Ion beam analysis of materials for water purification: Partitioning of inorganic ions in FT30 reverse osmosis membranes

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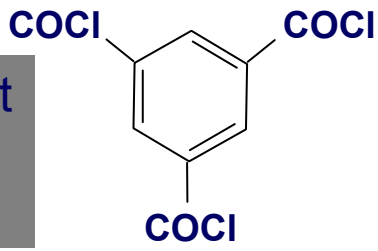
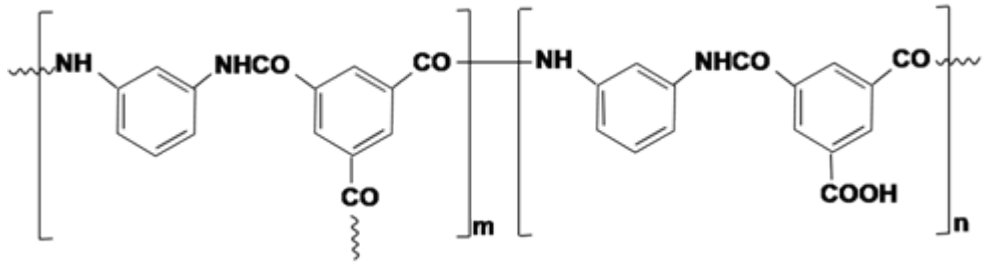
waterCAMPWS

Motivation: limited microscopic understanding of transport in interfacially polymerized membranes

- Technology of polyamide membranes for purifying water has seen only minor incremental changes in >30 years.

