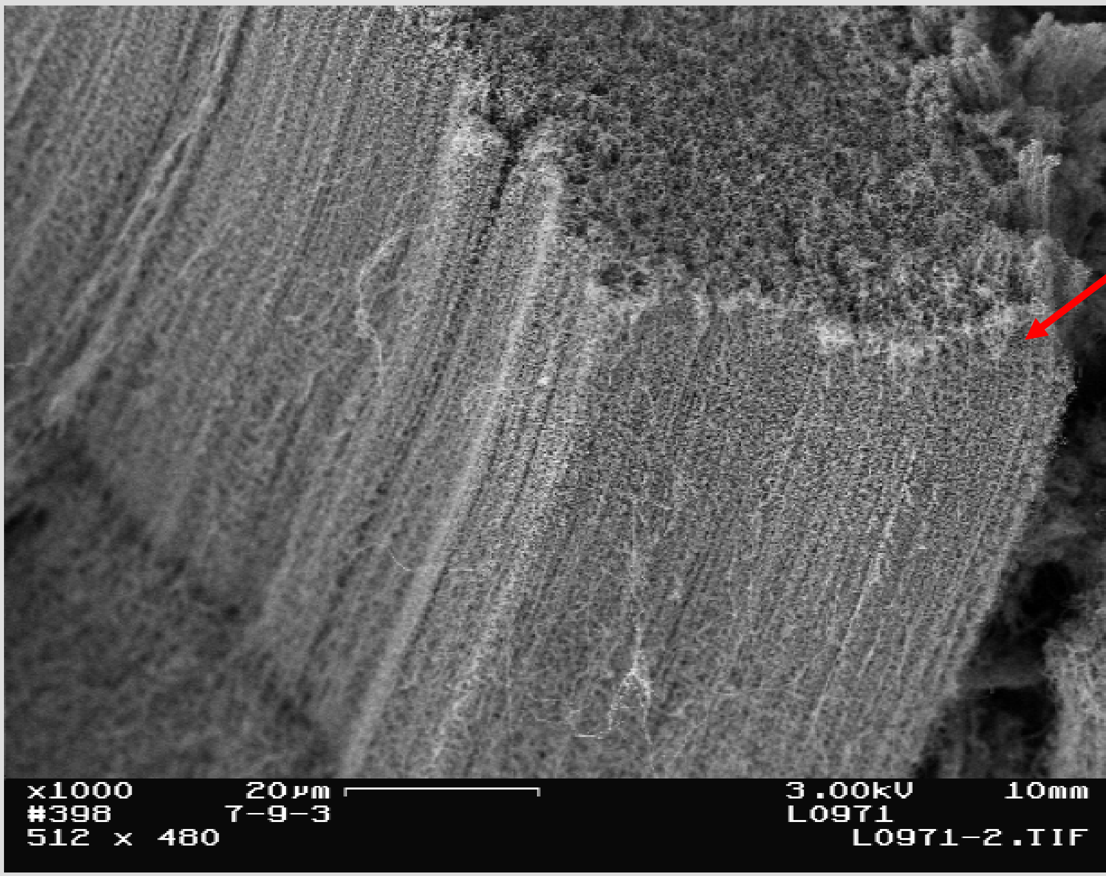


CNTs on Planar Surfaces

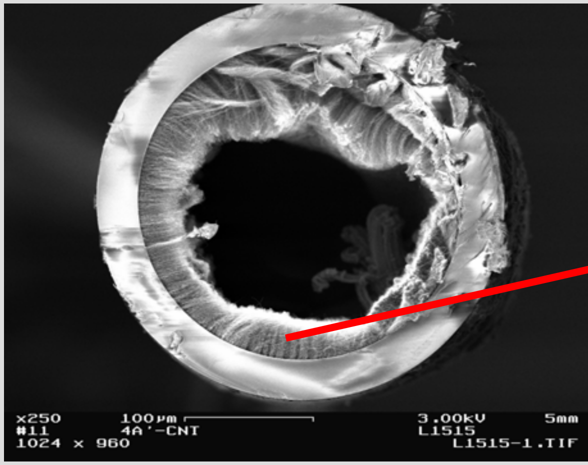
- 30 min.; 750 ºC
- CNTs arrays are about 0.1 – 0.2 mm
- Aligned CNTs are about 40 – 60 μm



