ANALYSIS OF NITROCELLULOSE BY GPC

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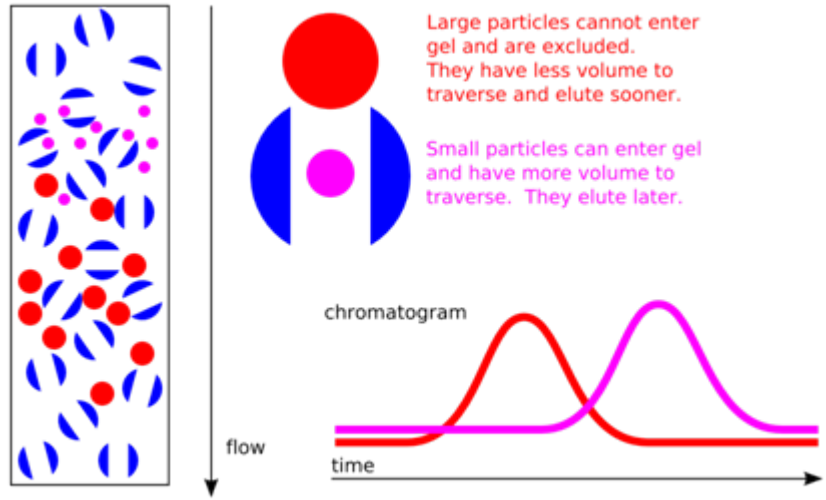


2001 Meetings

- 13th Feb 2001 – Viscotek Europe, Basingstoke
  - Cranfield Uni, MOD, ICI, Domino, BAE, DERA, AWE, Viscotek

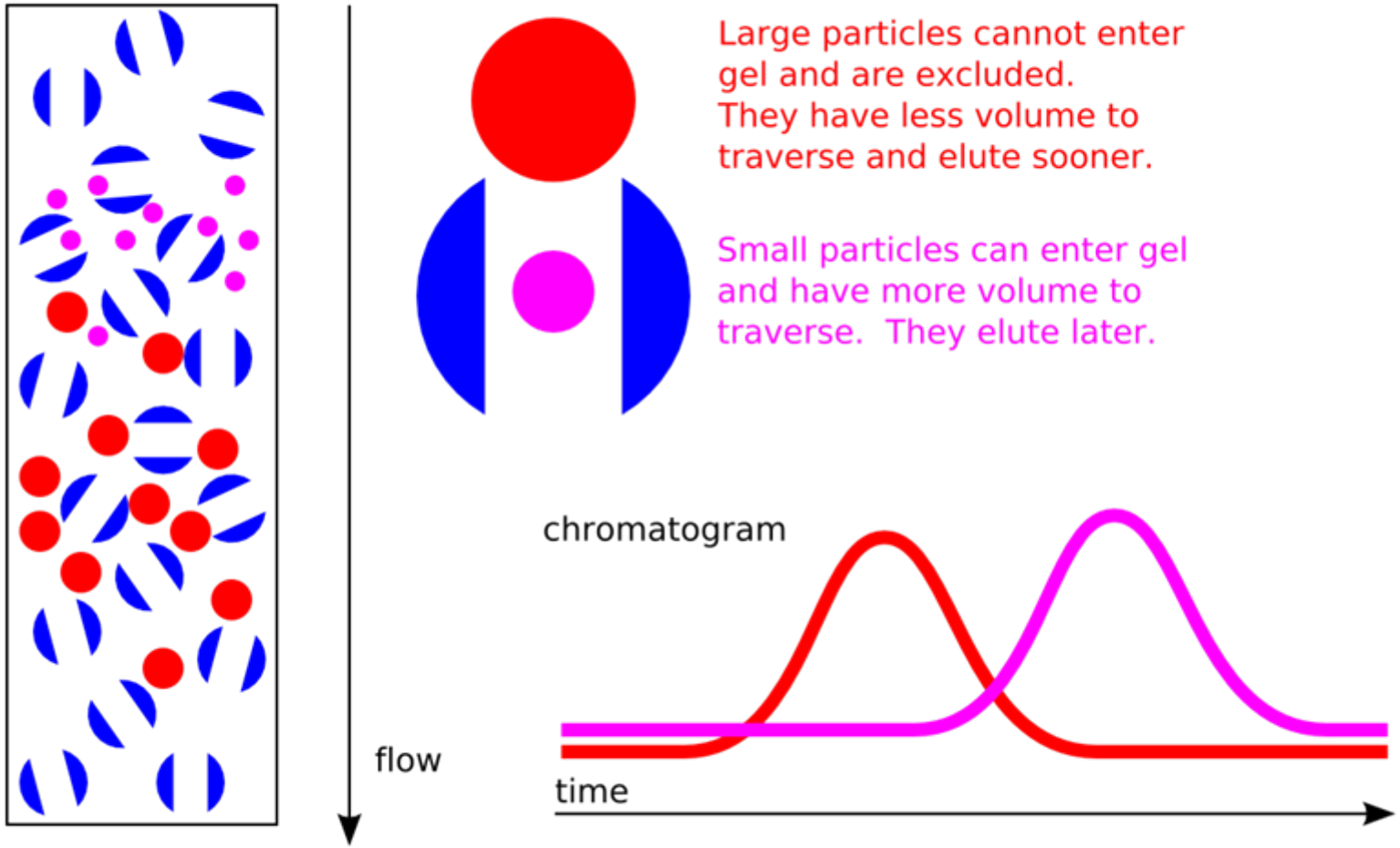
- 15th Nov 2001 – AWE/Viscotek, Portland House
  - AWE, BAE, Domino, FOI, ICI Nobel, DOSG, Nottingham Uni, Qinetiq, Cranfield Uni, Viscotek

Summary 2001 Meetings

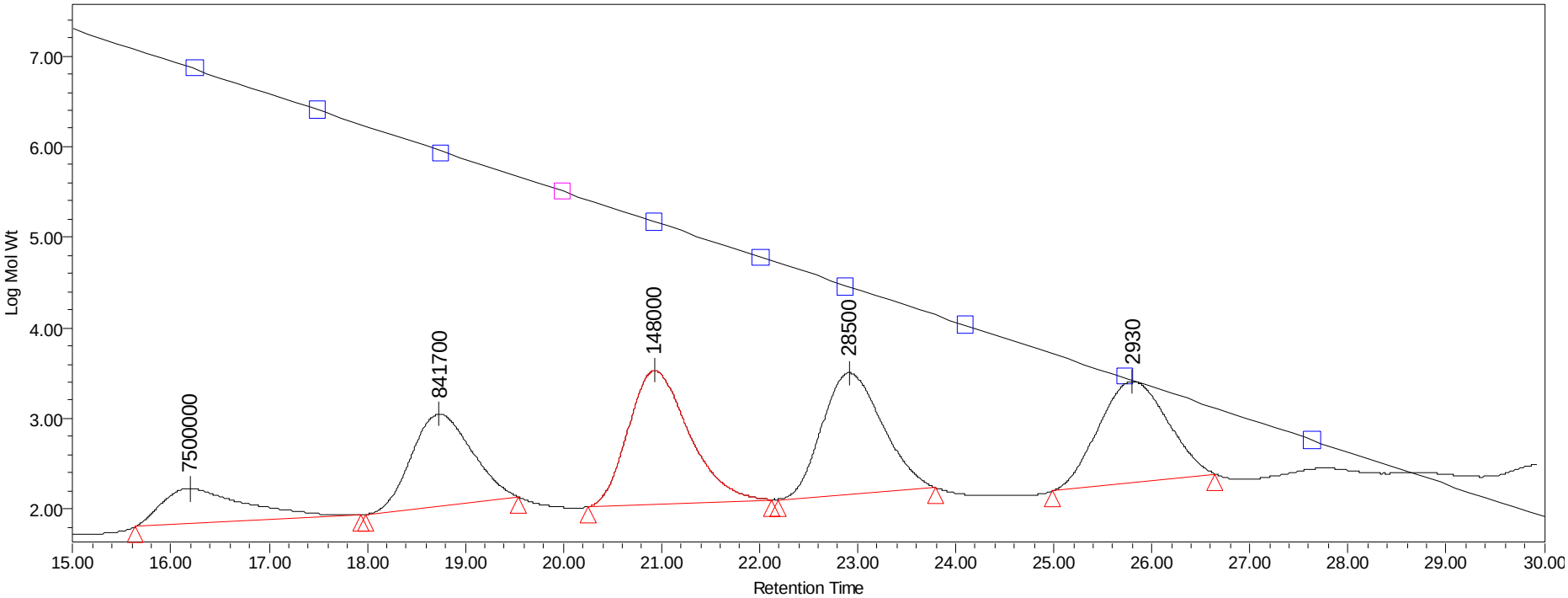
- **Problems**
- Polystyrene calibration problems (*relative*)
- Concentration effects
- Solvation effects

