Extraction Chromatography:

a microscopic view

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Eichrom User's Group Meeting / RRMC

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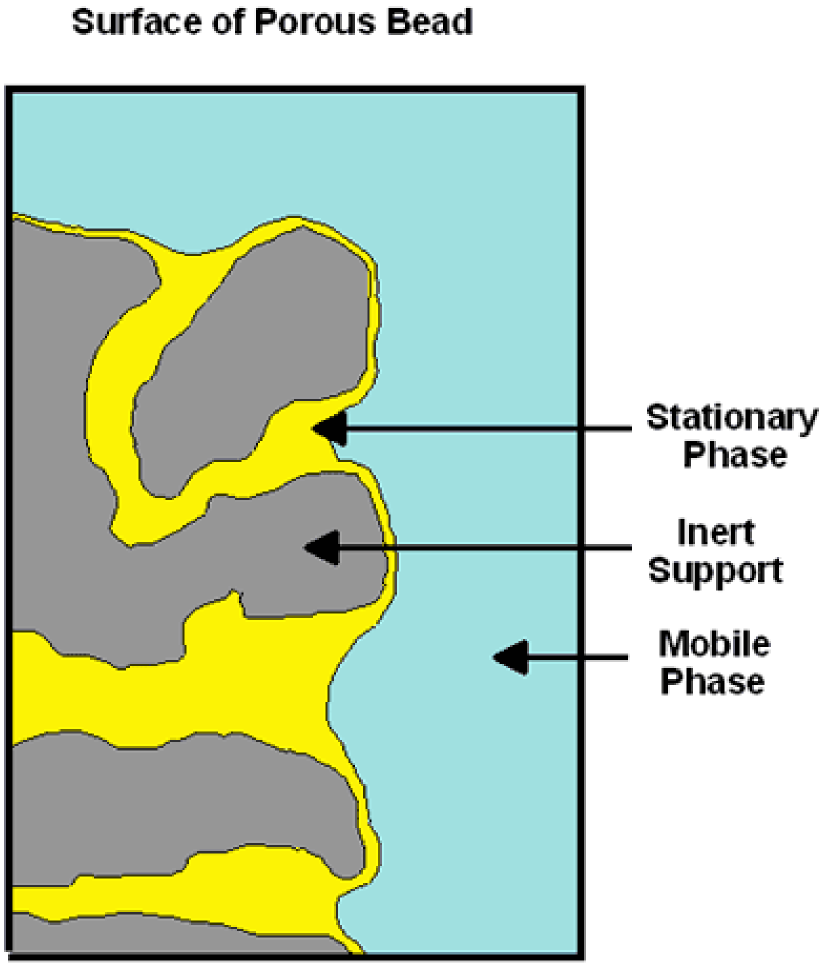
Topics to be covered

1. Aqueous and stationary phase diffusion
2. Column packing and flow phenomenon
3. Interfacial Structure
4. Temperature versus particle size

Depiction of Extraction Chromatography (EXC)



Relationship Between SX and EXC

$$k' = D_v \bullet \frac{v_s}{v_m}$$

k' = retention volume (FCV to peak maximum)

D_v = volume distribution ratio

v_s = volume of stationary phase

v_m = volume of mobile phases

Relationship between k′ and D_v

R = equilibrium fraction of solute in the mobile phase

1-R = equilibrium fraction of solute in the stationary phase

k′ = ratio of solute in the station phase to the mobile phase or number of free column volumes to peak maximum for a column.

$$\therefore \frac{1-R}{R} = k' \qquad (1)$$

If C_m and C_s are the concentrations in the mobile and stationary phase, respectivly and V_m and V_s are the corresponding volumes of these phases.

$$\frac{R}{1-R} = \frac{C_m V_m}{C_s V_s} \qquad (2)$$

C_s / C_m is the volume distribution ratio D_v

$$\therefore \frac{R}{1-R} = \frac{V_m}{D_V V_S} = \frac{1}{k'} \qquad (3)$$

$$\therefore k' = D_v \bullet v_s / v_m \qquad (4)$$

Relationship between k′ and D_w

$$D_w = \frac{A_o - A_s}{\text{Weight of Resin(g)}} \Big/ \frac{A_s}{\text{Volume of Solution (mL)}} \qquad (5)$$

$$D_v = \frac{A_o - A_s}{\text{Volume of Ext on Resin } (V_e)} \Big/ \frac{A_s}{\text{Vol of Sol (mL)}} \qquad (6)$$

Where D_w equals weight distribution ratio and D_v equals volume distribution ratio.

$$D_w = D_v \bullet V_e / g \qquad (7)$$

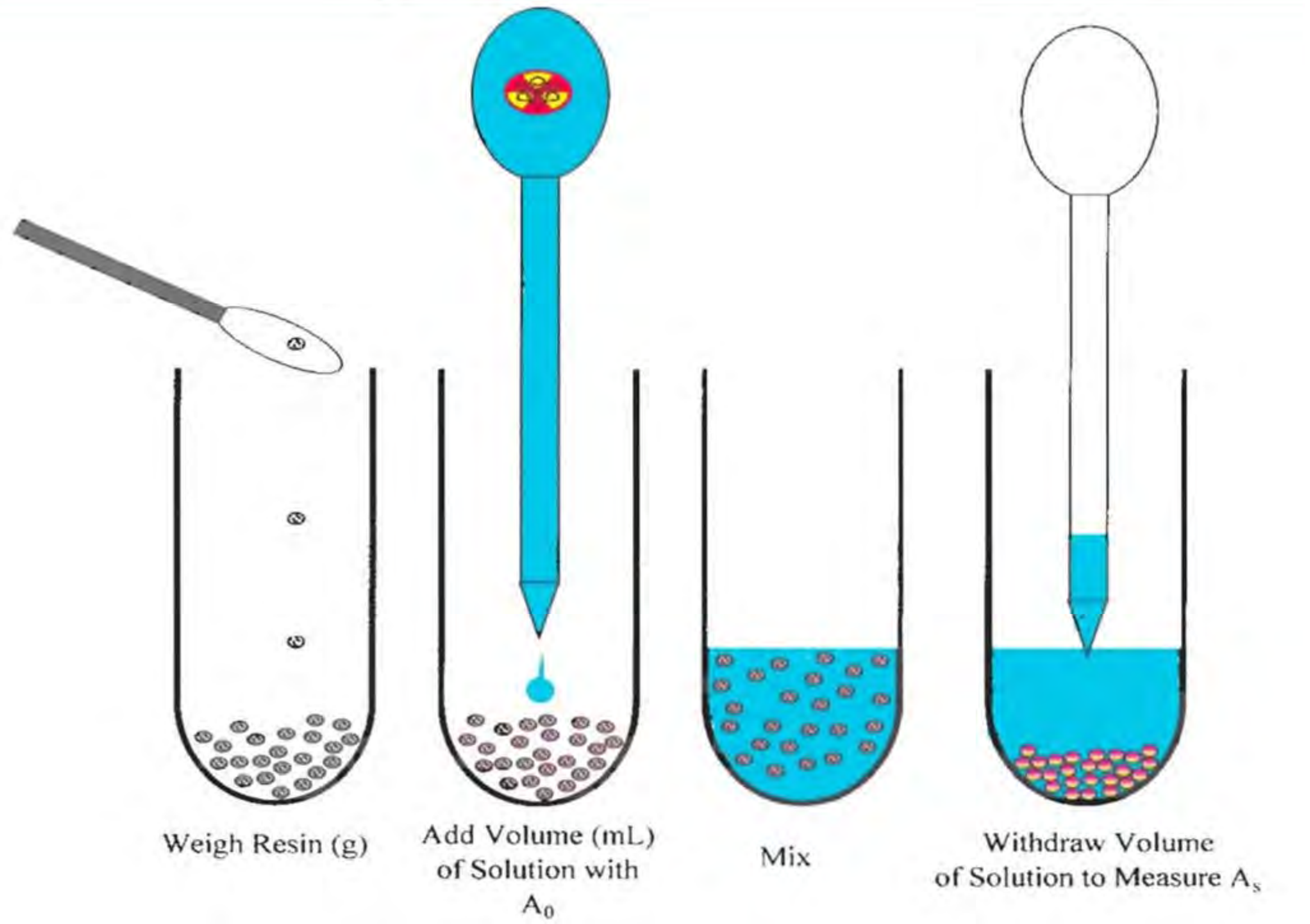
Assume extractant loading is 40 weight percent. Then one gram of resin contains 0.4g of extractant. Assume the extract has a density of 1 g/cc.

Then $D_v = D_w \times 2.5$ (8)

Assuming $v_s/v_v = 1/5$ which is close to the value obtained from packed column, substitute in eq. 4.

Then $k' = D_w \bullet 0.5$. (9)

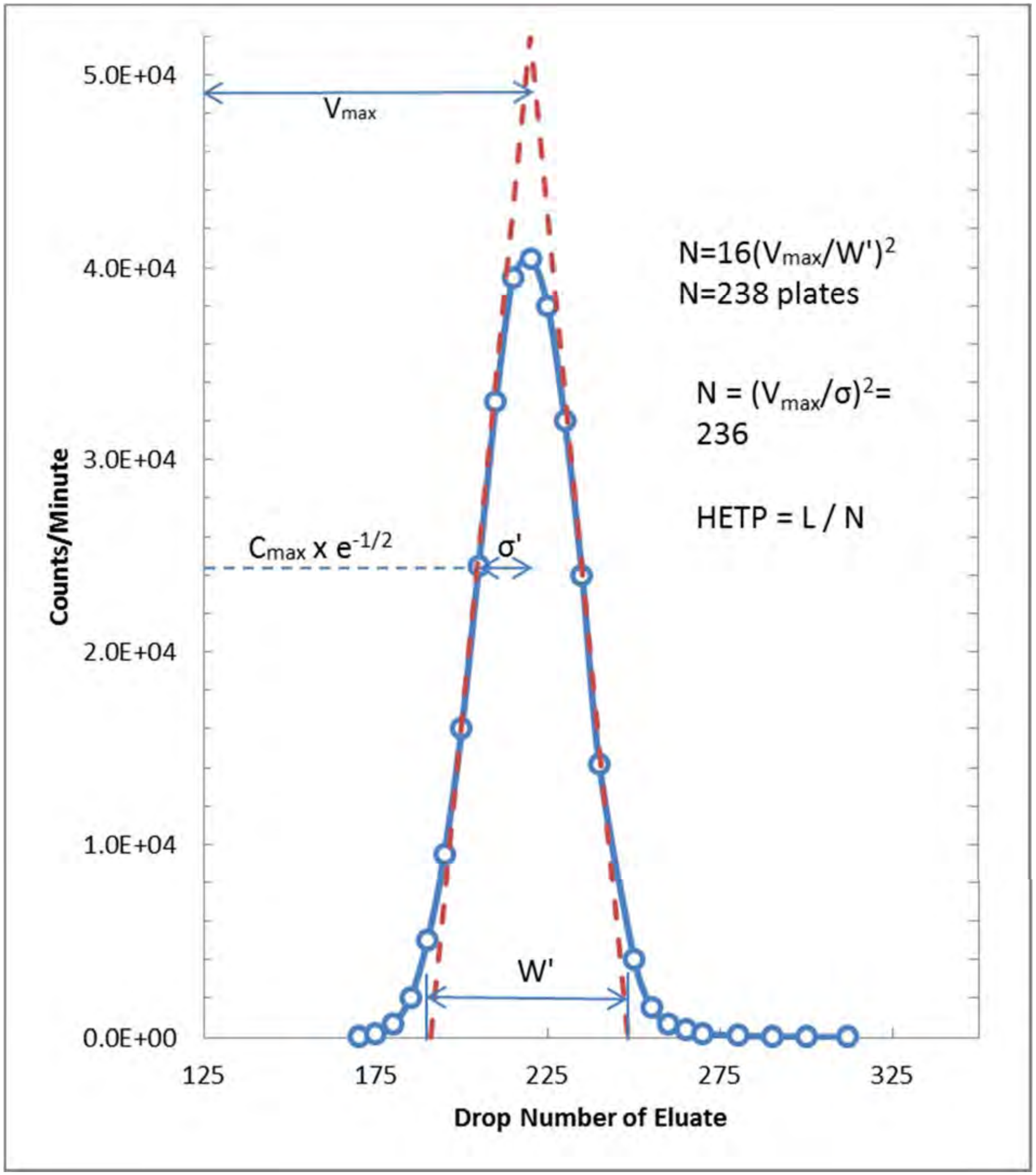
Dry Weigh Distribution Ratio



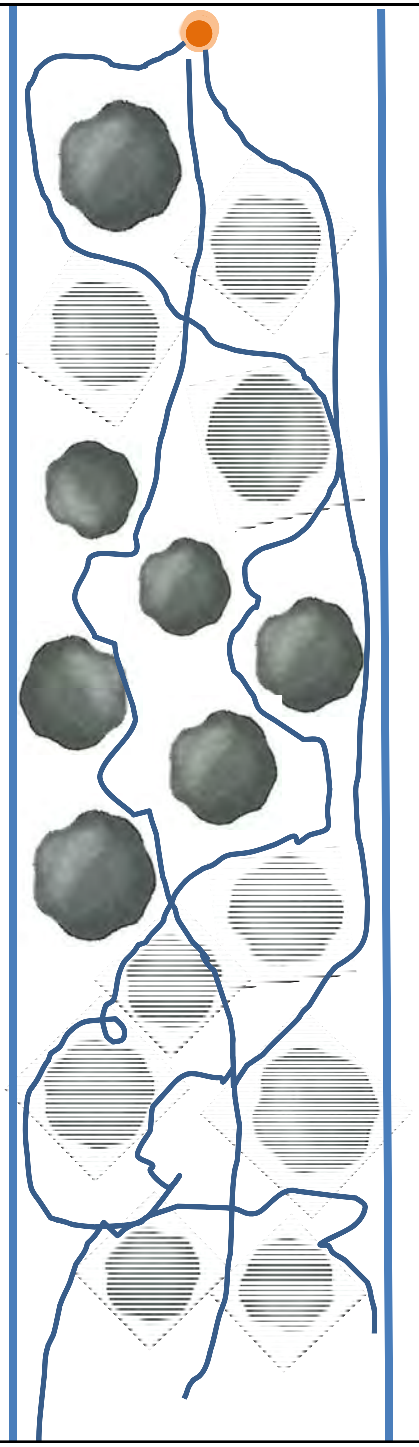
$$D_w = \frac{A_0 - A_s}{w(g)} \Big/ \frac{A_s}{v(mL)}$$