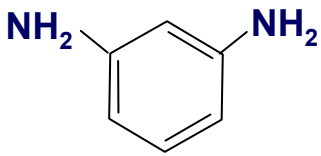
Organic solvent + acyl halide phase

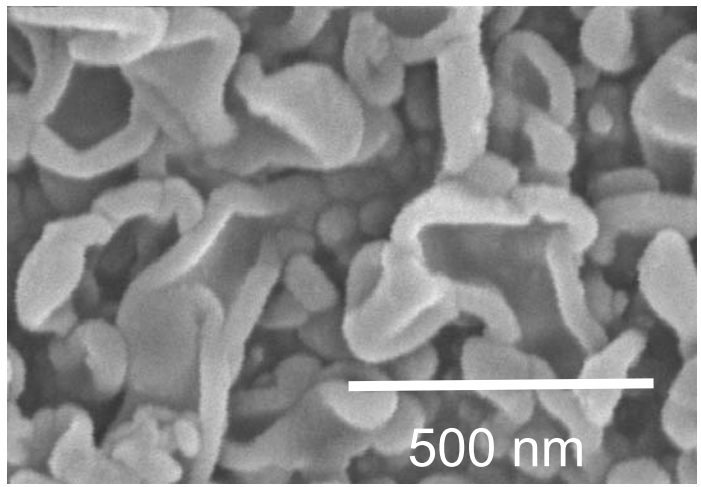




Polyamide ~100 nm

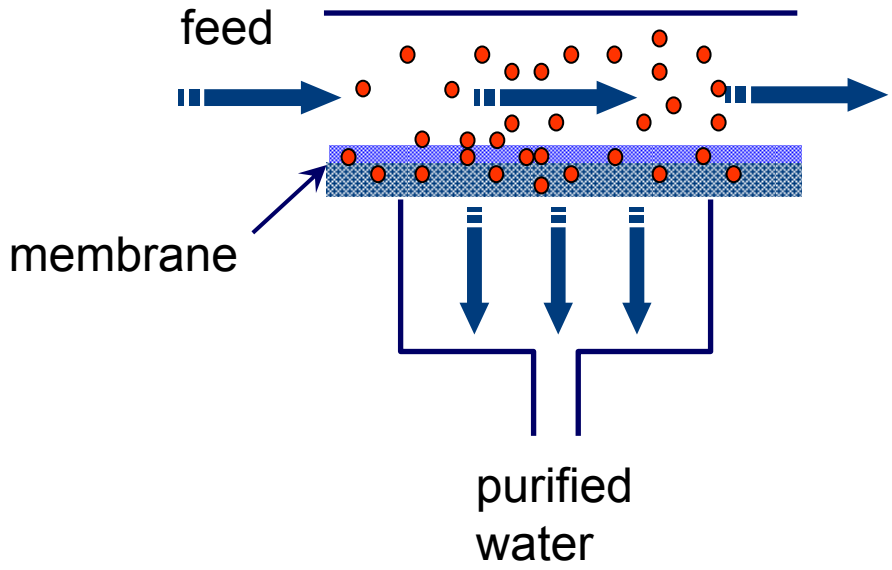