  "…..random number generators" (Sloan -2001)
- Fast eluting peaks/ pre-peaks
- Non-linearity of the Mark-Houwink-Sakurada Plot

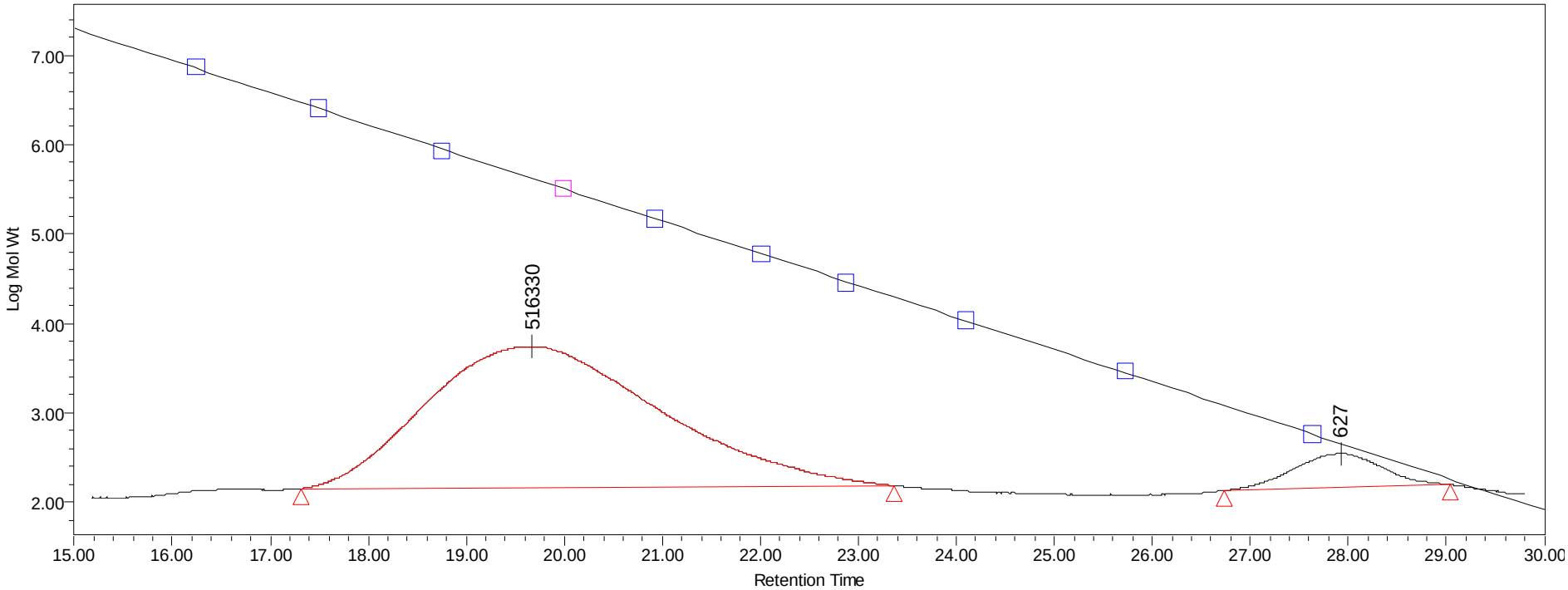
GPC/SEC


Large particles cannot enter gel and are excluded. They have less volume to traverse and elute sooner.
Small particles can enter gel and have more volume to traverse. They elute later.
flow
chromatogram
time