Comparison of K′ Calculated from D_w and K′ Obtained from Elution Curves

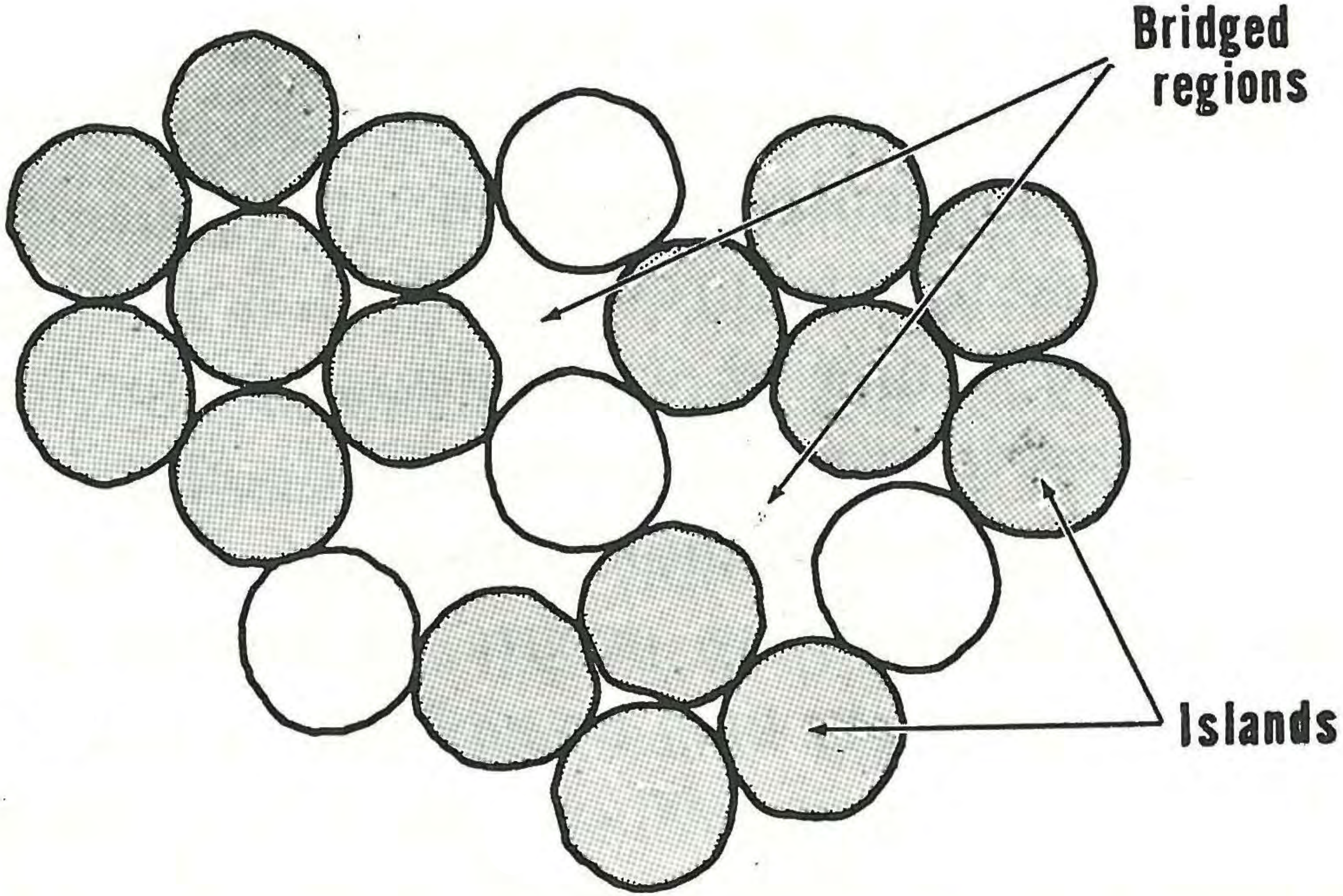
Element	$[HNO_3]$, M	k′ Calculated from D_w	k′ from Elution Curve
Nd	0.25	6.5 ± 0.8	6.0 ± 0.3
Pm	0.25	11 ± 1	13 ± 0.7
Sm	0.40	7.0 ± 0.8	6.5 ± 0.3
Eu	0.40	13 ± 2	14 ± 0.7
Gd	0.40	25 ± 3	23 ± 1


5.0E+04
4.0E+04
3.0E+04
2.0E+04
1.0E+04
0.0E+00
Counts/Minute
125
175
225
275
325
Drop Number of Eluate
V_{max}
$N=16(V_{max}/W')^2$
N=238 plates
$N = (V_{max}/\sigma)^2=$
236
HETP = L / N
$C_{max} \times e^{-1/2}$
σ'
W'

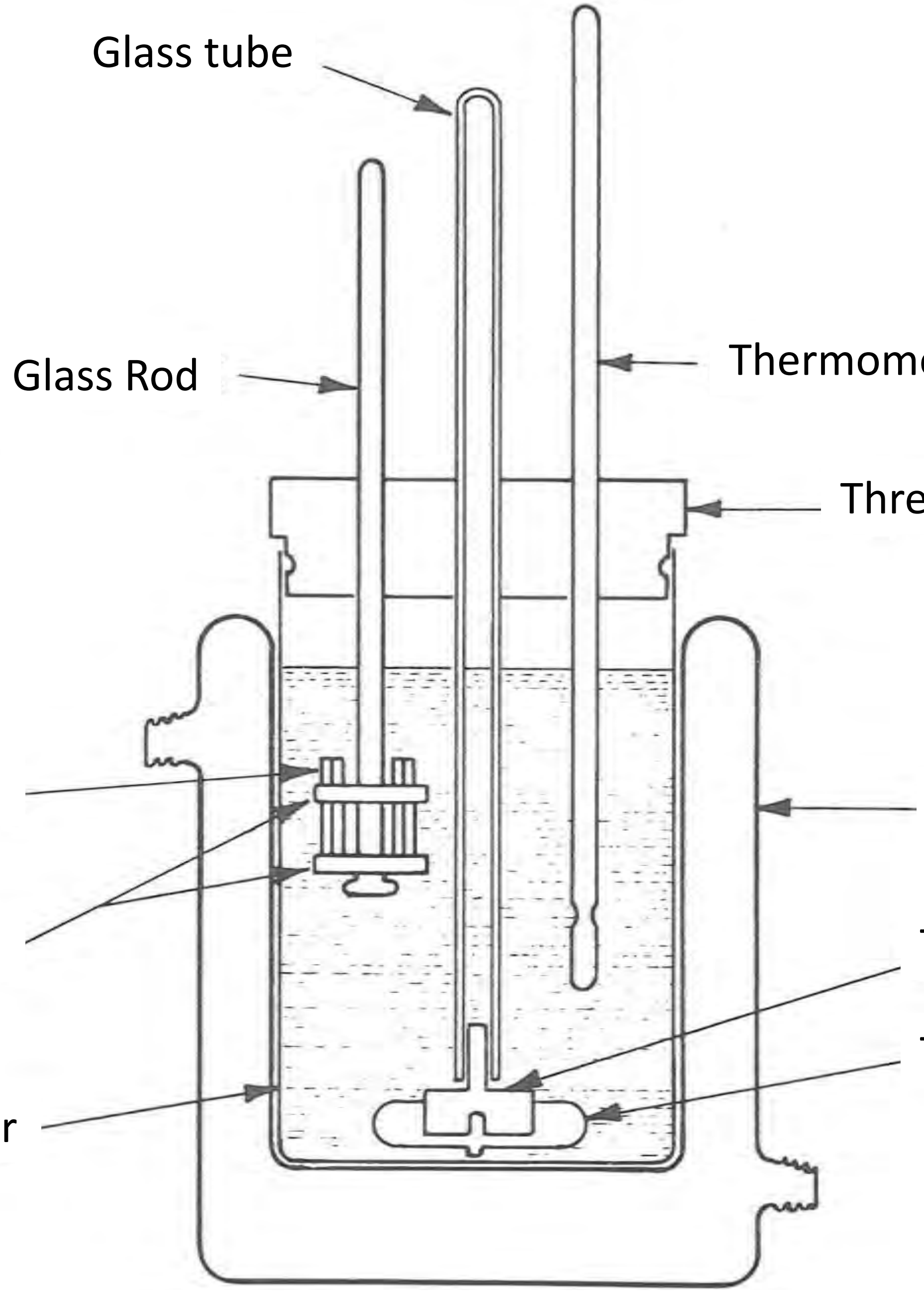
Depiction of streamlines erratically veering around particles in a packed bed.



Bridging Illustrated by a two-dimensional model



Open-end Capillary technique used to measure diffusion coefficients



Glass tube

Glass Rod

Thermometer

Three Holed Teflon Stopper

Diffusion Capillaries

Thermostated Jacket

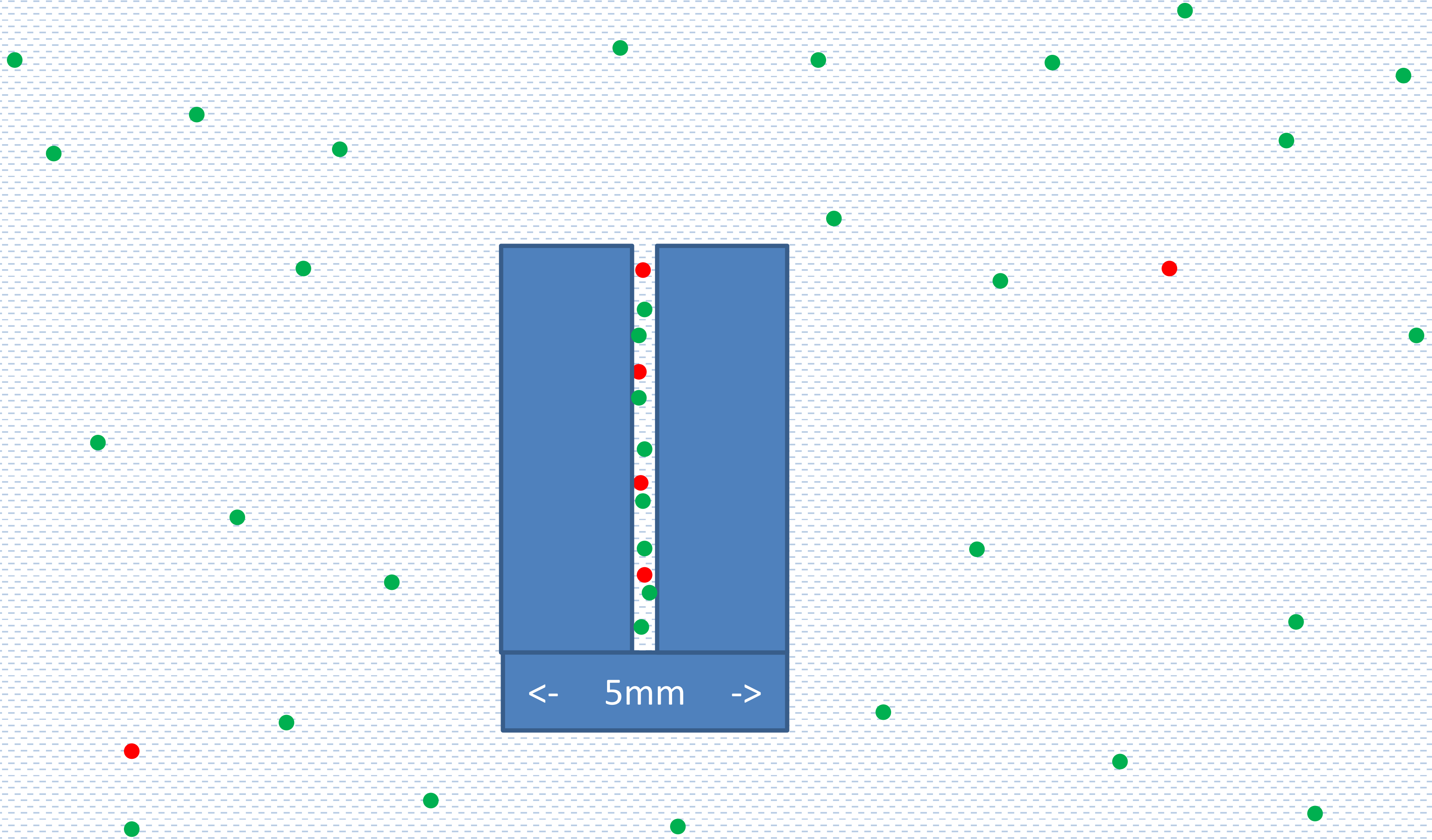
Teflon Discs (2)