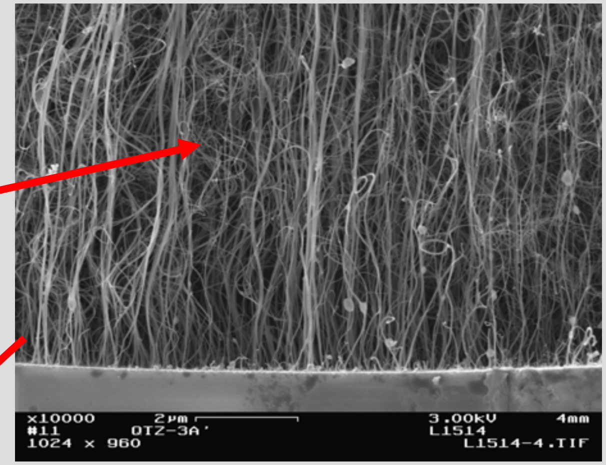
10X



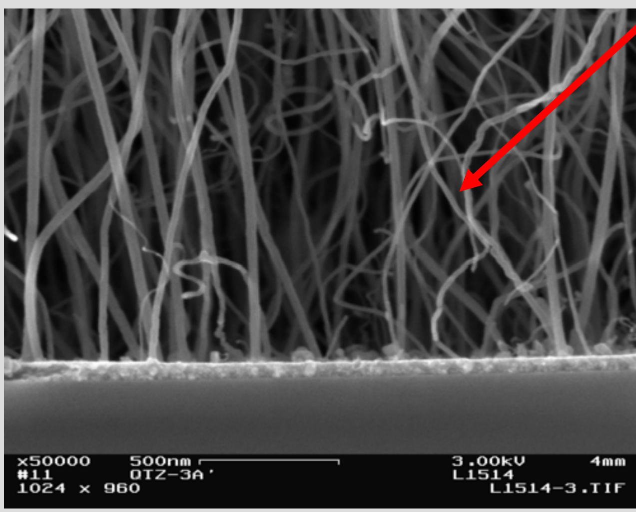
CNTs in Quartz Capillary Tubes



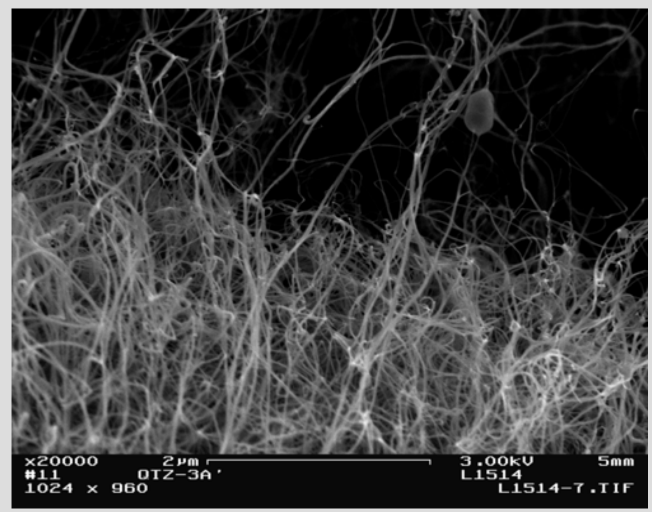
CNT-coated quartz capillary tube



Alignment of CNTs coated inside a quartz capillary tube