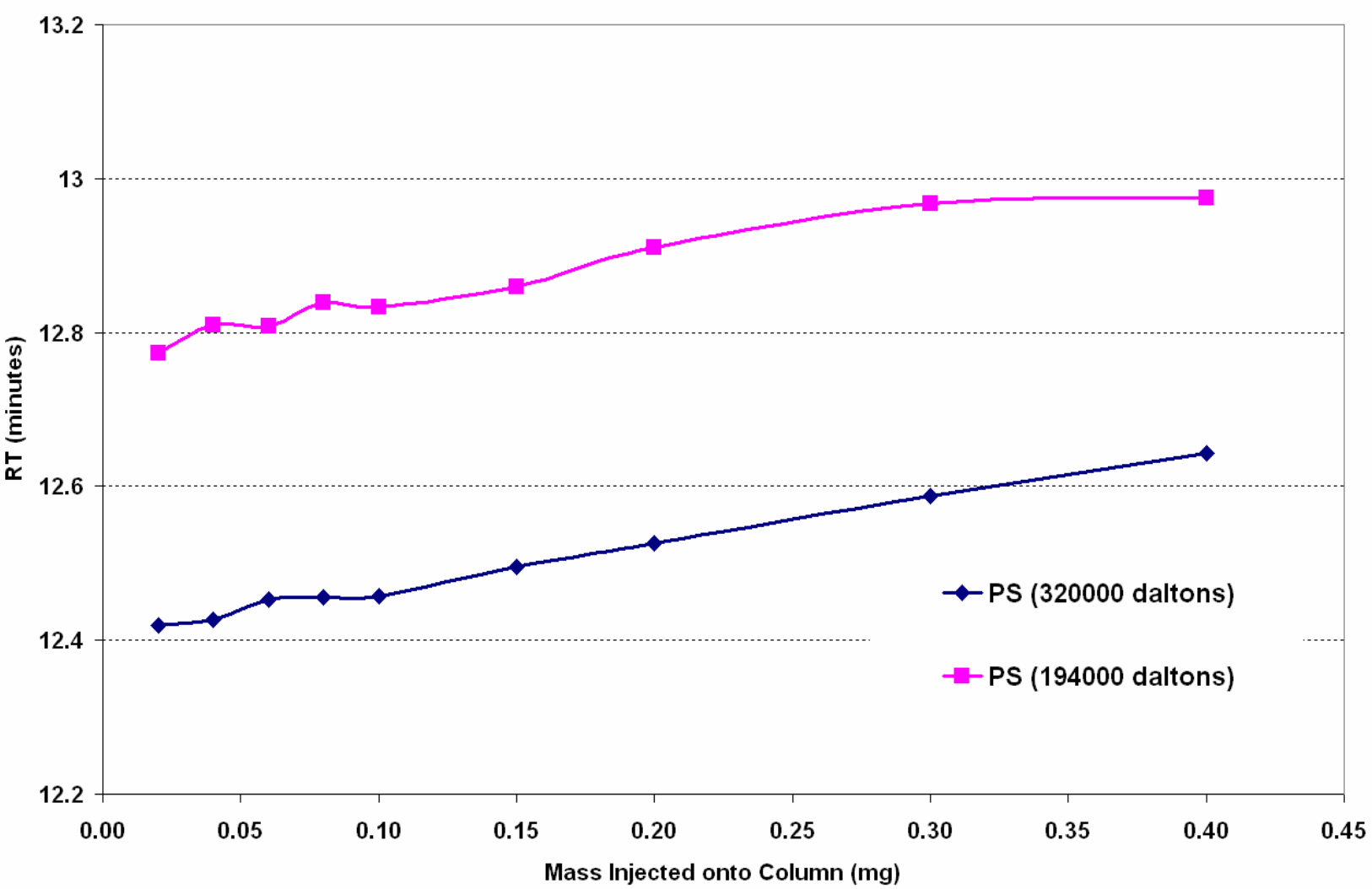
Polystyrene Calibration



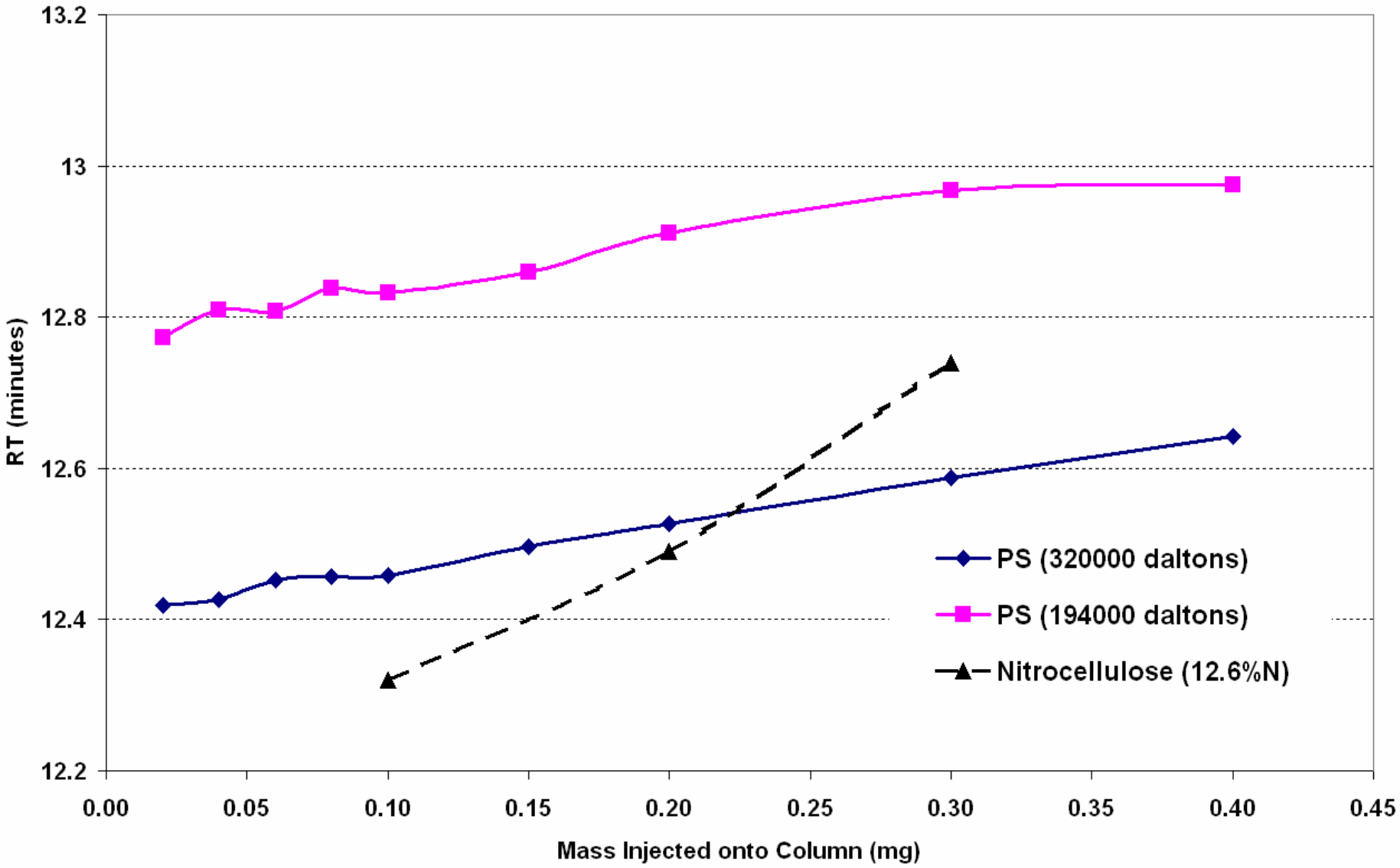
Polystyrene Calibration



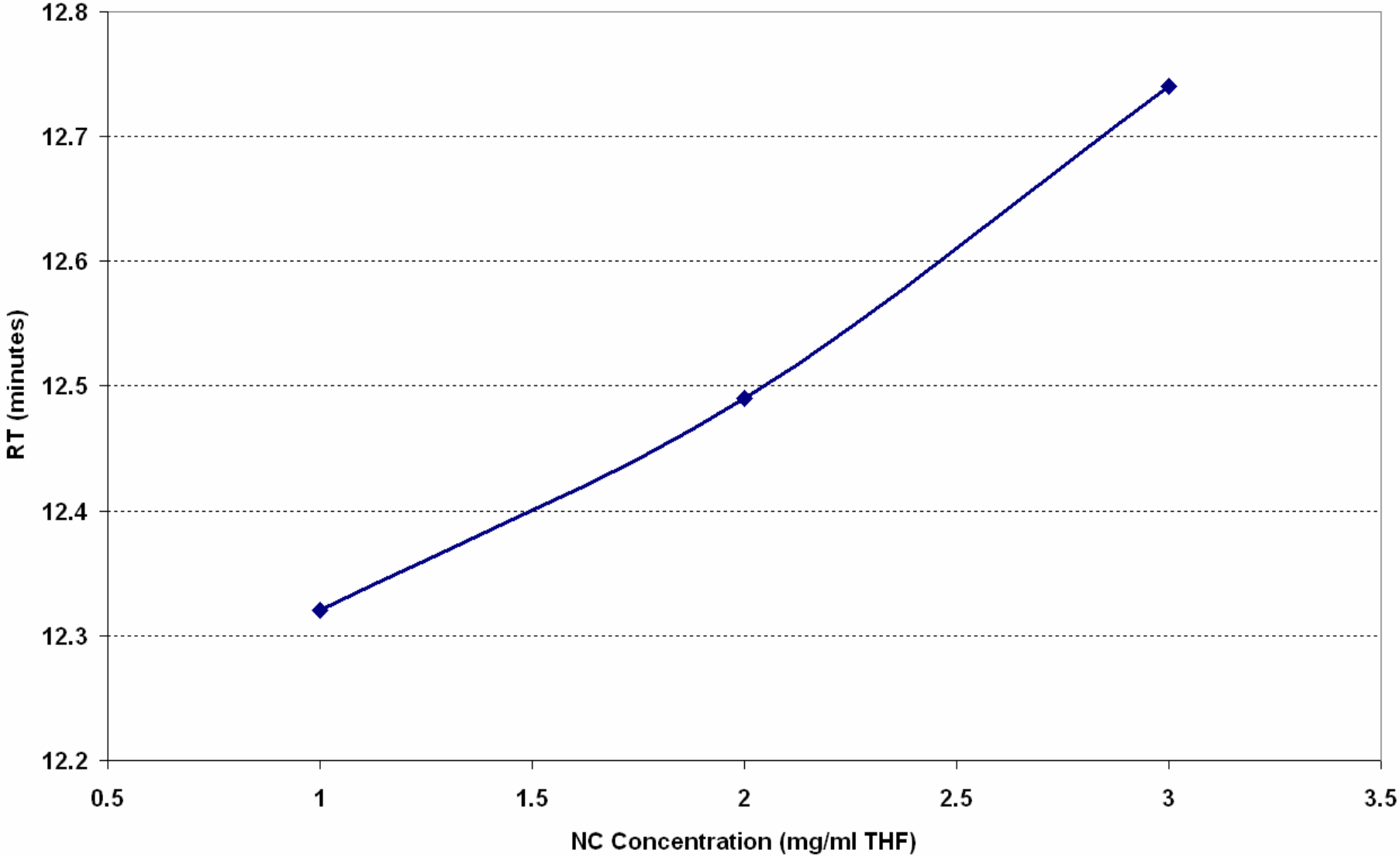