Teflon Jacket

Teflon Stirring Bar

Flat Top Glass Beaker

Self Diffusion from open end capillary



D calculated from the following equation

$$\frac{\bar{C}}{C_0} = \gamma = \frac{8}{\pi^2}\left(e^{-\theta} + \frac{e^{-9\theta}}{9} + \frac{e^{-25\theta}}{25} + \frac{e^{-49\theta}}{49}\right)$$

$$\theta = \frac{\pi^2 D t}{4l^2}$$

Where:

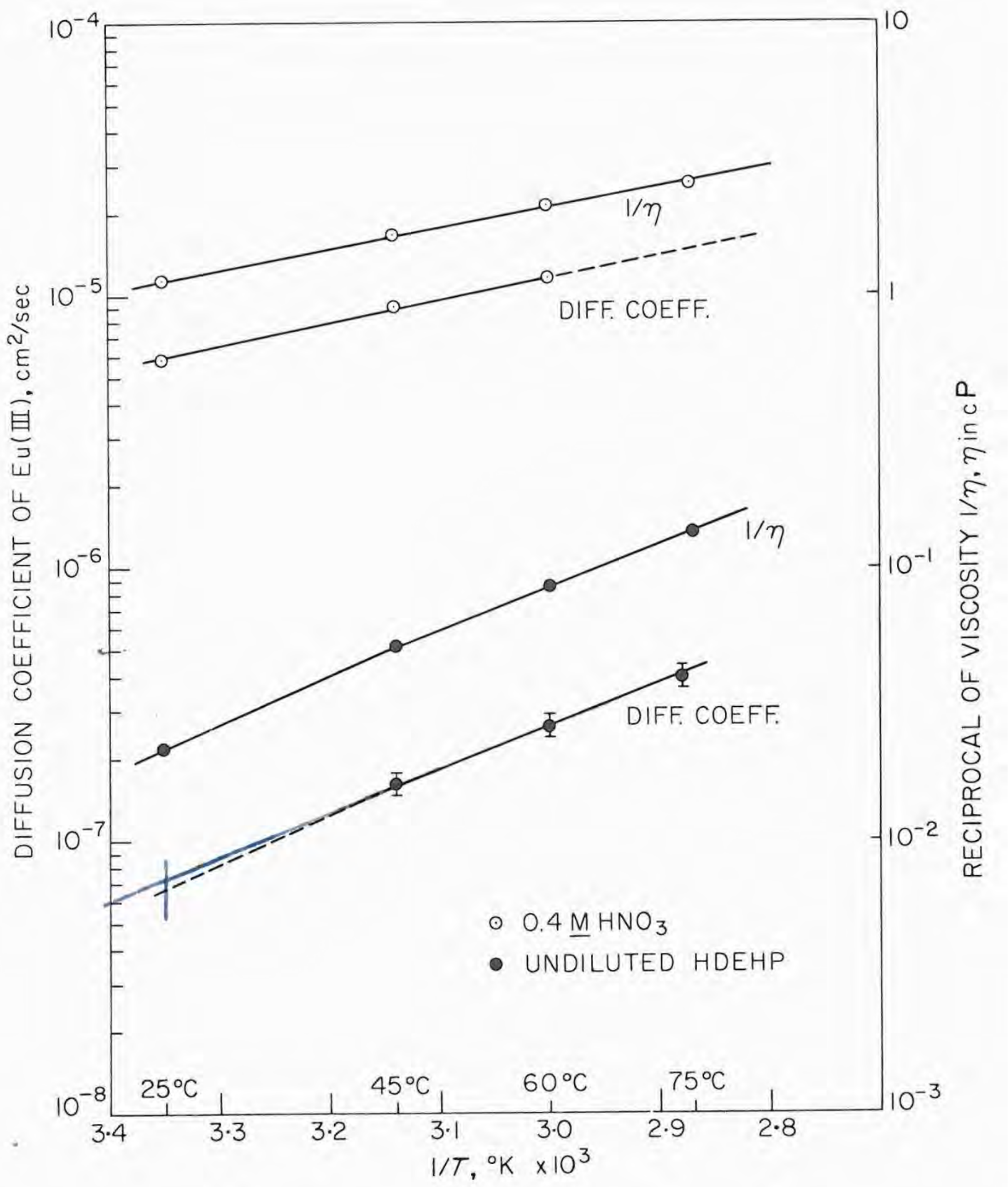
C_0: [Eu] in capillary before diffusion

$\bar{C}$: [Eu] in the capillary after diffusion

t: time of diffusion

l: length of the capillary

The effect of temperature on the viscosity and diffusion coefficient



Average time, t*, needed for M^{3+} in dilute HNO_3 to diffuse a particle diameter distance

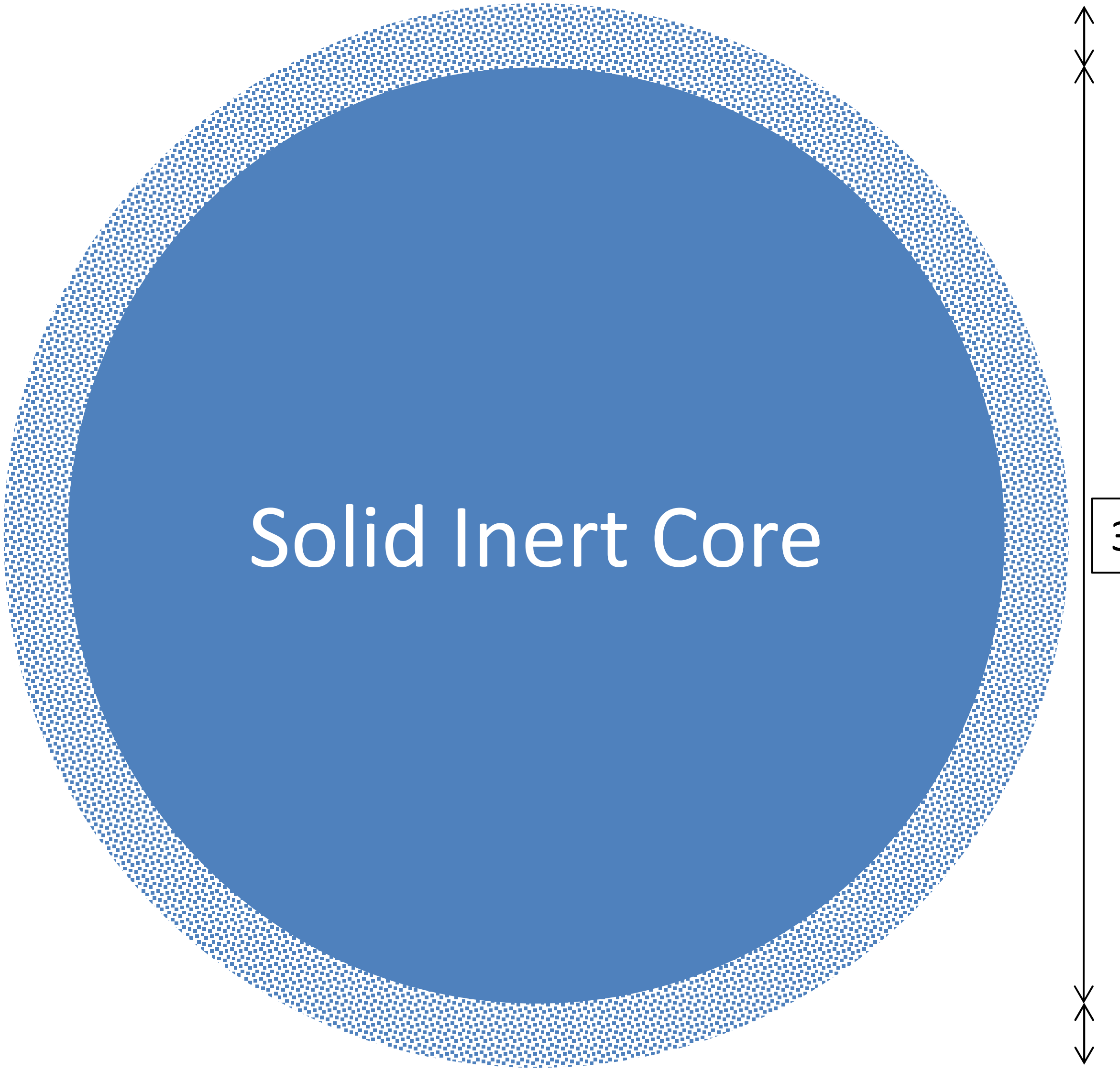
Average Particle Diameter in µ	Time in Sec
A – grade (125)	7.8
S – grade (75)	2.8
F – grade (39)	0.76
VF – grade (18)	0.16

* $t = \omega^2 d_p^2 / 2D_m$

Where Dm is the diffusion coefficient and ω is a structure parameter

$D = 1 \times 10^{-5}$ cm^2/sec, $\omega \sim 1$

Drawing Of Pellicular Support



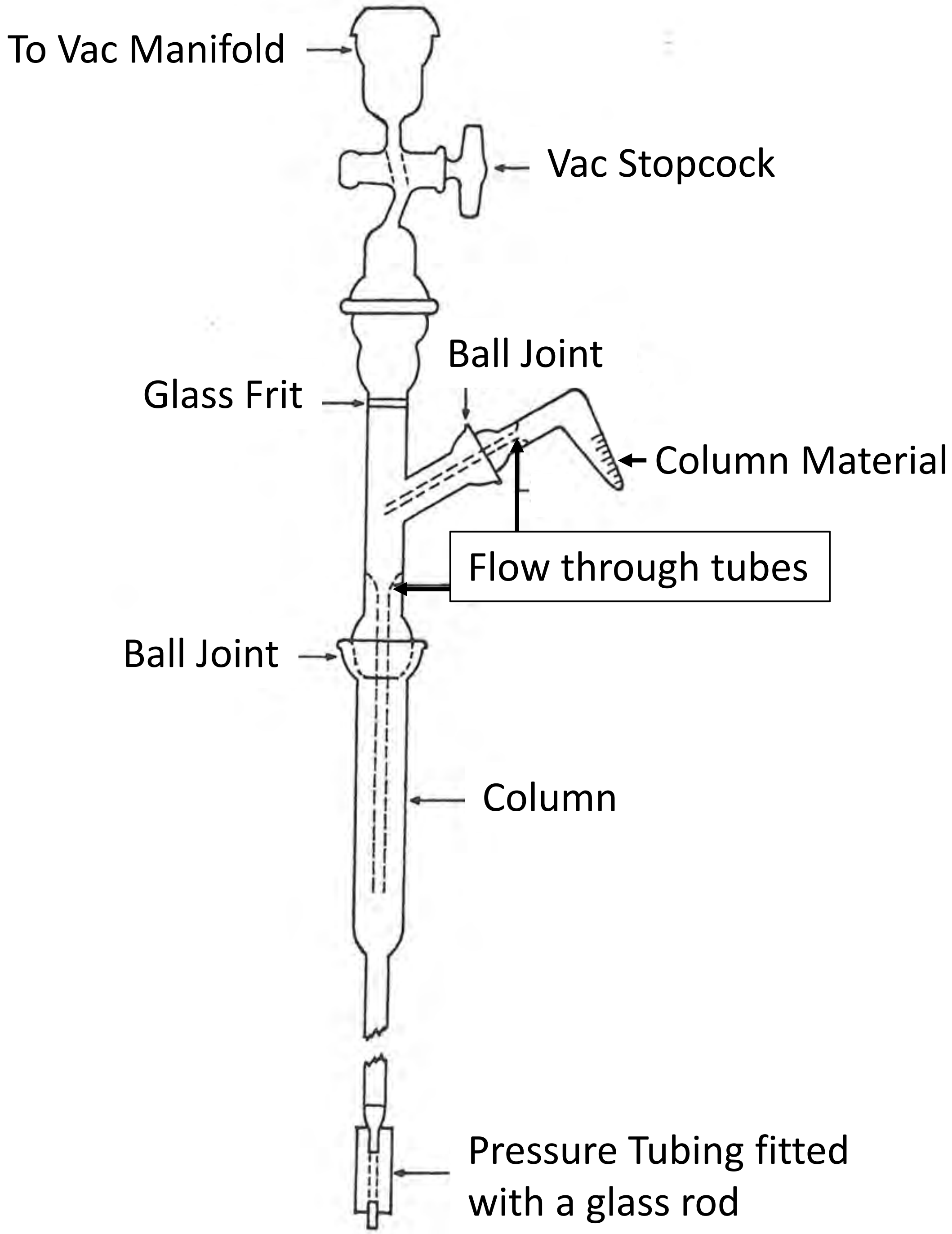
Factors Affecting Band Spreading in EXC

Stationary phase diffusion:

$$H = q \bullet \frac{k'}{(1+k')^2} \bullet \frac{{d_\ell}^2 v}{D_s}$$

H = plate height (HETP)
q = geometrical configuration factor
k' = FCV to peak maximum
d_ℓ = depth of stationary phase
D_s = diffusion coefficient in the stationary phase
v = interstitial flow velocity