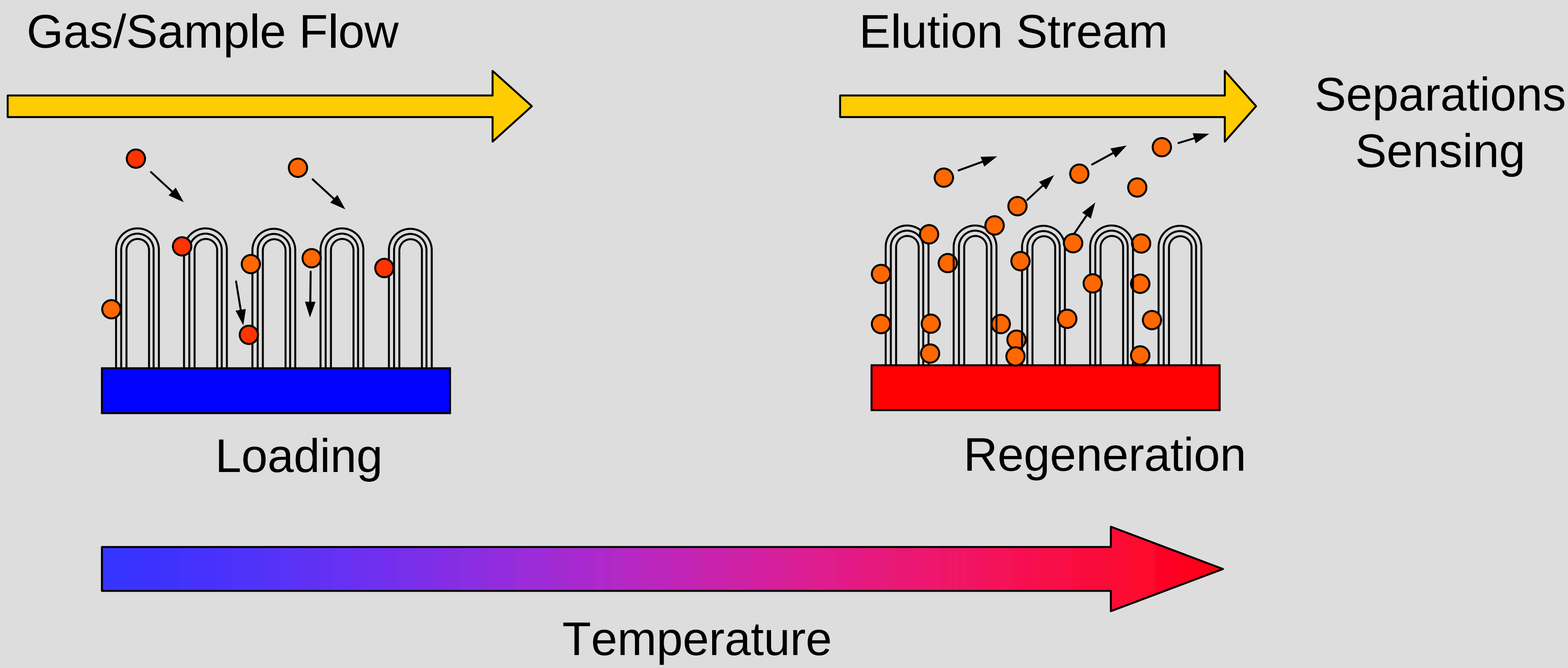


Alignment of CNTs coated inside a quartz capillary tube (high mag.)



Alignment of CNTs' tips coated inside a quartz capillary tube

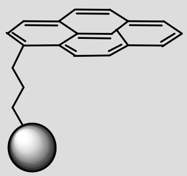
Preconcentration with CNT Structures and Thermal Swing Adsorption