Polystyrene Calibration



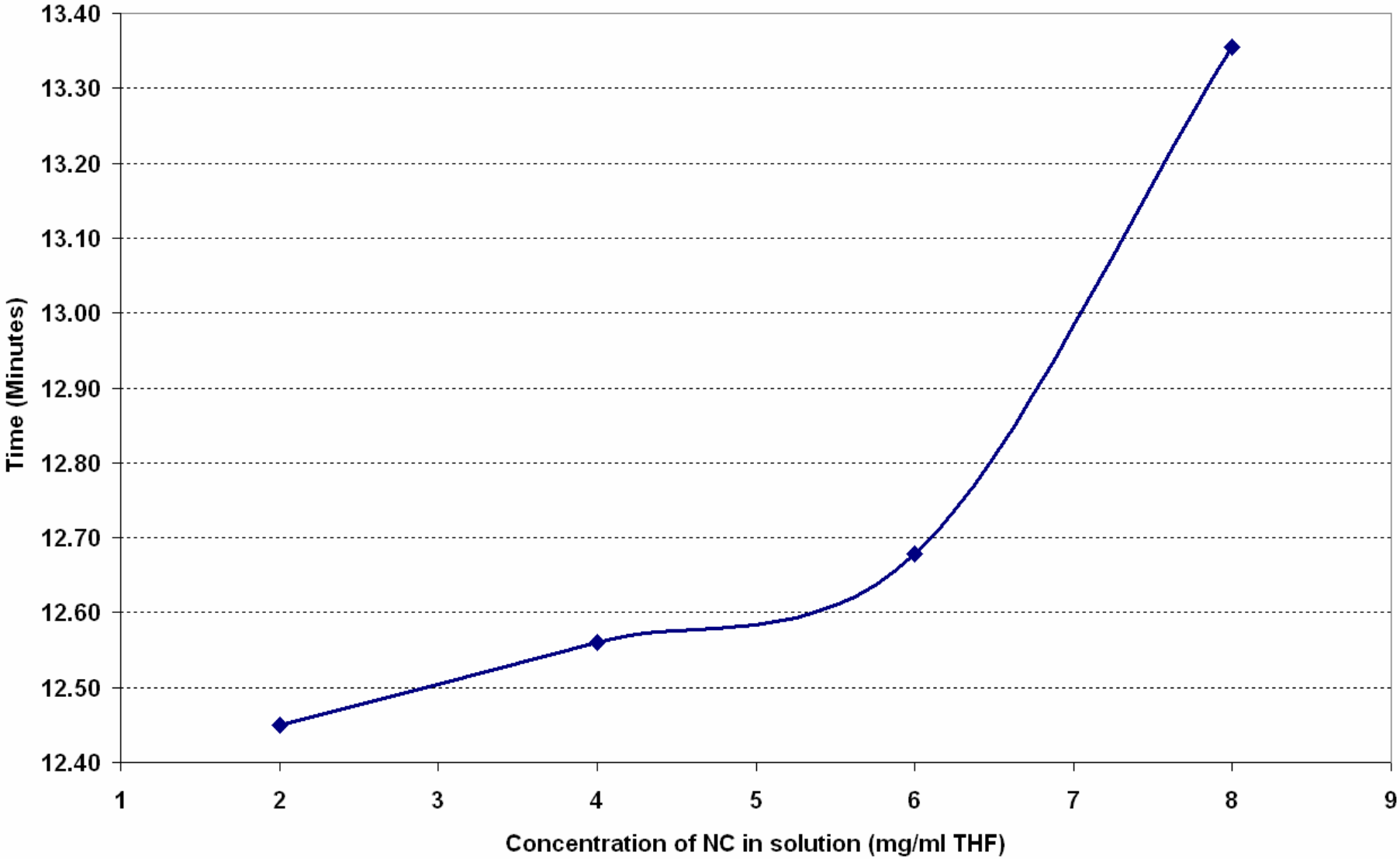
Polystyrene Calibration



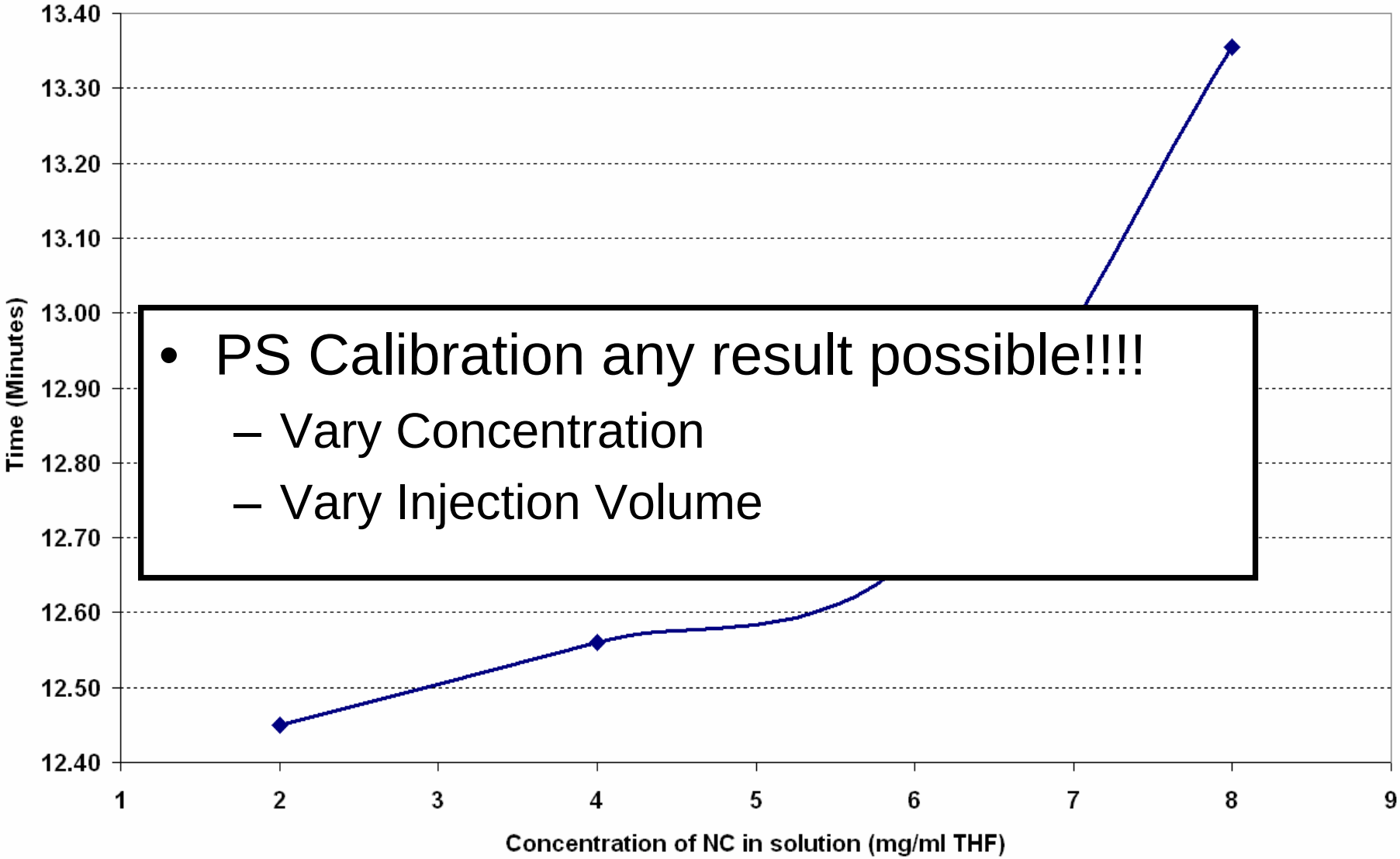
Concentration effects (100µl)



Concentration effects (0.2mg)