Apparatus for dry packing in a vacuum



EXC System Used To Evaluate Packing Efficiency

$$Cd^{2+} + 2HCl + \overline{2R_4N^+Cl^-} \leftrightarrows \overline{(R_4N^+)_2CdCl_4^{2-}} + H^+$$

Calculation of Theoretical Elution Curve

$$(c)_v = c_{max} \exp - \frac{N(V_{max} - V)^2}{2V_{max} \cdot V}$$

Theoretical points calculated using the equation above:

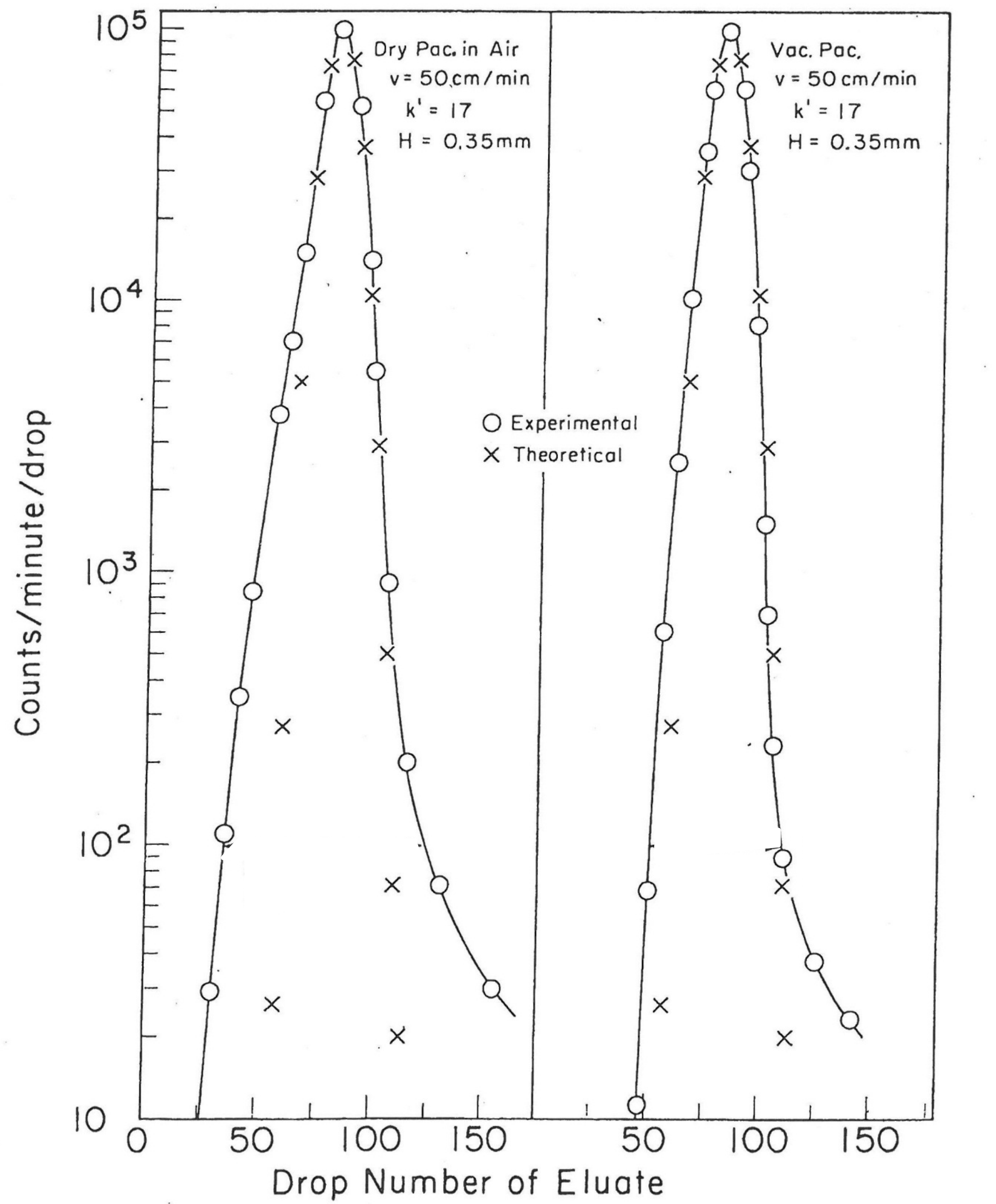
Where:

$(c)_v$ = Concentration of solute at the corresponding elution volume (V)

C_{max} = Peak concentration

V_{max} = Elution volume at C_{max}

N = Number of theoretical plates



Elution curves of Cd^{2+} at high v for two different column pack procedures.

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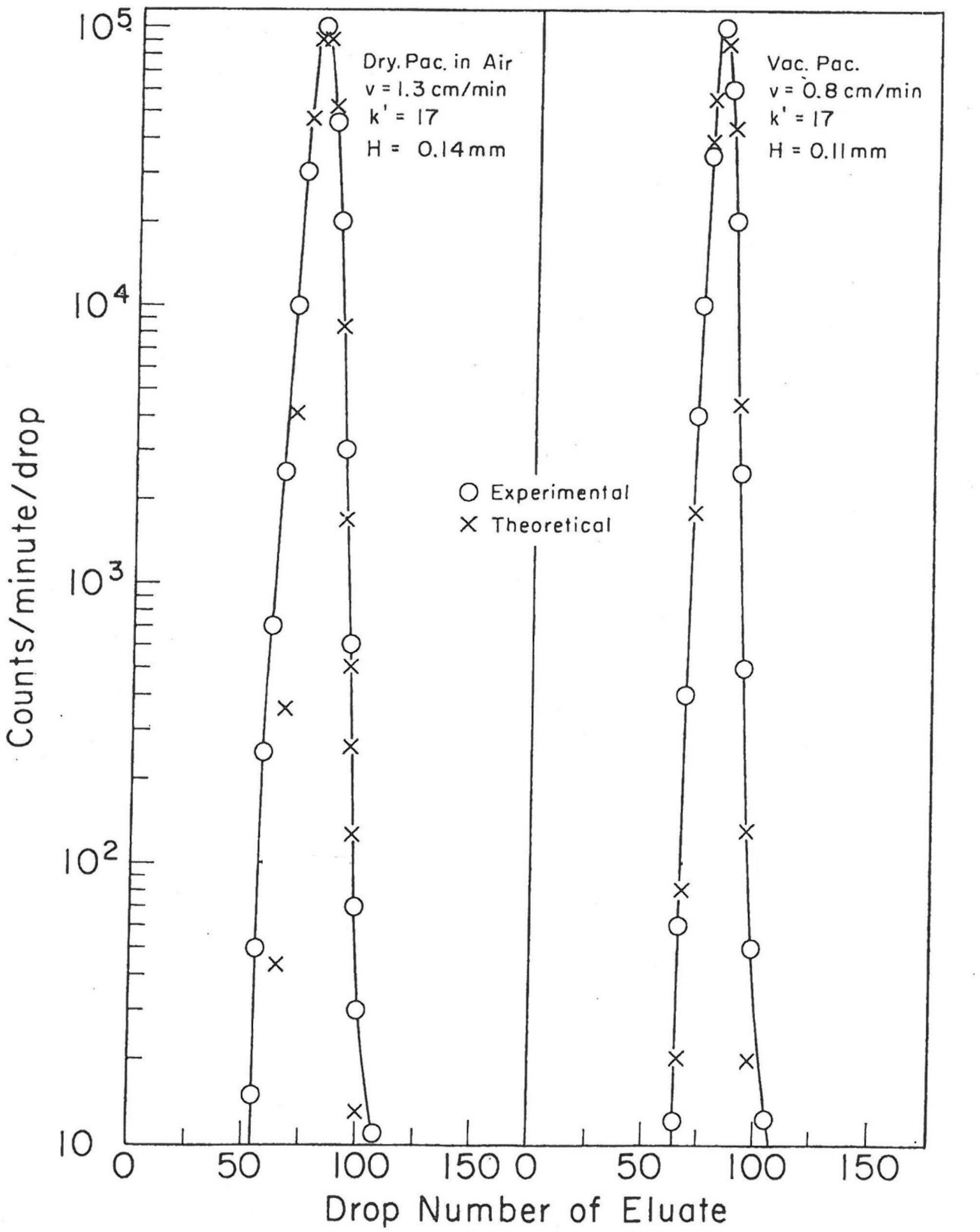
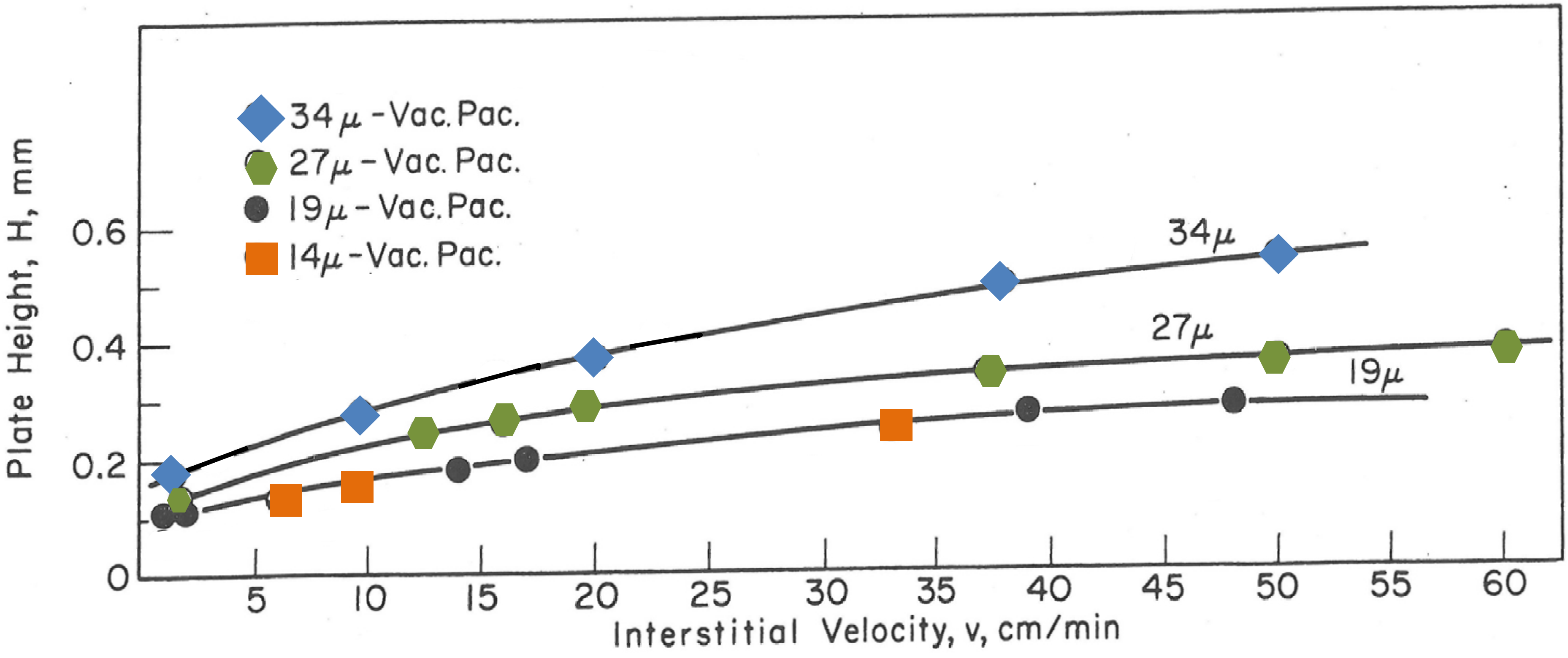


Elution curves of Cd^{2+} at high v for two different column pack procedures.