Water + amine phase



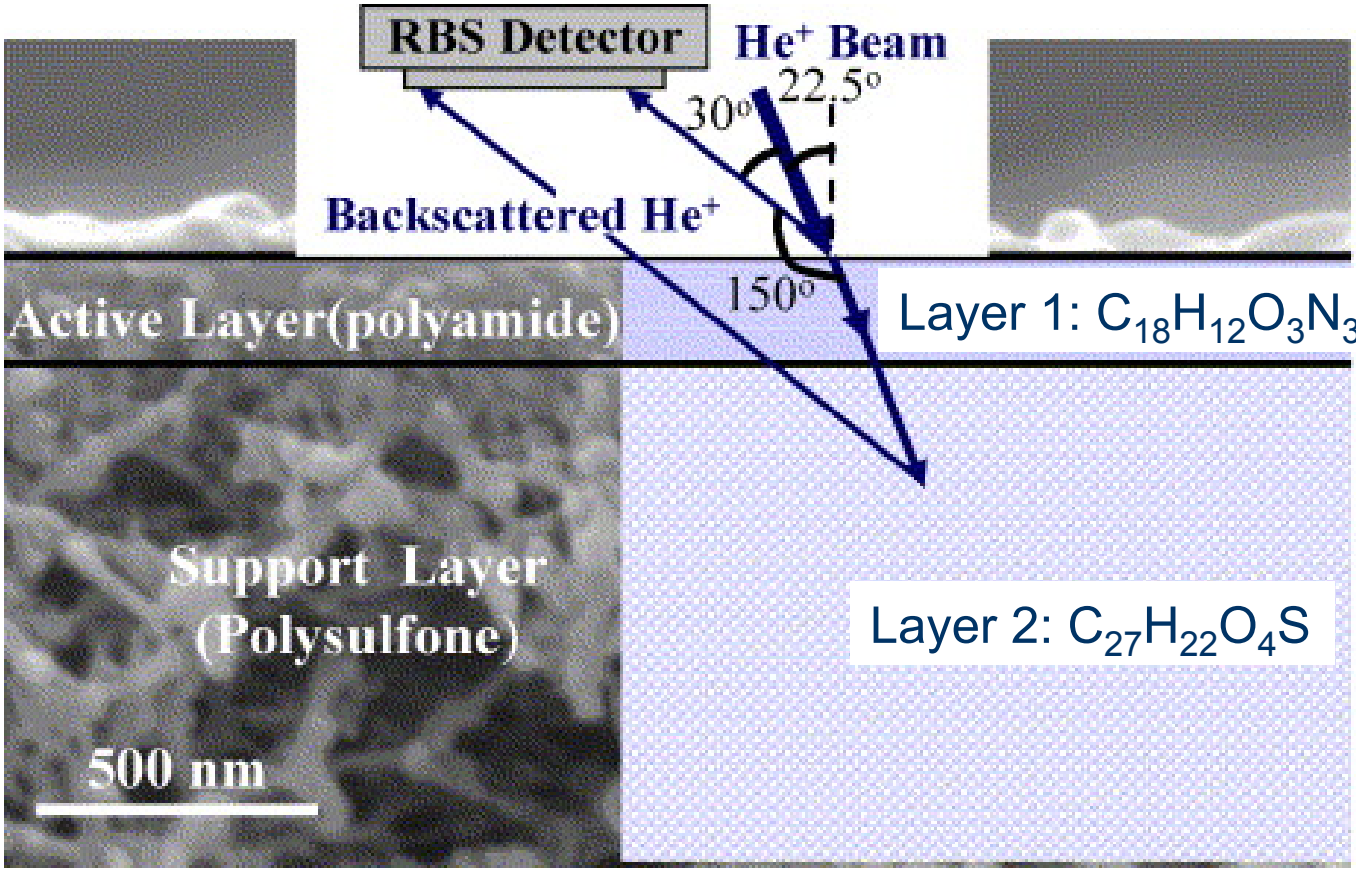


Permeability is the product of solubility (i.e., partition coefficient K) and diffusion constant D.