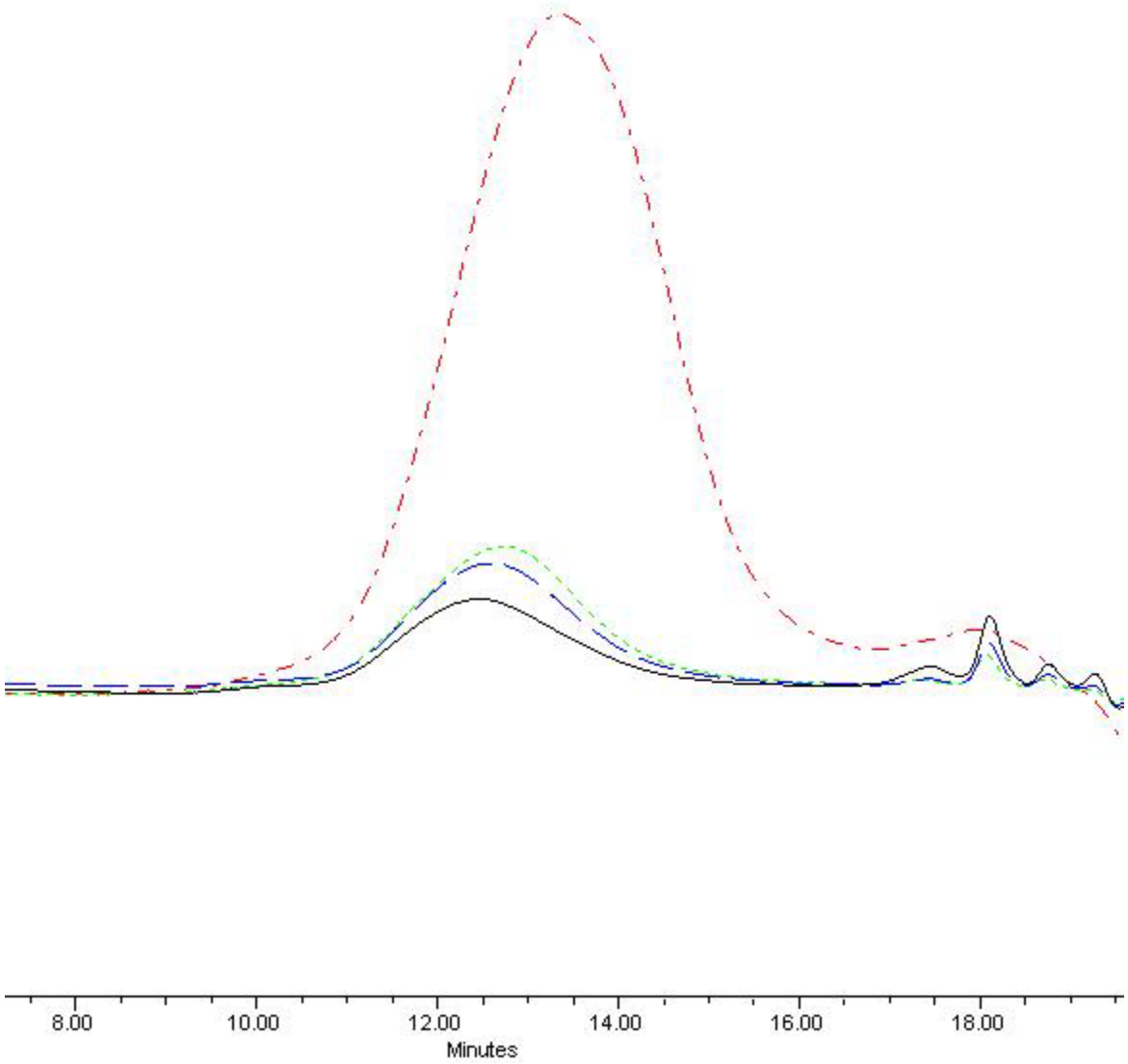


Concentration effects (0.2mg)



- PS Calibration any result possible!!!!
  - Vary Concentration
  - Vary Injection Volume

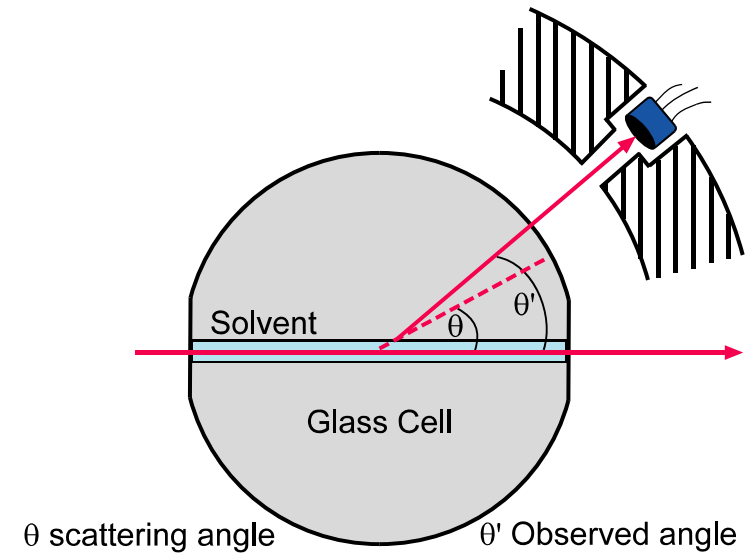
Concentration effects (0.2mg)