The effect of particle size on H vs v I w/o TCMA • Cl on Zipax, mobile phase 7.1M, HCl 60°C, k’ = 17



Factors Affecting Band Spreading in EXC

Flow phenomena:

$$H = \frac{1}{1/2\lambda_i d_p + D_m/\omega_i {d_p}^2 v}$$

H = plate height (HETP)
d_p = particle diameter
D_m = mobile phase diffusion coefficient
v = interstitial flow velocity
λ_i, ω_i = geometrical constants related to particle size and shape

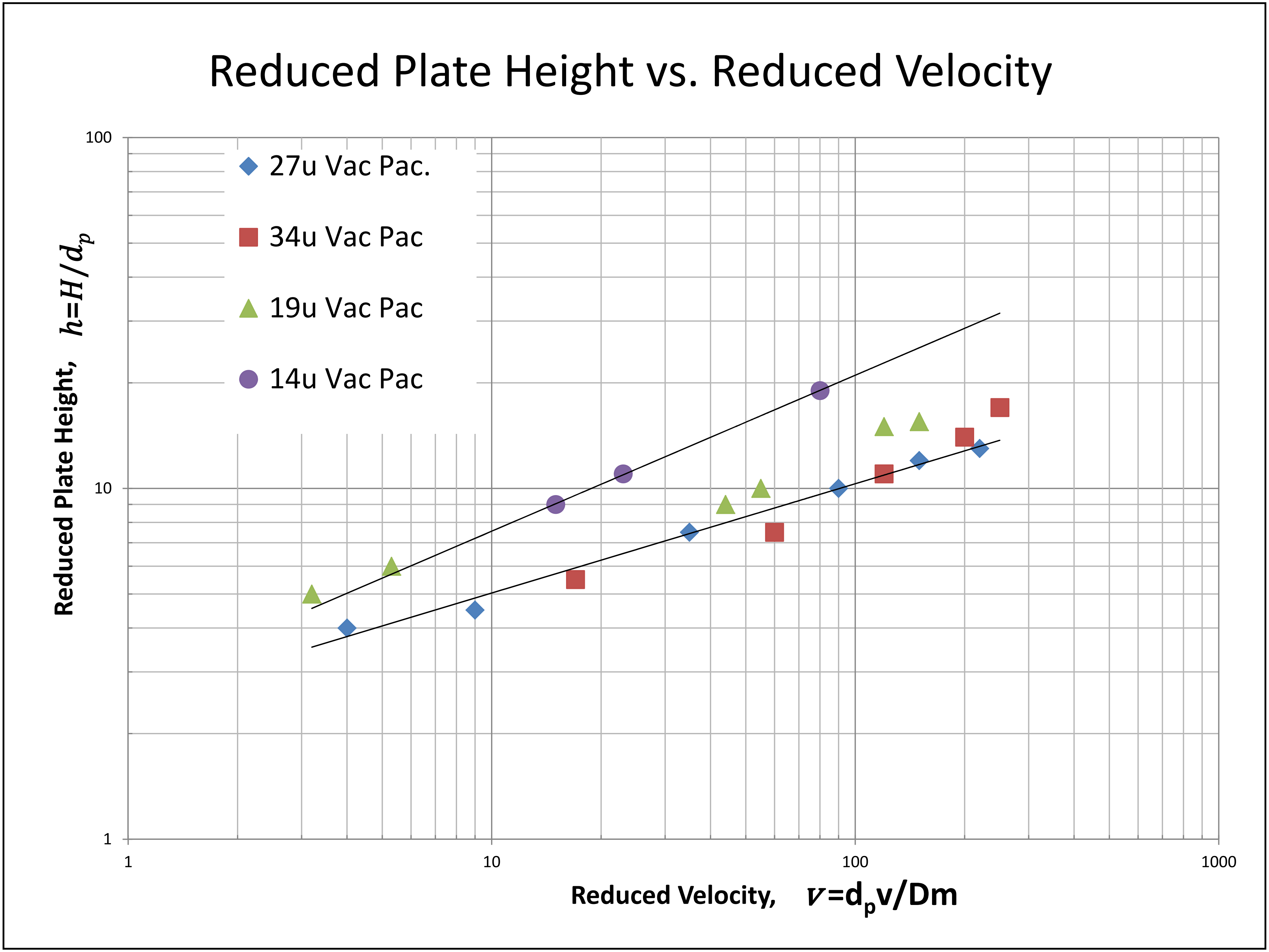
Flow phenomenon in terms of reduced parameters

Flow phenomena:

$$\mathrm{H} = \frac{1}{1/2\lambda_i d_p + D_m/\omega_i d_p{}^2 v}$$

Divide both sides by d_p and rearrange

$$\mathrm{h} = \frac{\mathrm{H}}{d_p} = 2\lambda + \frac{\omega d_p v}{D_m}$$


Reduced Plate Height vs. Reduced Velocity
◆ 27u Vac Pac.
■ 34u Vac Pac
▲ 19u Vac Pac
● 14u Vac Pac
100
10
1
1
10
100
1000
Reduced Plate Height, $h = H/d_p$
Reduced Velocity, $\nu = d_p v/Dm$

Factors Affecting Band Spreading in EXC

Extraction kinetics:

$$\mathrm{H} = 2 \bullet \frac{\mathrm{k}'}{(1 + \mathrm{k}')^2} \bullet \frac{\mathrm{v}}{\mathrm{k_{oa}}}$$

H = plate height (HETP)

k' = FCV to peak maximum

v = interstitial flow velocity

k_{oa} = organic to aqueous rate constant

Interfacial mass transfer coefficients: k_{ao} and k_{oa}

1. $$-\frac{d[\overline{M}]}{dt} = \frac{Q}{V}\left(k_{oa}[\bar{M}] - k_{ao}[M^{3+}]\right)$$
2. $$ln\left(1 - \frac{[\bar{M}]}{[\bar{M}]_e}\right) = -\left(\frac{\mathrm{Q}}{\mathrm{V}}\right)(k_{oa} + k_{ao})t$$
3. $$K_d = \frac{[\bar{M}]_e}{[M^{3+}]_e} = \frac{k_{ao}}{k_{oa}}$$
4. $$ln\left(1 - \frac{[\bar{M}]}{[\bar{M}]_e}\right) = -\left(\frac{Q}{V}\right)(1 + K_d)k_{oa}t$$

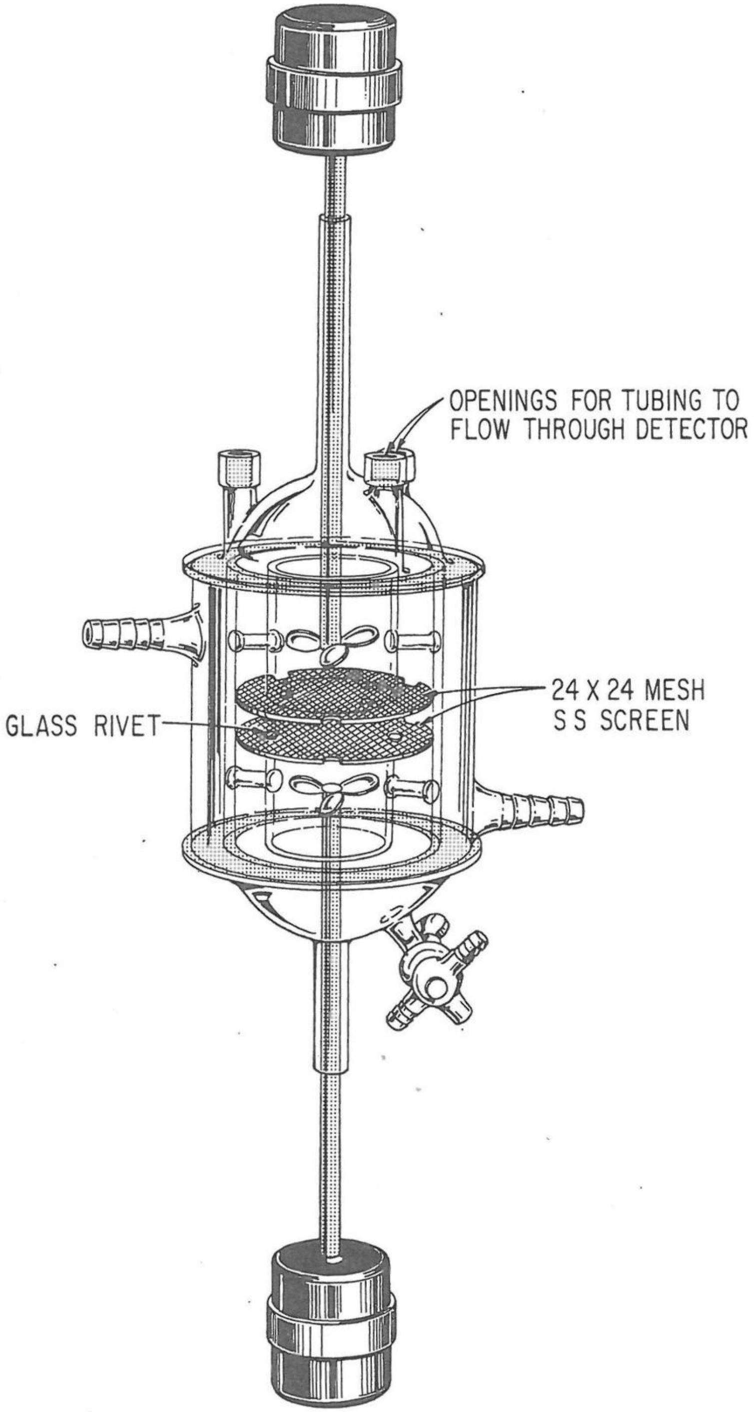
A. [M] and $[M^{3+}]$ are the concentration in the organic and aqueous phase respectively

B. $\bar{\mathrm{M}}$and $\bar{\mathrm{M}}_e$ are the organic concentrations at time t and at equilibrium

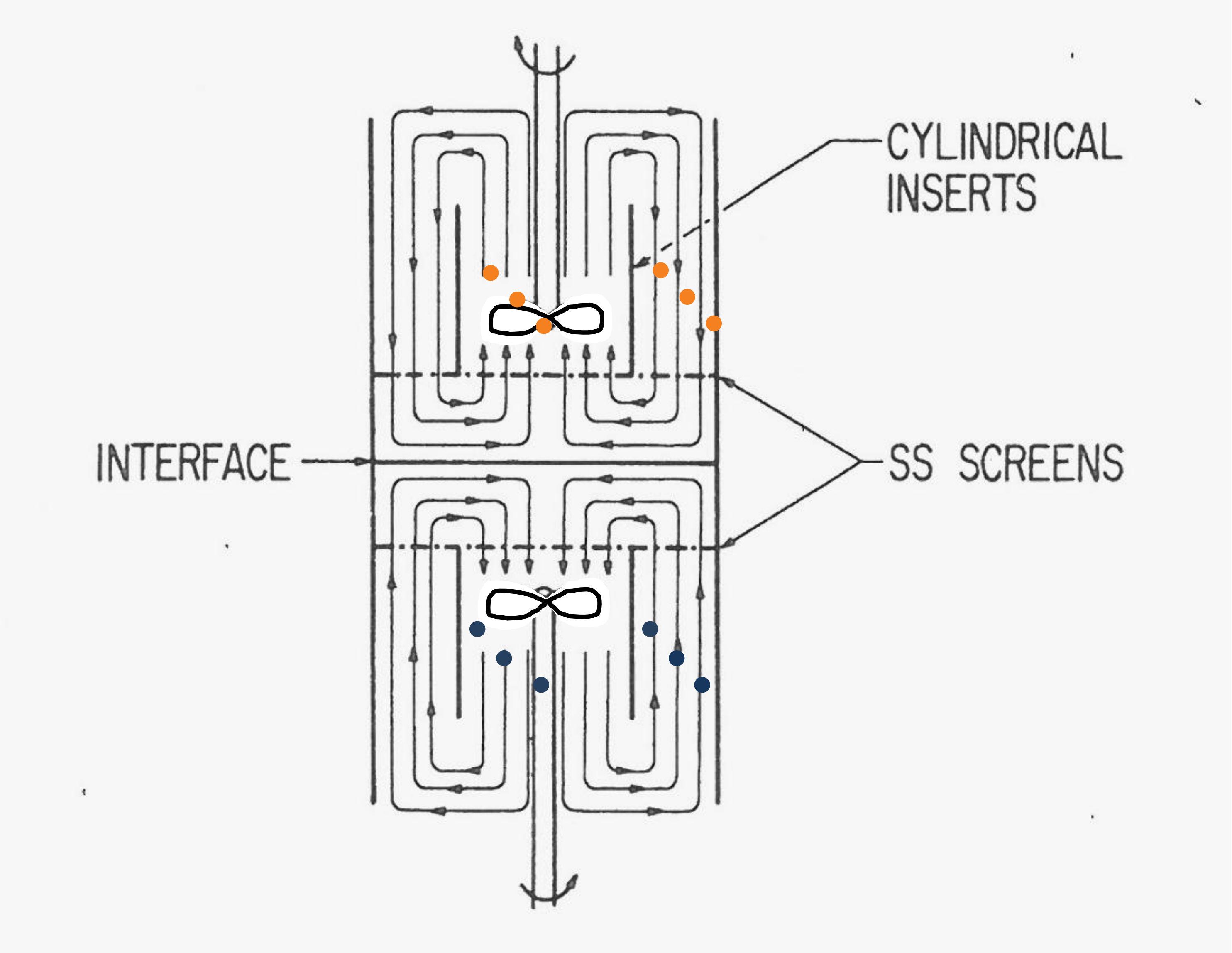
C. V(cm^3) is the volume of either the aqueous or organic phase