- Goal is high rejection of salts and contaminants
  - Need high permeability to water (solvent) but low permeability to contaminants (solute)
- Steady-state transport measurements cannot distinguish between small partition coefficient K and small diffusivity



Use ion beam analysis (RBS) to measure K of salt ions

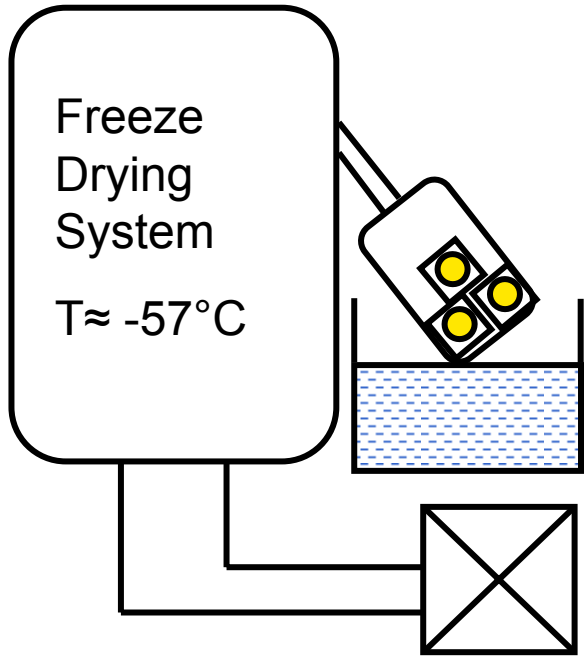


FT30 reverse osmosis membrane, Dow Liquid Separations

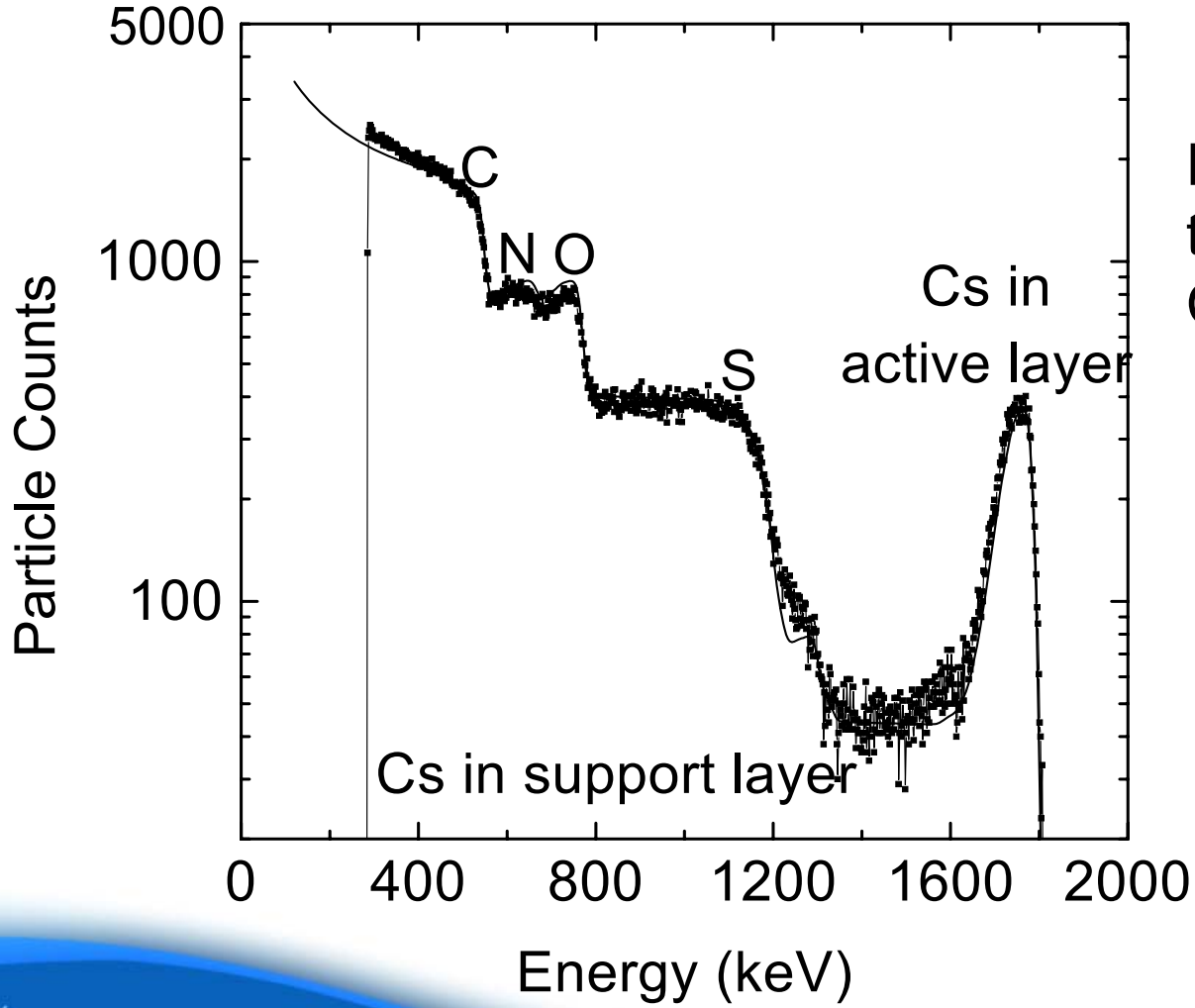
Conventional wisdom is K<<1; we find K≈5.