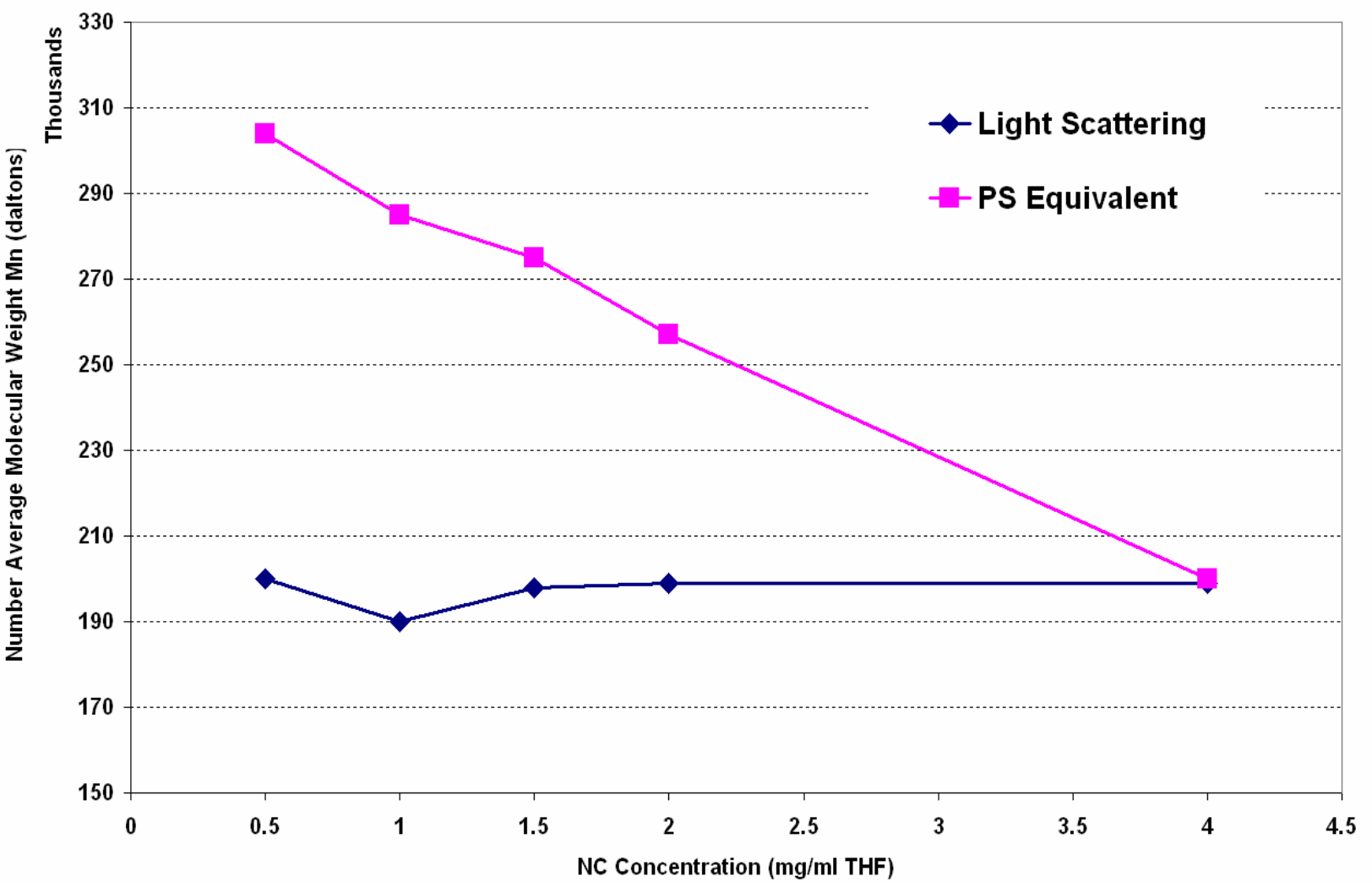
Concentration Effects of Nitrocellulose

- PS Calibration any result possible
  - Vary Concentration
  - Vary Injection Volume

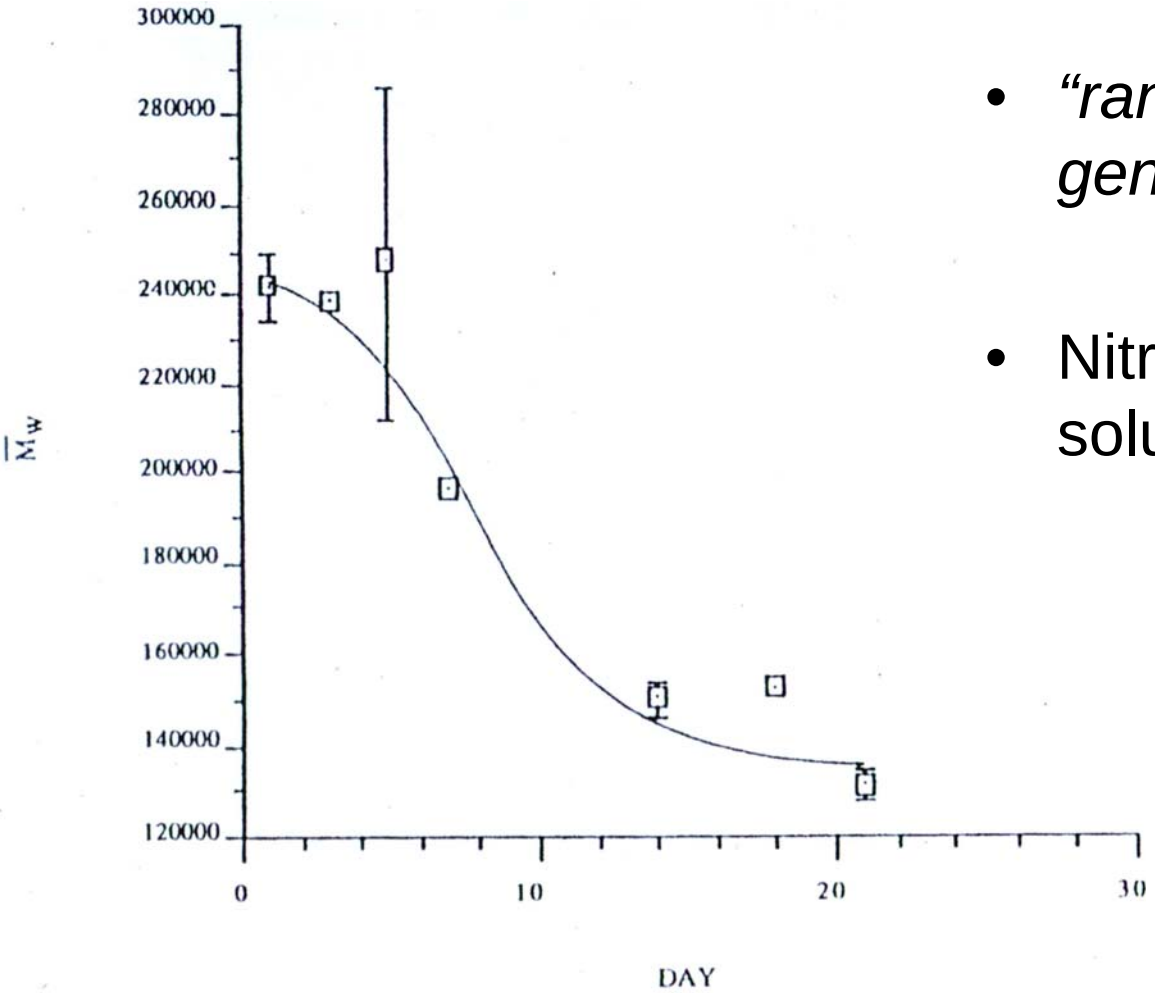
- Light Scattering Data
  - Independent of Concentration
  - & SEC effects



Concentration effects (Light Scattering Data)



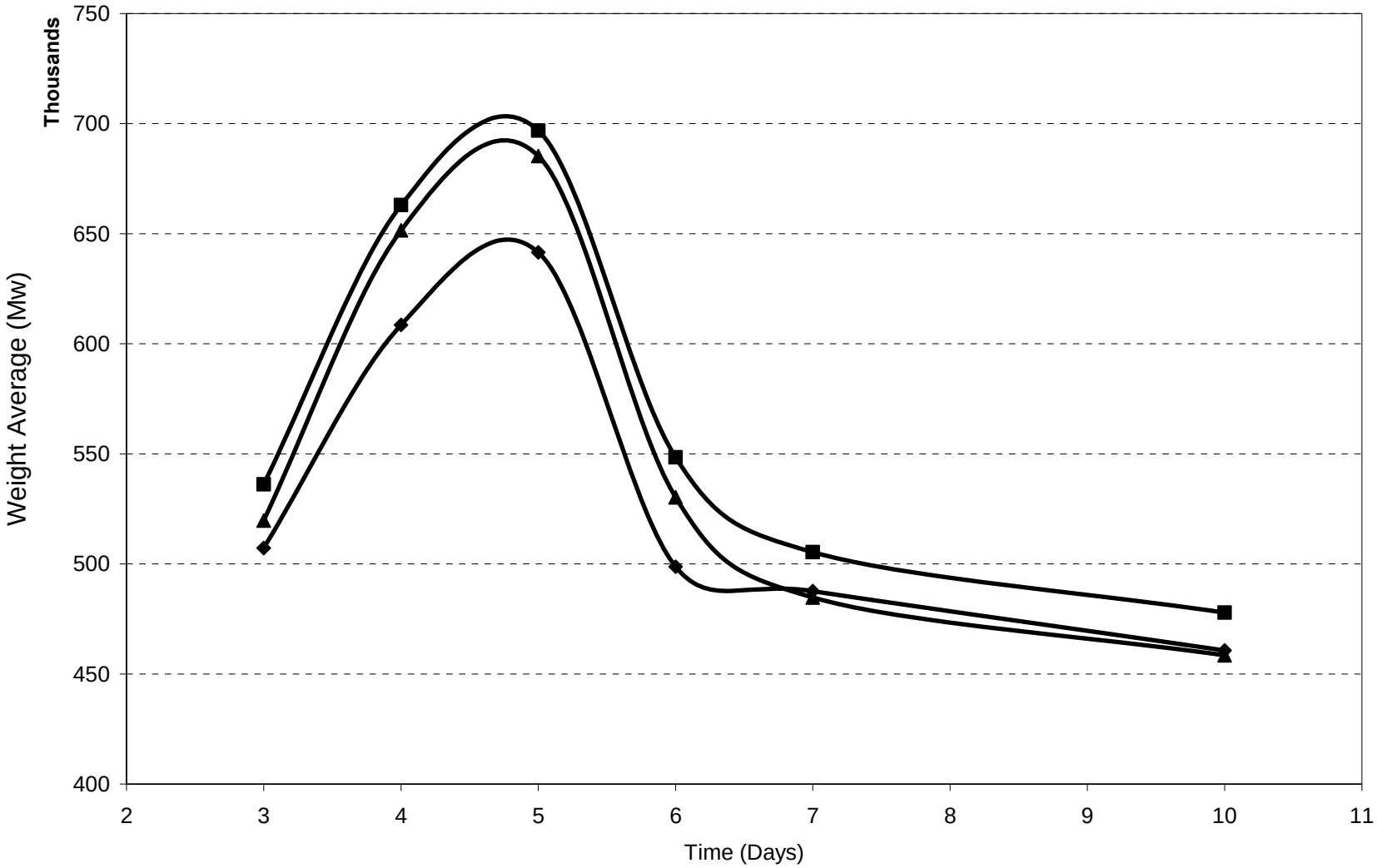
Solvation effects



- *"random number generators" –Sloan 2001*
- Nitrocellulose changes in solution over time