D. Q(cm^2) is the interfacial area

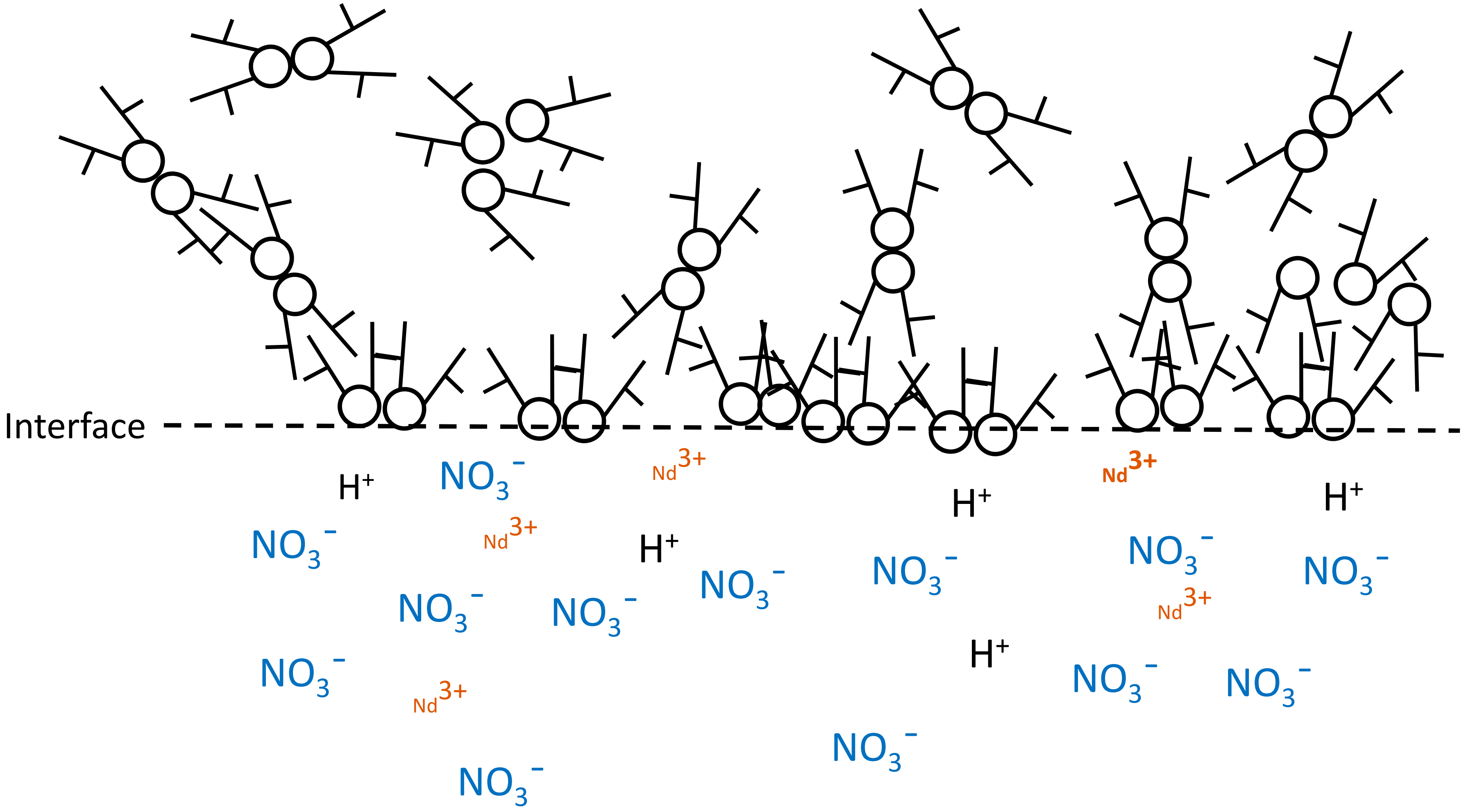
Forced convection, constant-interfacial-area stirred cell (ARMOLLEX)



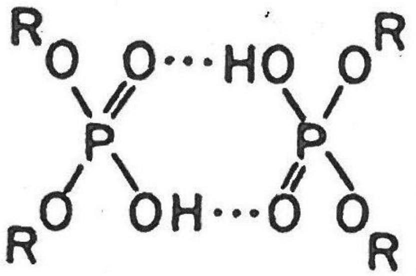
Convection inside the ARMOLLEX cell



Interface and bulk organic phase structure
10^{-1} F HDEHP

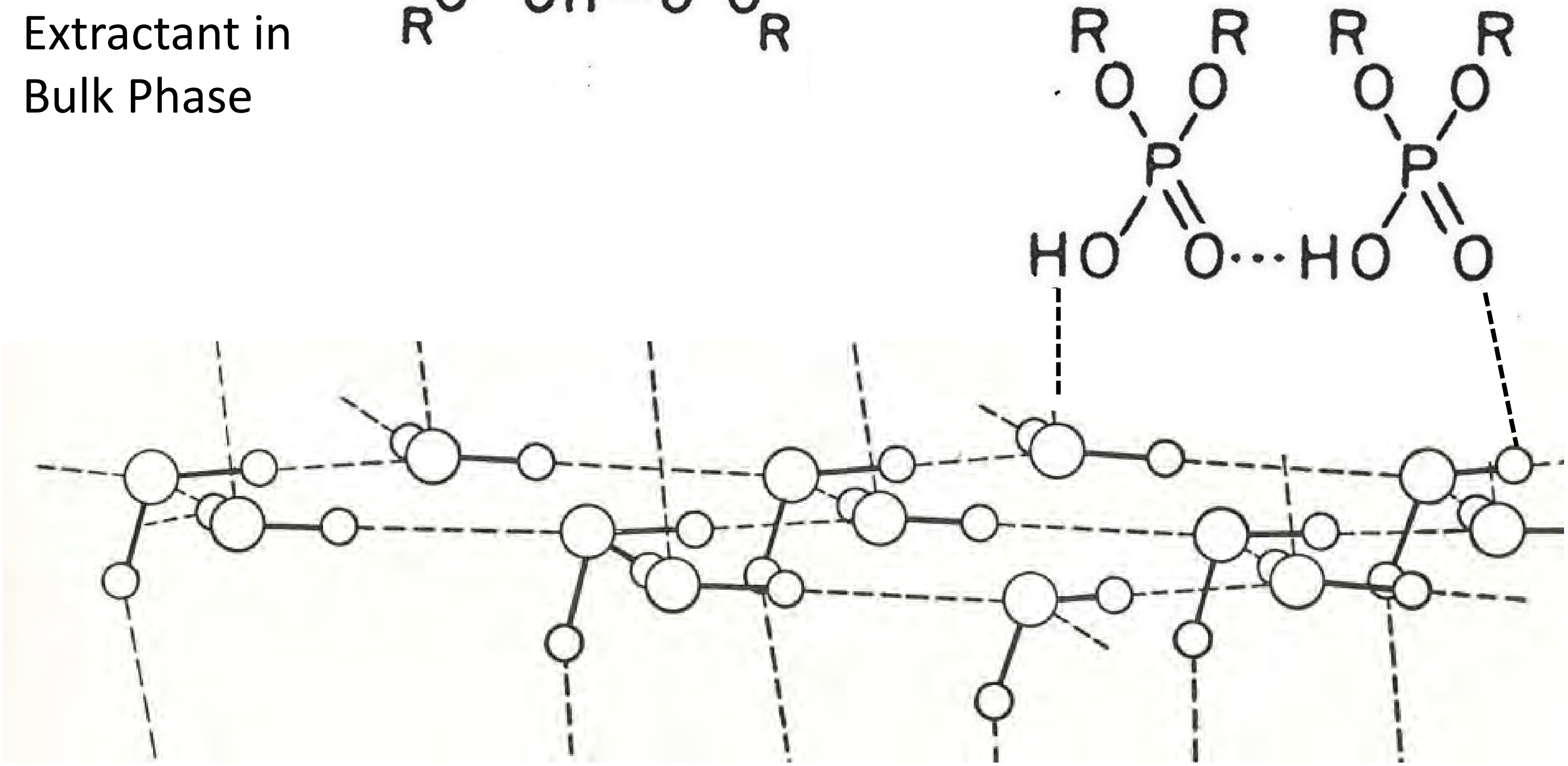


Configuration of singe layer of water molecules and HDEHP at the aqueous–organic interface