Sample preparation is critical

- Use high Z ions to increase sensitivity
  - Cs^+ in CsCl
  - Br^- in KBr
  - WO_4^{2-} in Na_2WO_4
- Freeze-dry to remove water without disturbing the ion distribution
- Polysulfone is highly susceptible to ion beam damage
  - Scan RBS beam to minimize ion dose



RBS can determine both the K of the active layer and the porosity of the support layer



FT30 membrane treated in 0.05 M CsCl solution.

Ion Concentrations in Active Layers and Support Layers

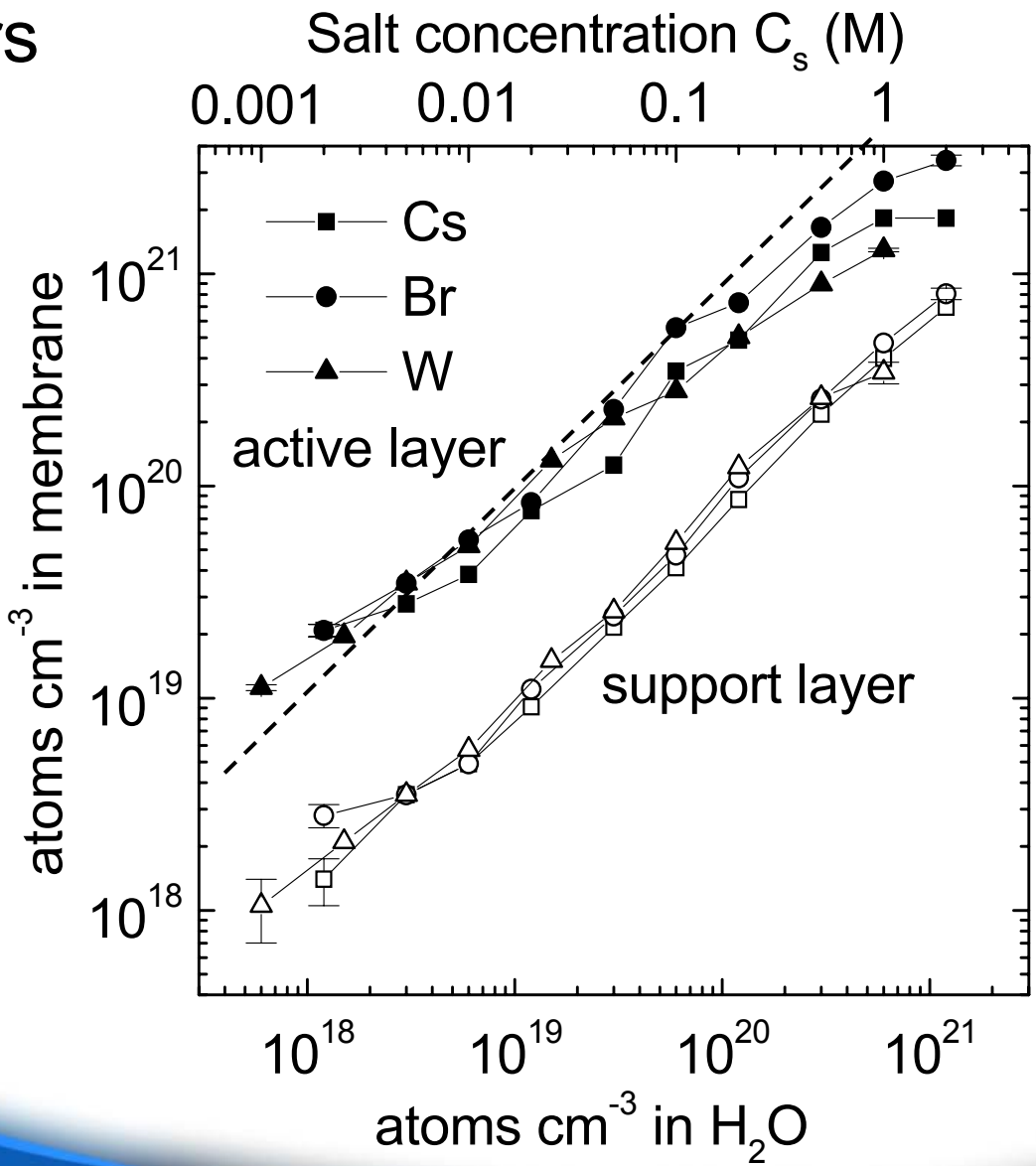
Cs^+ in CsCl

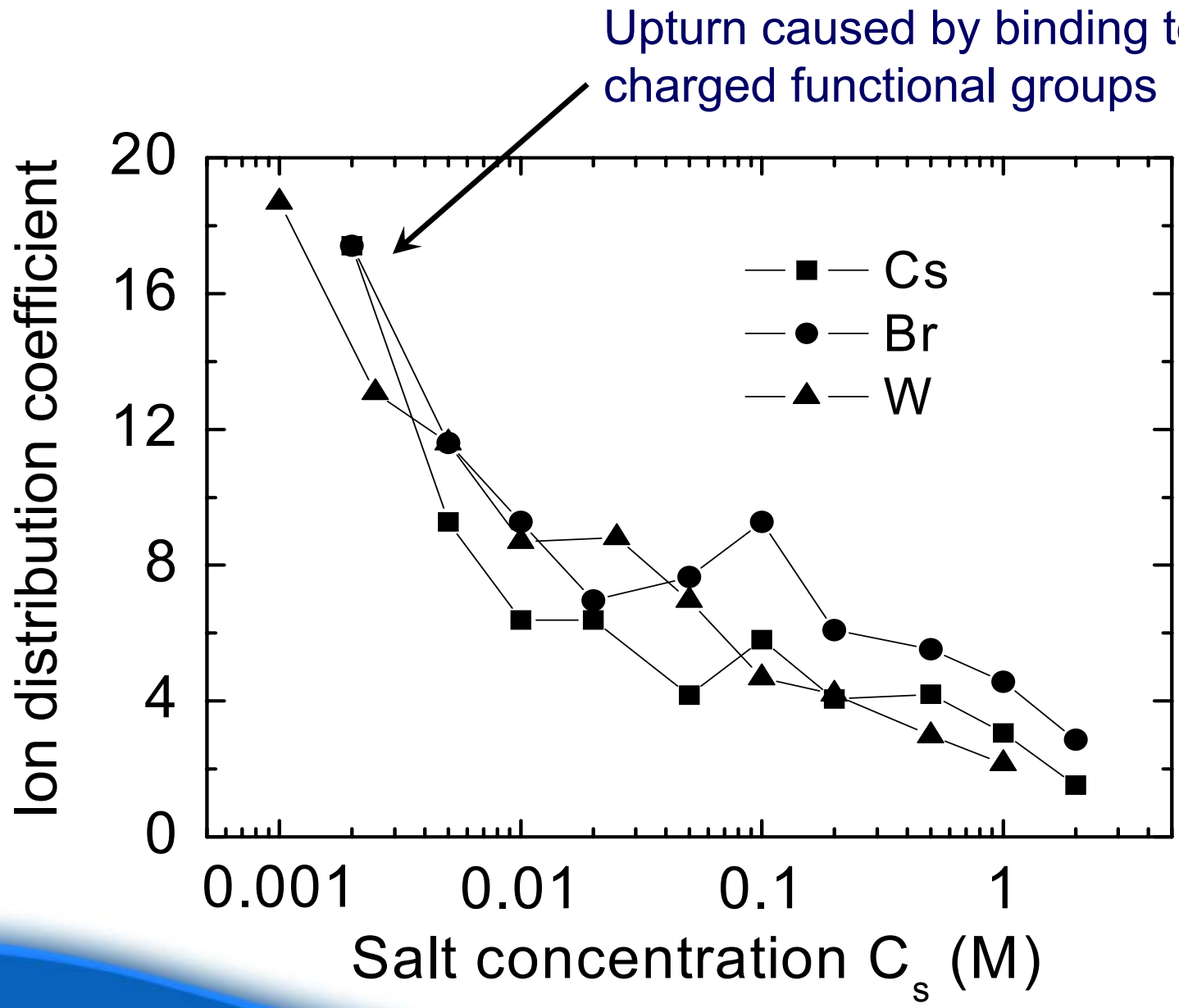
Br^- in KBr

WO_4^{2-} in Na_2WO_4

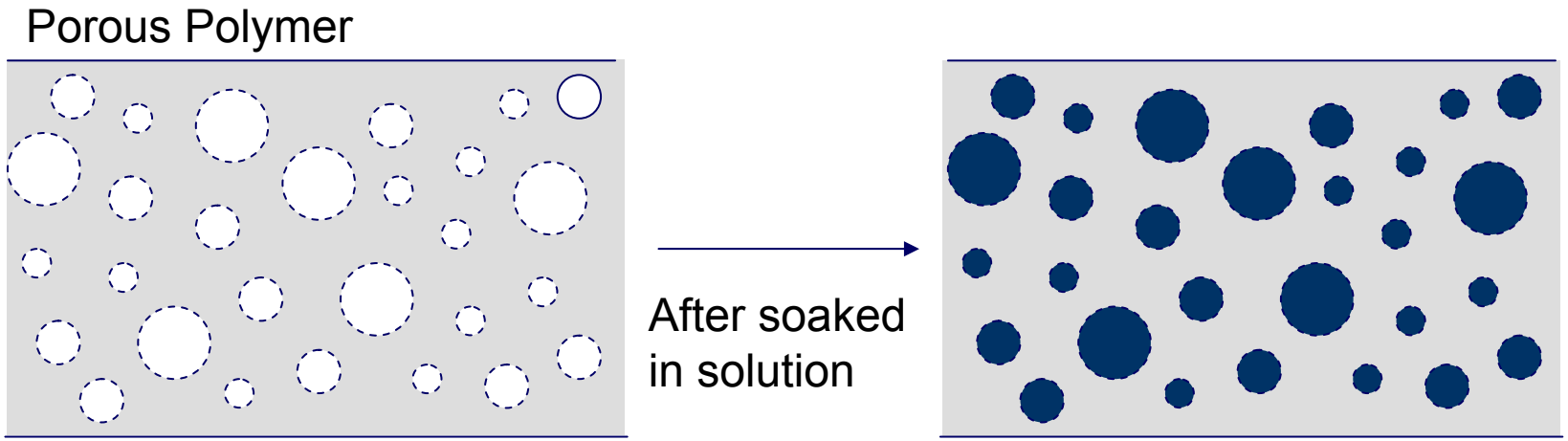
Cs^+, Br^- r = 3 Å

WO_4^{2-} r = 4 Å




Upturn caused by binding to charged functional groups
Ion distribution coefficient
20
16
12
8
4
0
0.001
0.01
0.1
1
Salt concentration C_s (M)
Cs
Br
W

RBS can depth profile the porosity of the support layer



Atomic density of key element in solution: N_i. For example, 0.05 M equals to 3×10^{19} cm^{-3}