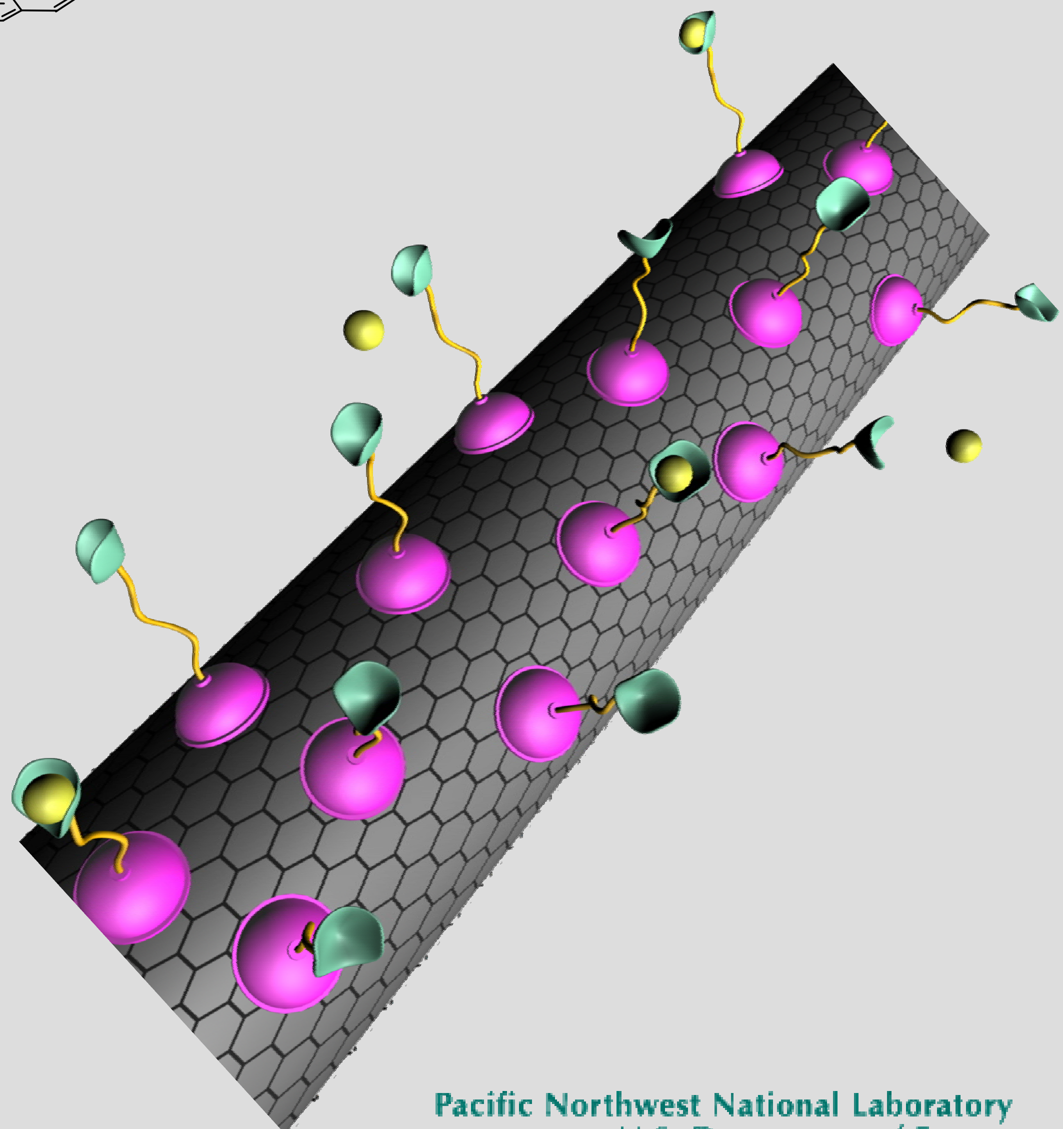
- High Surface Area/Capacity
- Rapid Cycle time
- Not selective….

Chemically Selective CNTs?

- Pyrene "anchors"
  - Pi-stacking
  - Strong enough to hold macromolecules
  - Does not disrupt CNT structure