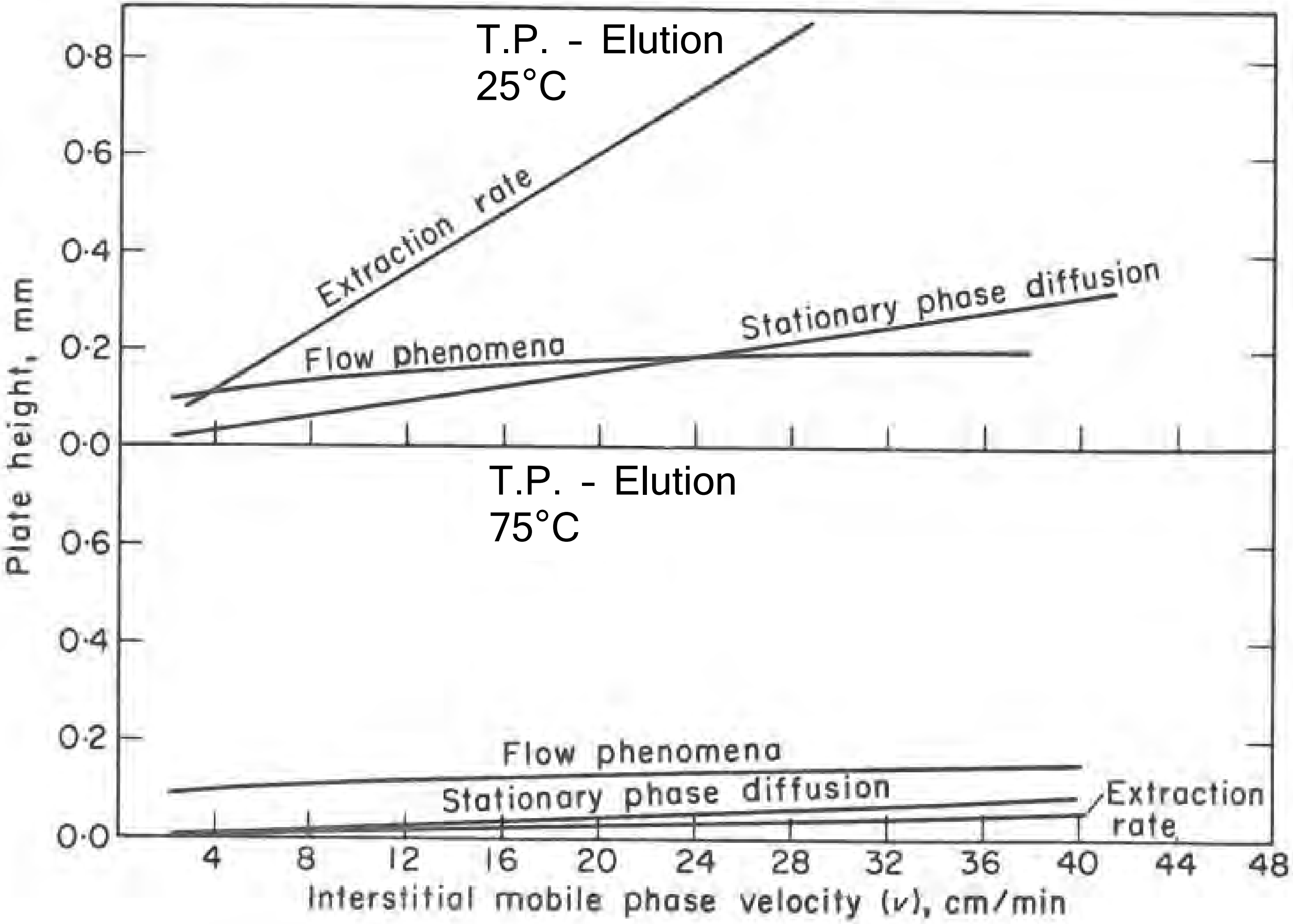


Extractant in
Bulk Phase

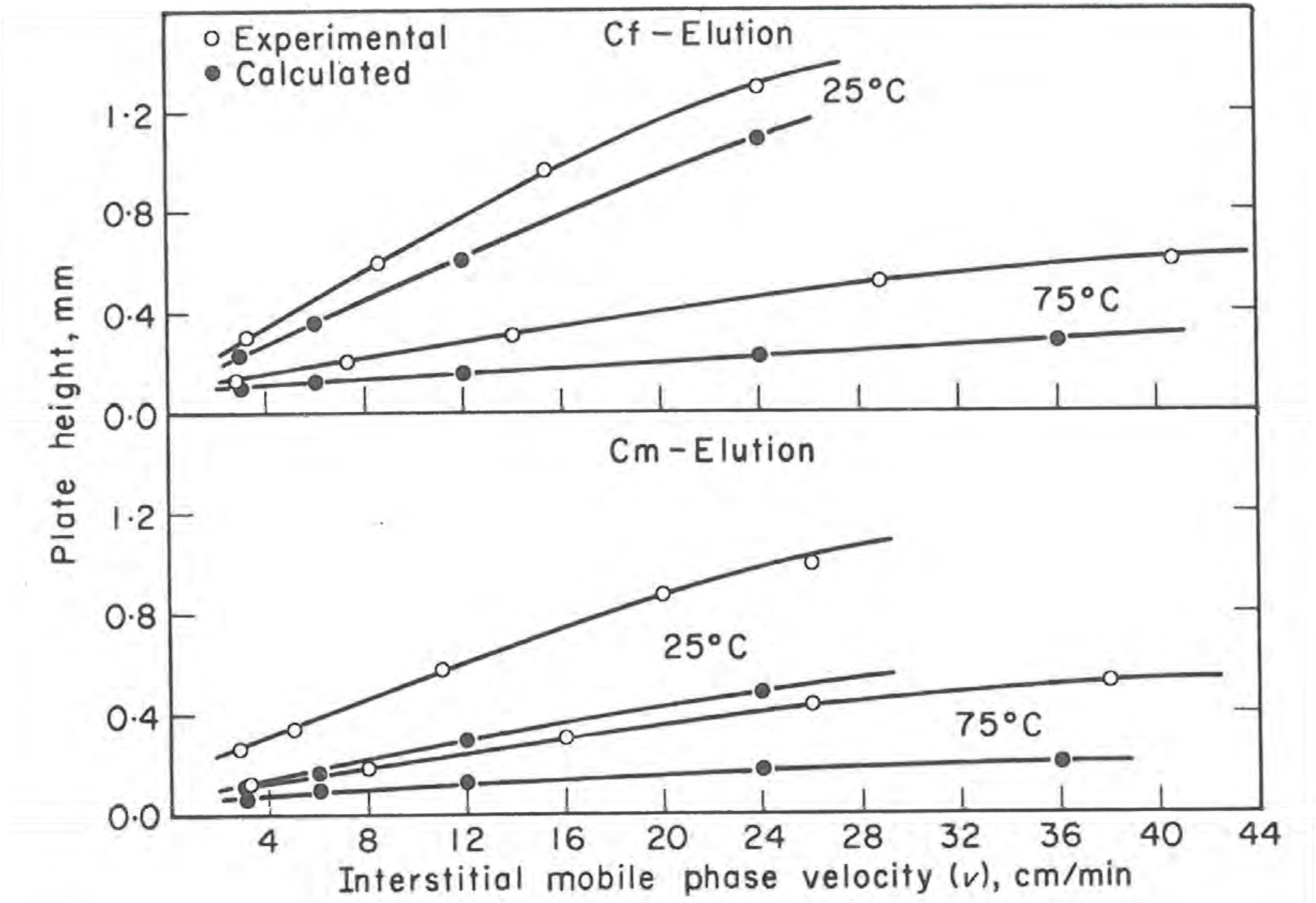
Extractant at
Interface

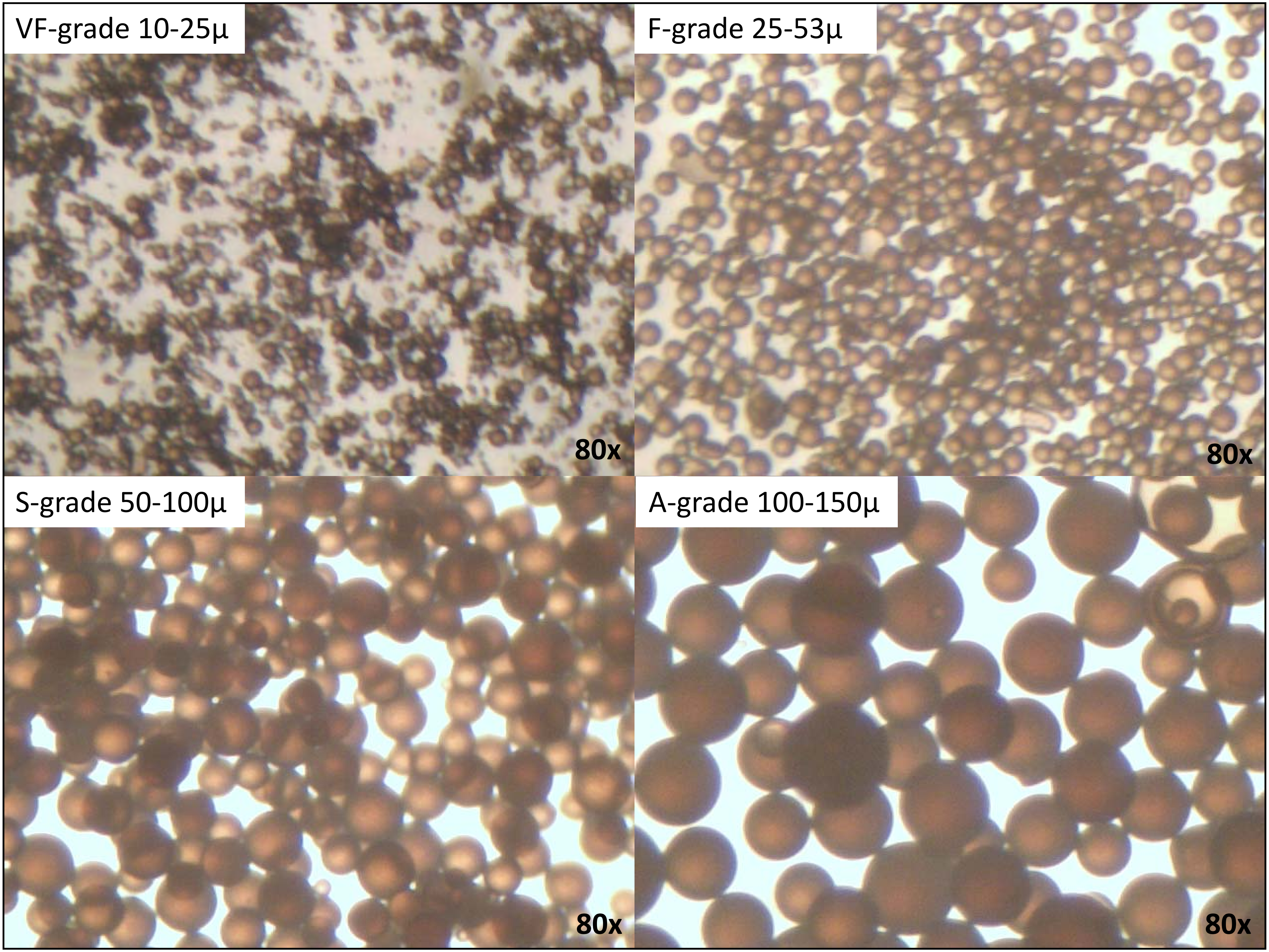


Comparison of the relative contributions of flow phenomena, stationary phase diffusion and extraction rate to the plate height for the elution of T.P.s from HDEHP on 35µ Celite.

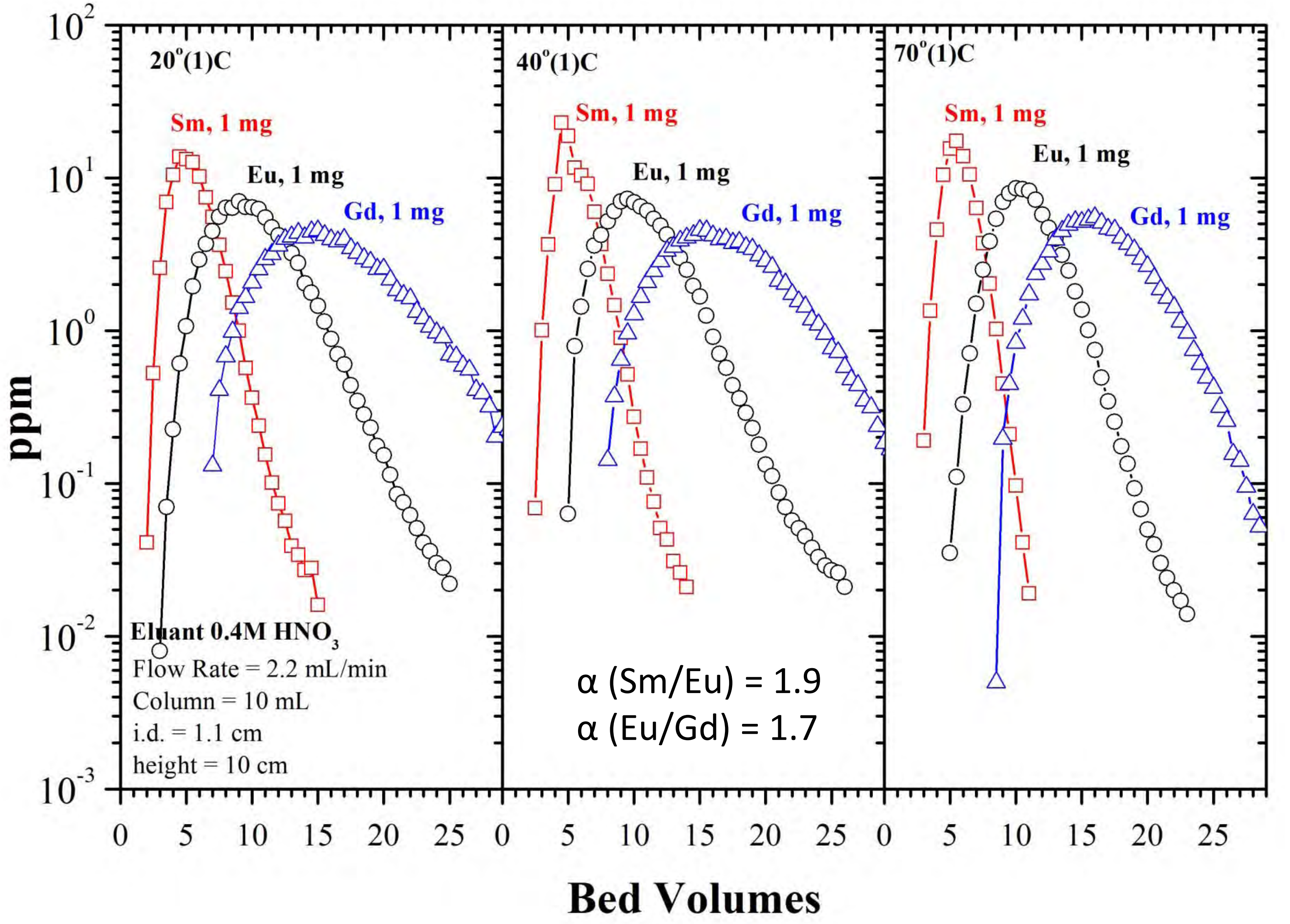


Comparison of calculated and experimental H vs V curves for the elution of Cm(II) and Cf(III) from HDEHP on 35µ Celite at 25°C and 75°C




VF-grade 10-25µ
80x
F-grade 25-53µ
80x
S-grade 50-100µ
80x
A-grade 100-150µ
80x

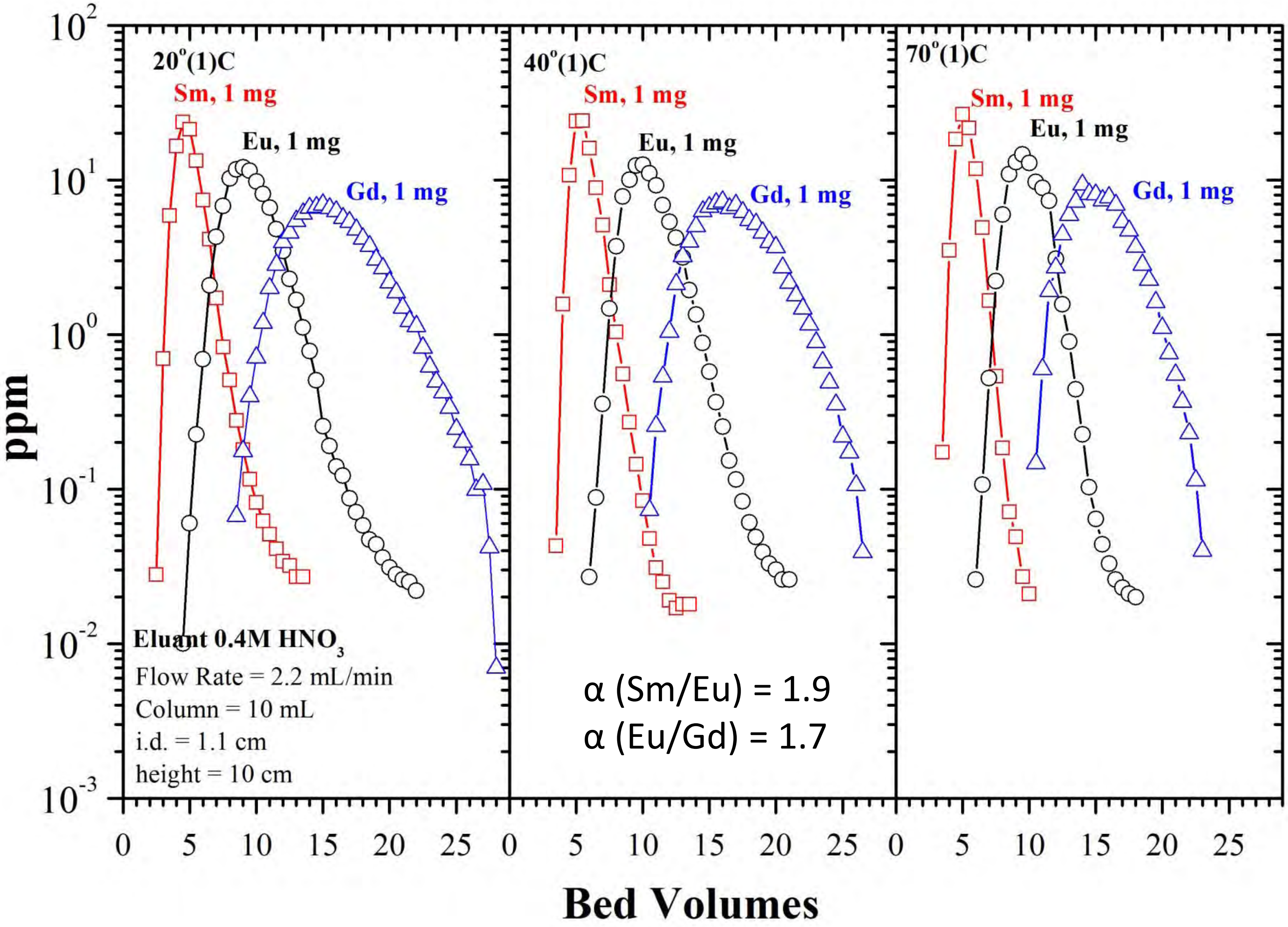
Slurry Packed LN Resin (A-grade), 100-150 µm