Siochi & Ward (1989)

Solvation effects



Fast eluting peaks/ pre-peaks

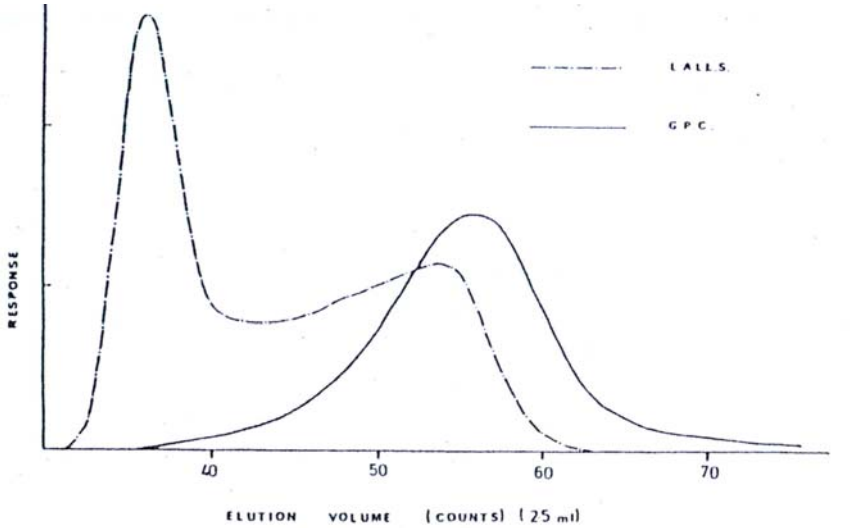


FIG. 16. Output from GPC/LALLS analysis of cellulose nitrate [21].

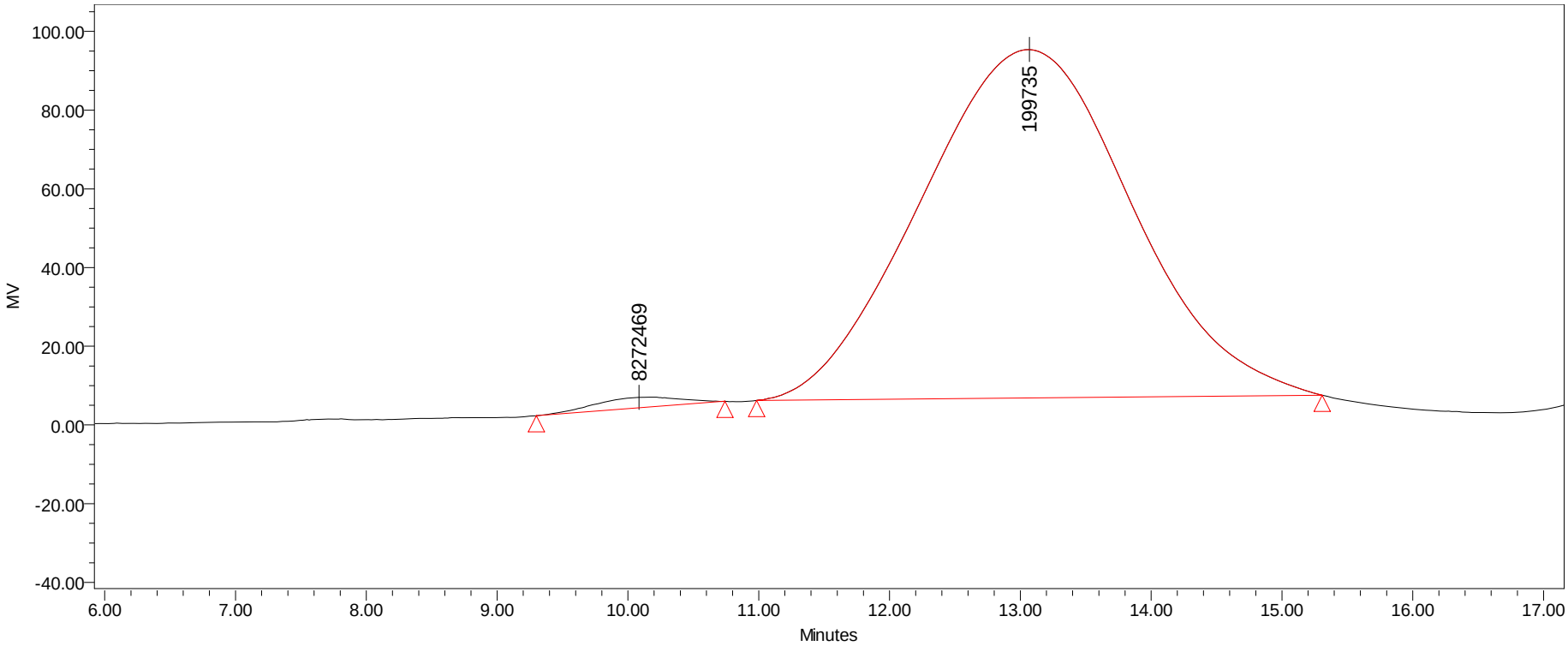
- Greater response with LS
  - Low concentration
  - Large Size
- Incompletely nitrated materials aggregated together?