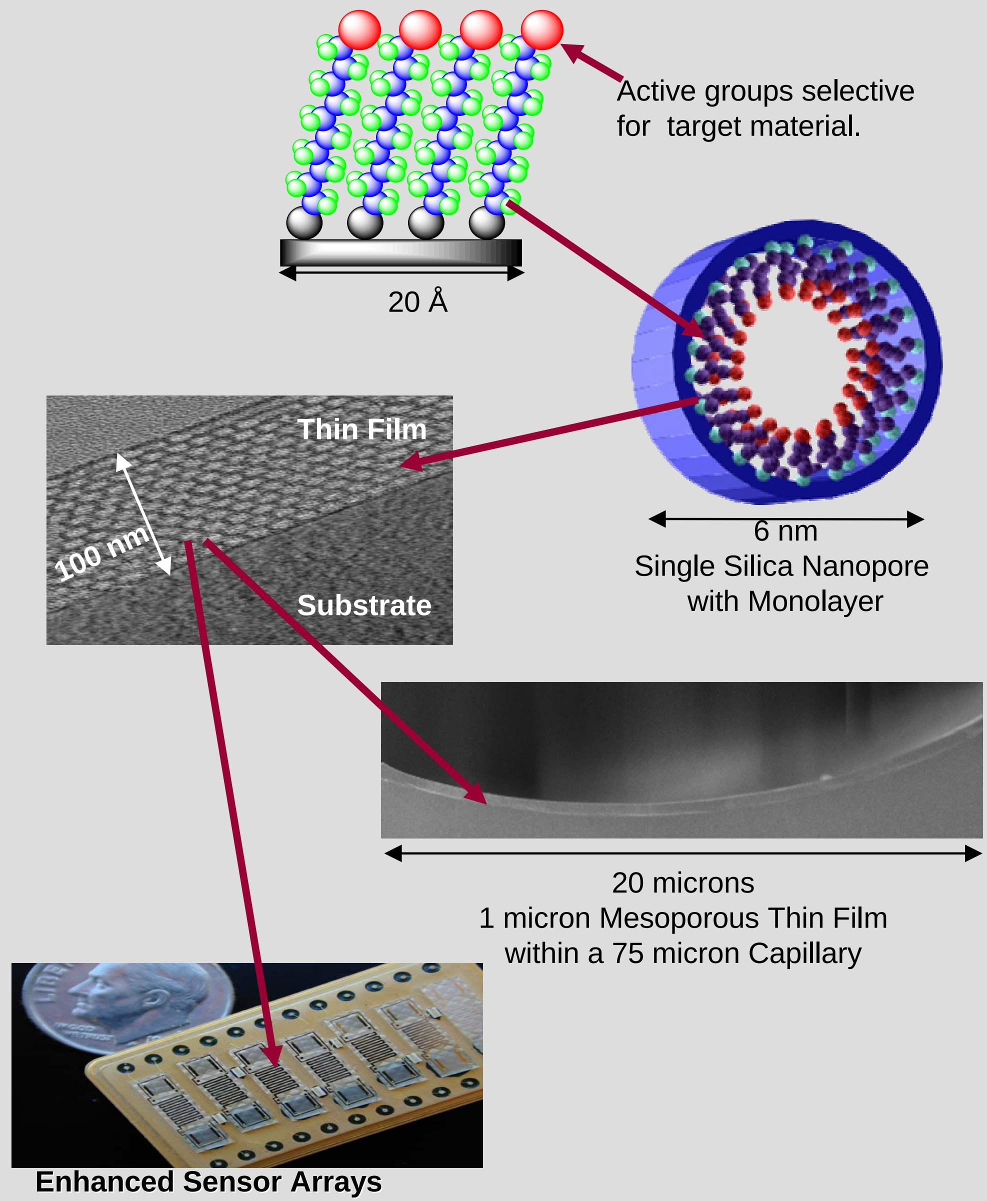
- Chemically active groups can be tethered to pyrene
- Loading density can be greater than monolayer coverage!(?)
- Mixed Functionality



Conclusions

Hierarchically ordered materials can enable leaps in sampling and sensing.

- **Nanostructure Materials can provide:**
  - High surface areas (capacity)
  - Open pore structure (speed)
  - Flexible surface chemistry (selectivity)
  - High functional density (capacity)
  - Can be integrated into macrostructures
    - Capillaries
    - Planar Thin films
    - Particles
    - Monoliths
  - "Orthogonal" Enhancement
    - Sensitivity, Selectivity, Simplicity, Speed



- **Other Nanobuilding Blocks Emerging**
  - Mesoporous Carbon
  - Metal Oxide Frameworks
  - Metal Nanoparticles
  - Quantum Dot Emitters
  - Modified Enzymes