α (Sm/Eu) = 1.9

α (Eu/Gd) = 1.7

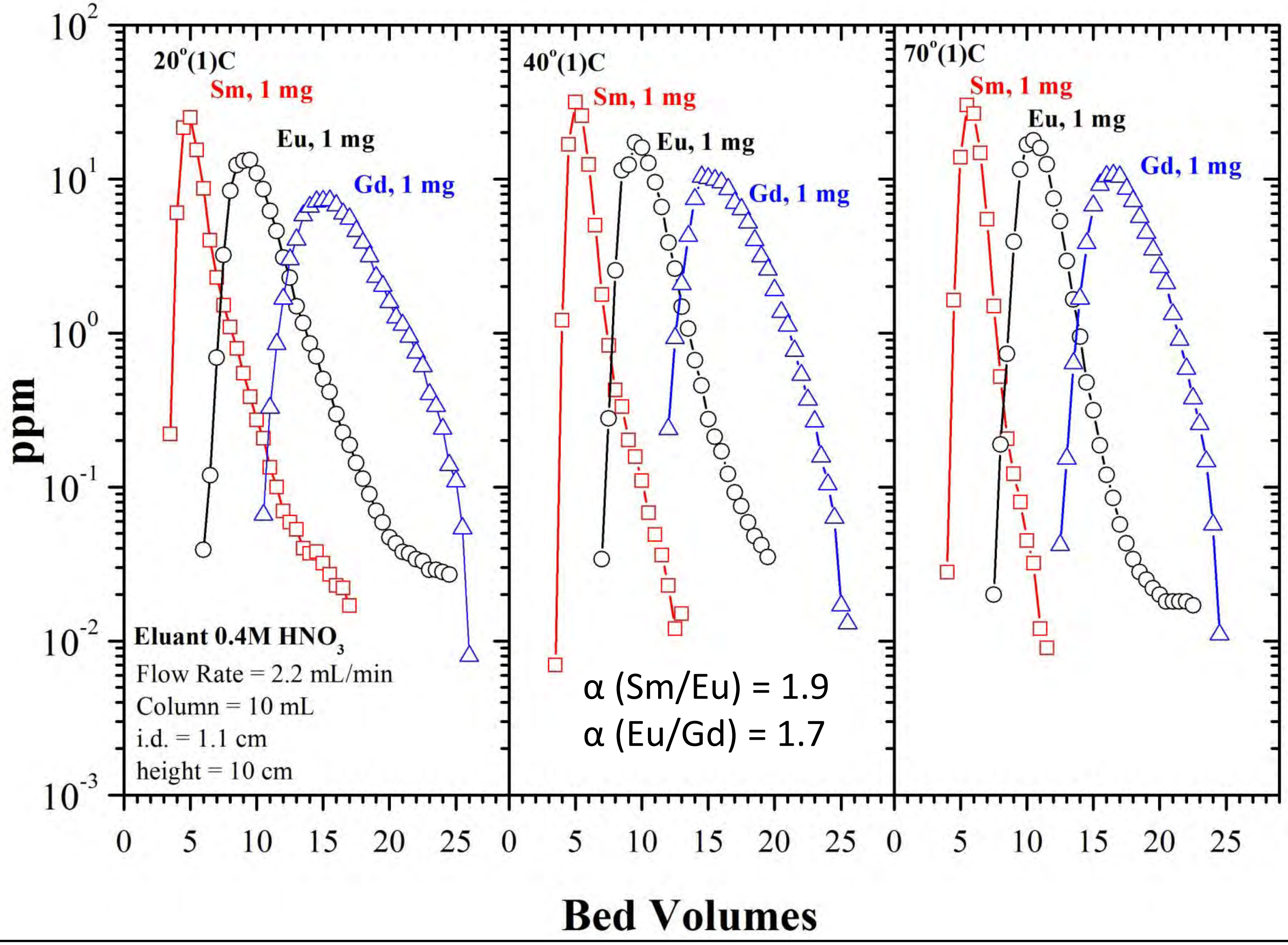
Slurry Packed LN Resin (S-grade), 50-100µm



α (Sm/Eu) = 1.9

α (Eu/Gd) = 1.7

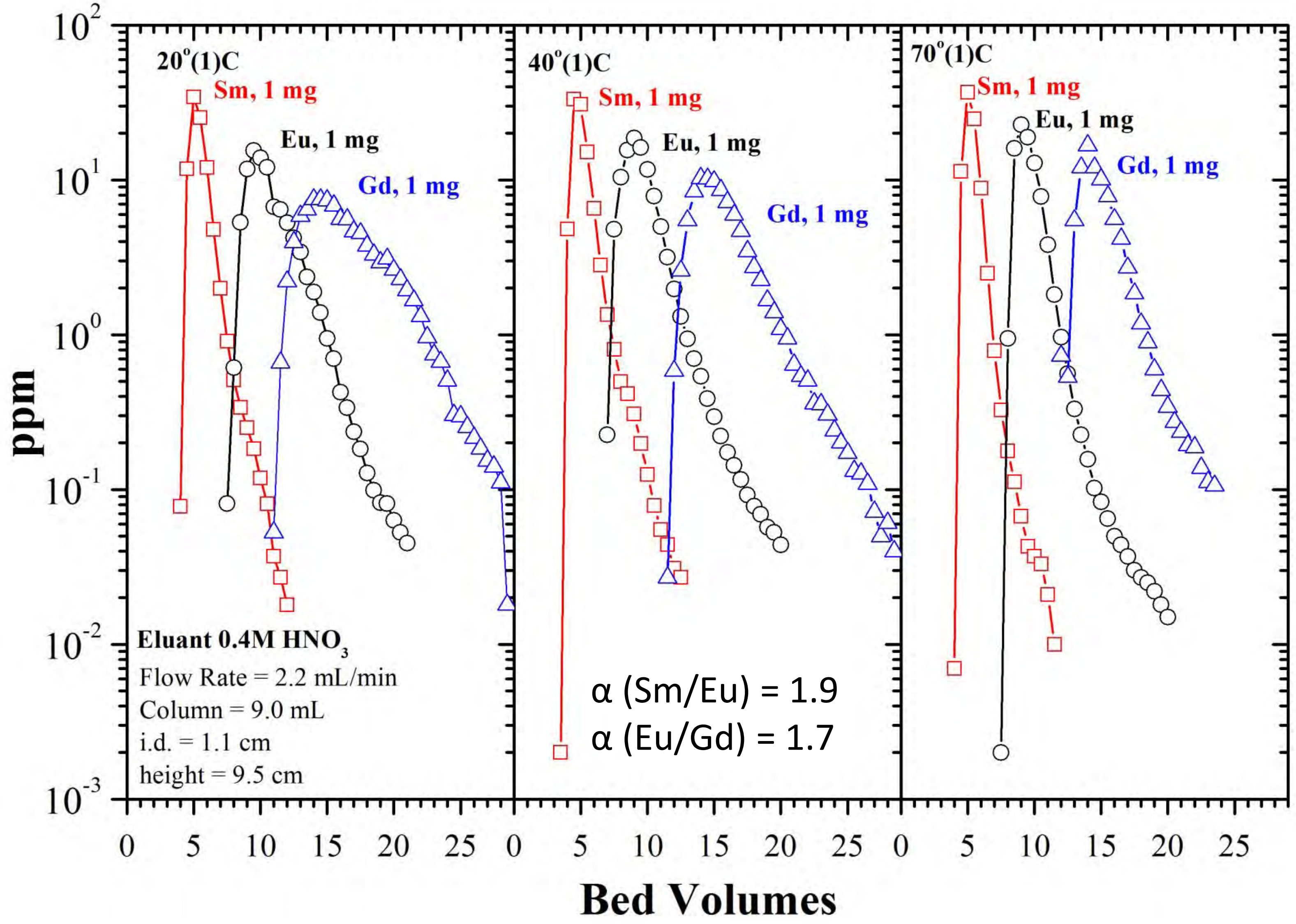
Slurry Packed LN Resin (F-grade), 25-50μm



α (Sm/Eu) = 1.9

α (Eu/Gd) = 1.7

Slurry Packed LN Resin (VF-grade), 10-25μm

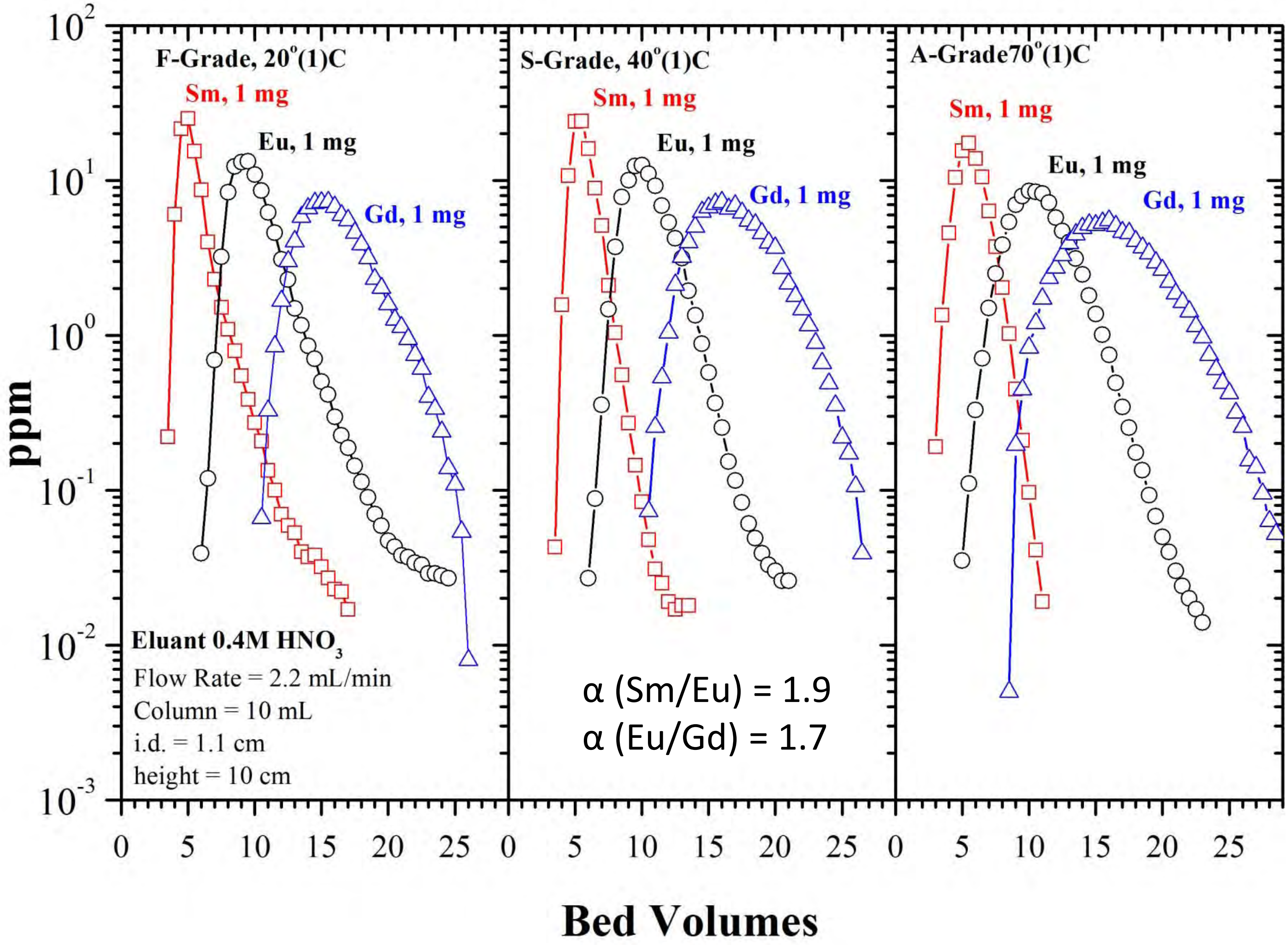


α (Sm/Eu) = 1.9

α (Eu/Gd) = 1.7

Particle Size (µm)	Col Length (mm)	Temp (°C)	Average HETP (mm)
VF 10-25	95	20	1.0
		40	1.0
		70	0.6
F 25-53	110	20	2.2
		40	1.6
		70	1.2
S 50-100	110	20	4.0
		40	2.6
		70	2.3
A 100-150	110	20	10.7
		40	6.9
		70	4.3

Slurry Packed LN Resin
Particle Size vs Temperature



α (Sm/Eu) = 1.9

α (Eu/Gd) = 1.7

Ref #	Reference	Slide #
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