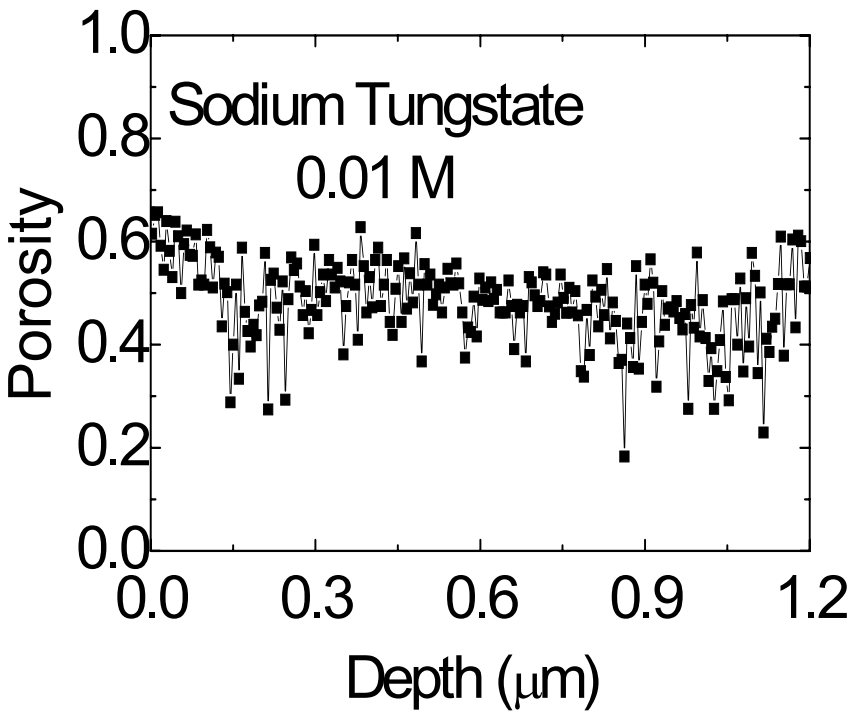
Atomic density in polymer: $N_p \approx 9\times10^{22}$ cm^{-3}

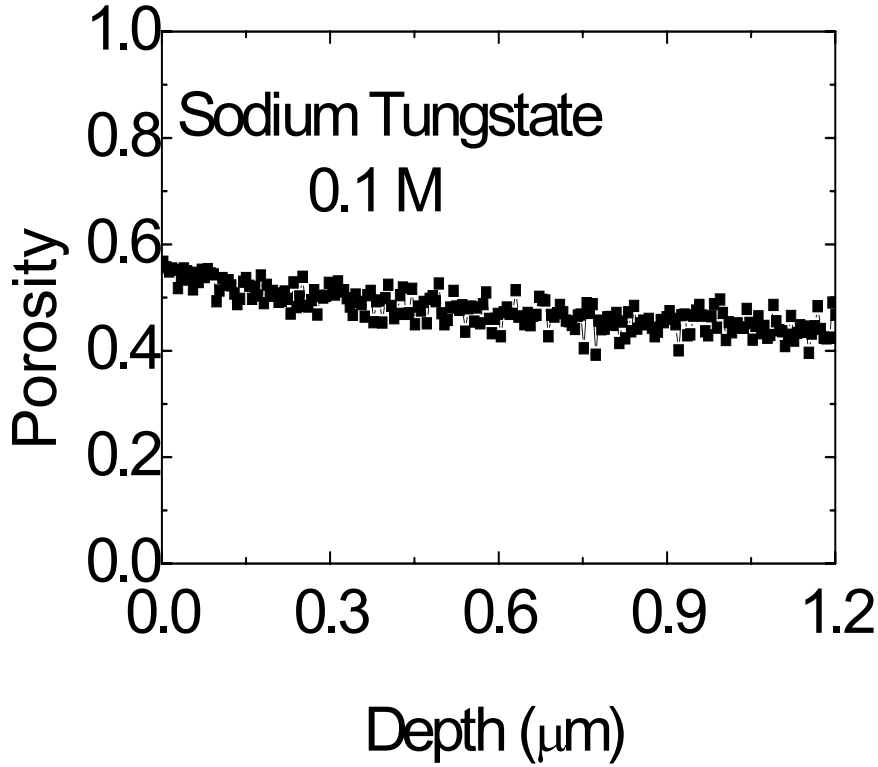
Volume of pores V_o and volume of polymer V_p

Atomic percentage of the key element in polymer $x = V_o N_i / V_p N_p$

$$\text{Porosity } \phi = V_o/(V_p+V_o) = \frac{x\frac{N_p}{N_i}}{1+x\frac{N_p}{N_i}}$$

Profile of porosity in the support layer





Summary

- Ion beam analysis has much to offer the field of "materials for water purification"
- Freeze-drying is a critical step in sample preparation but are there still issues of ion redistribution?
- Partition coefficient of salt ions in the active layer is surprisingly high, K≈6, much larger expected based on conventional wisdom.
- Greater depth resolution would be helpful since interfacially polymerized membranes are thin (<200 nm) and highly inhomogeneous.