LALLS - - - - -

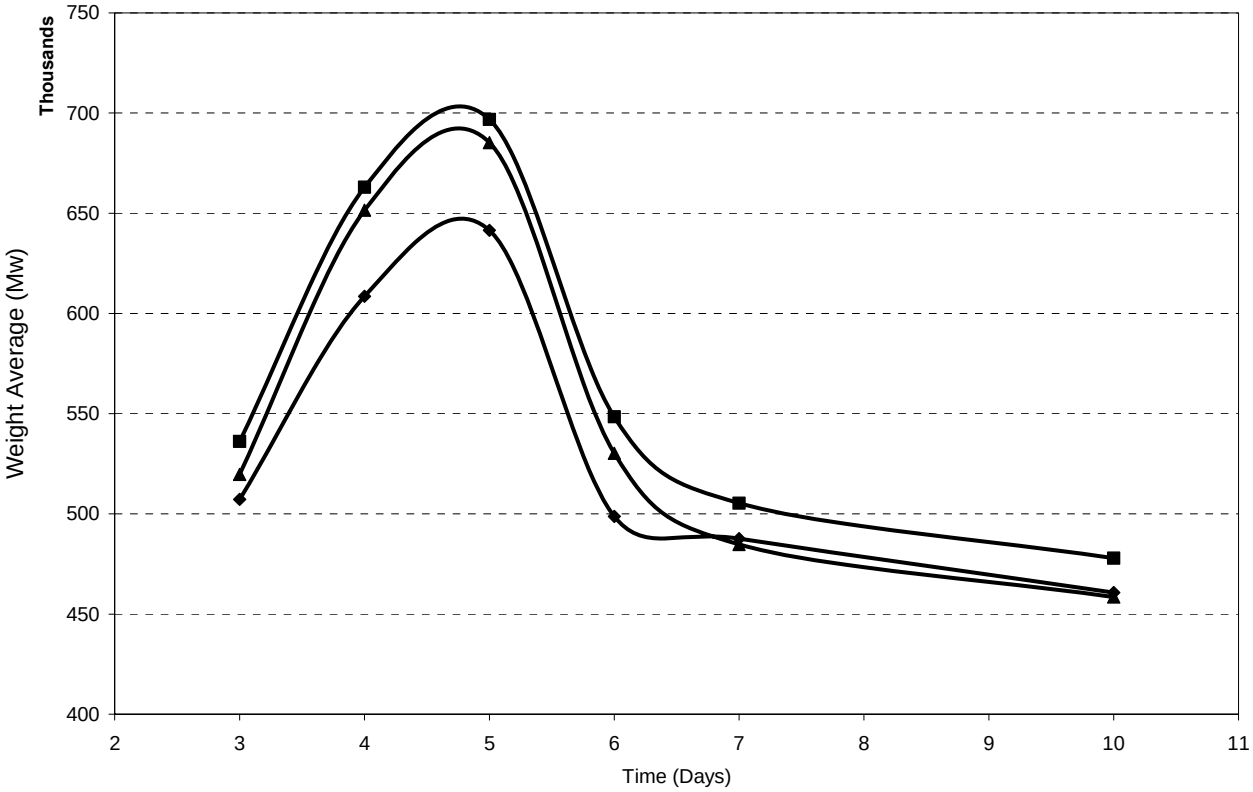
GPC ————

Siochi & Ward (1989)

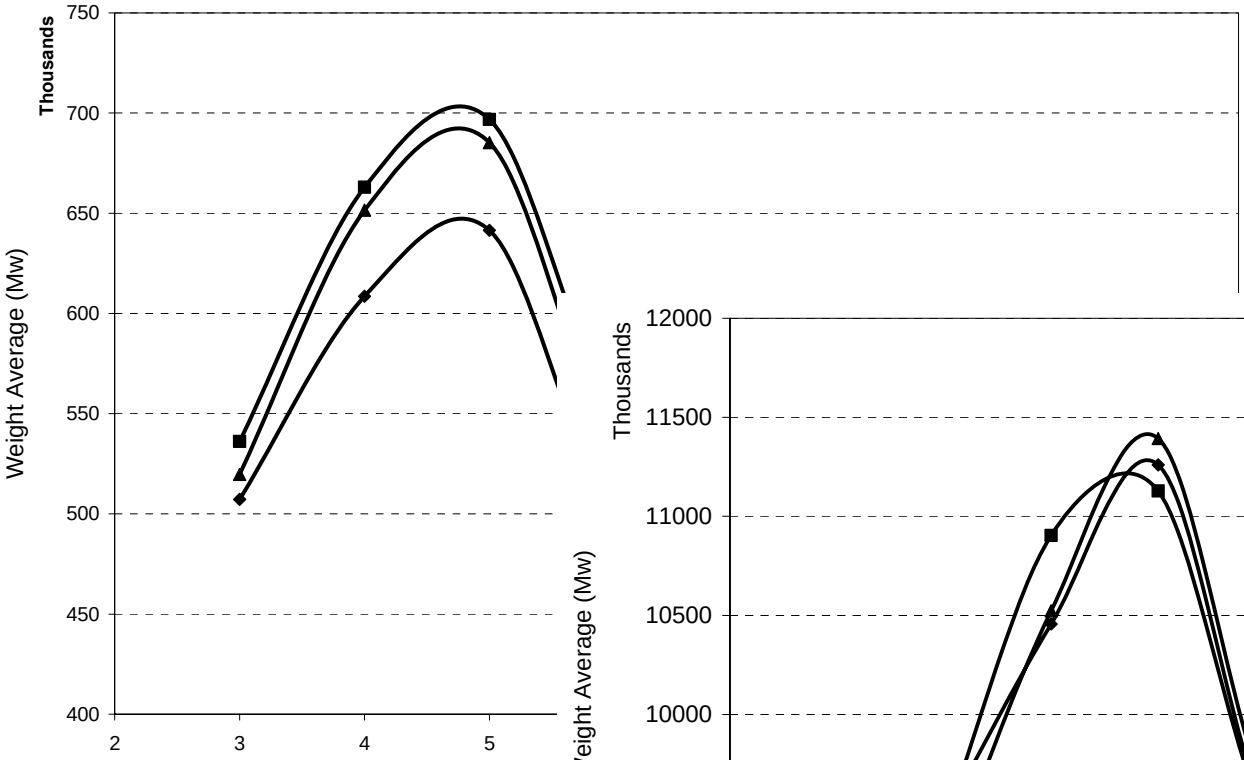
Apparent High Mass pre-peak

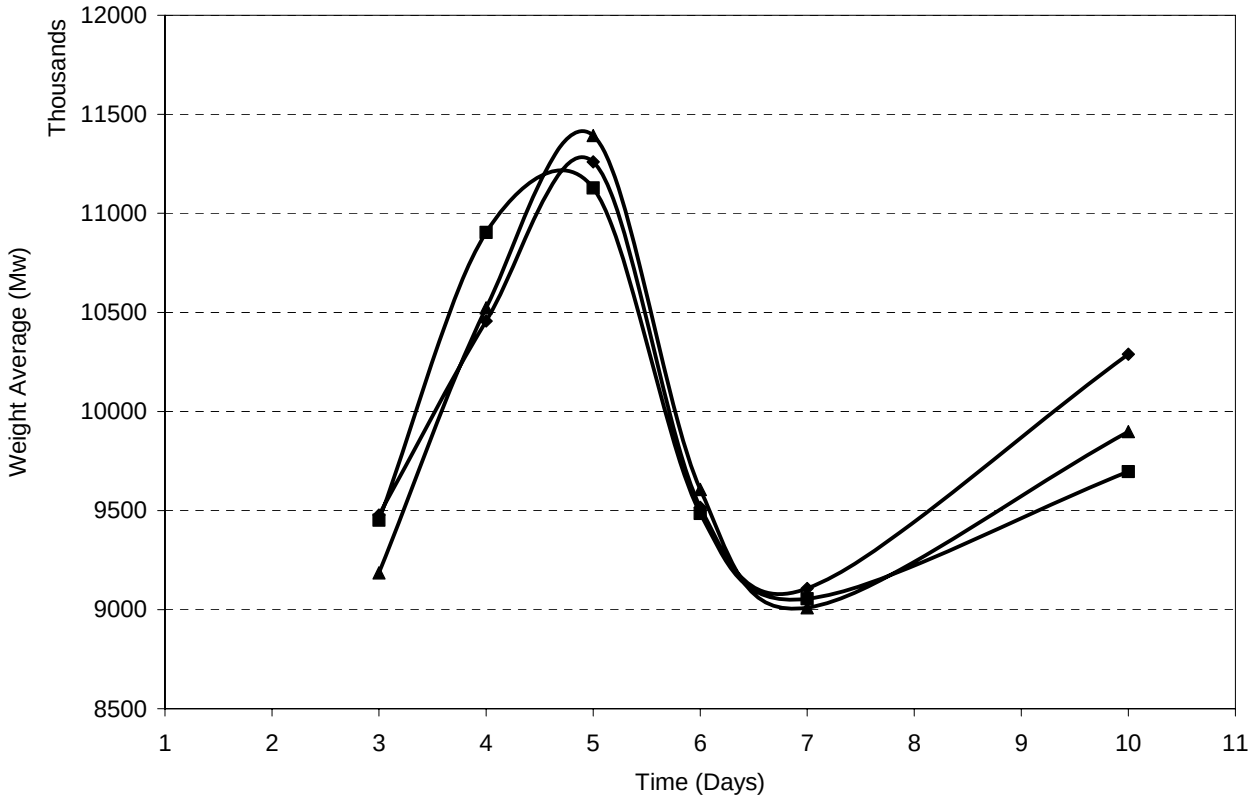


Follows same solvation effect as main peak

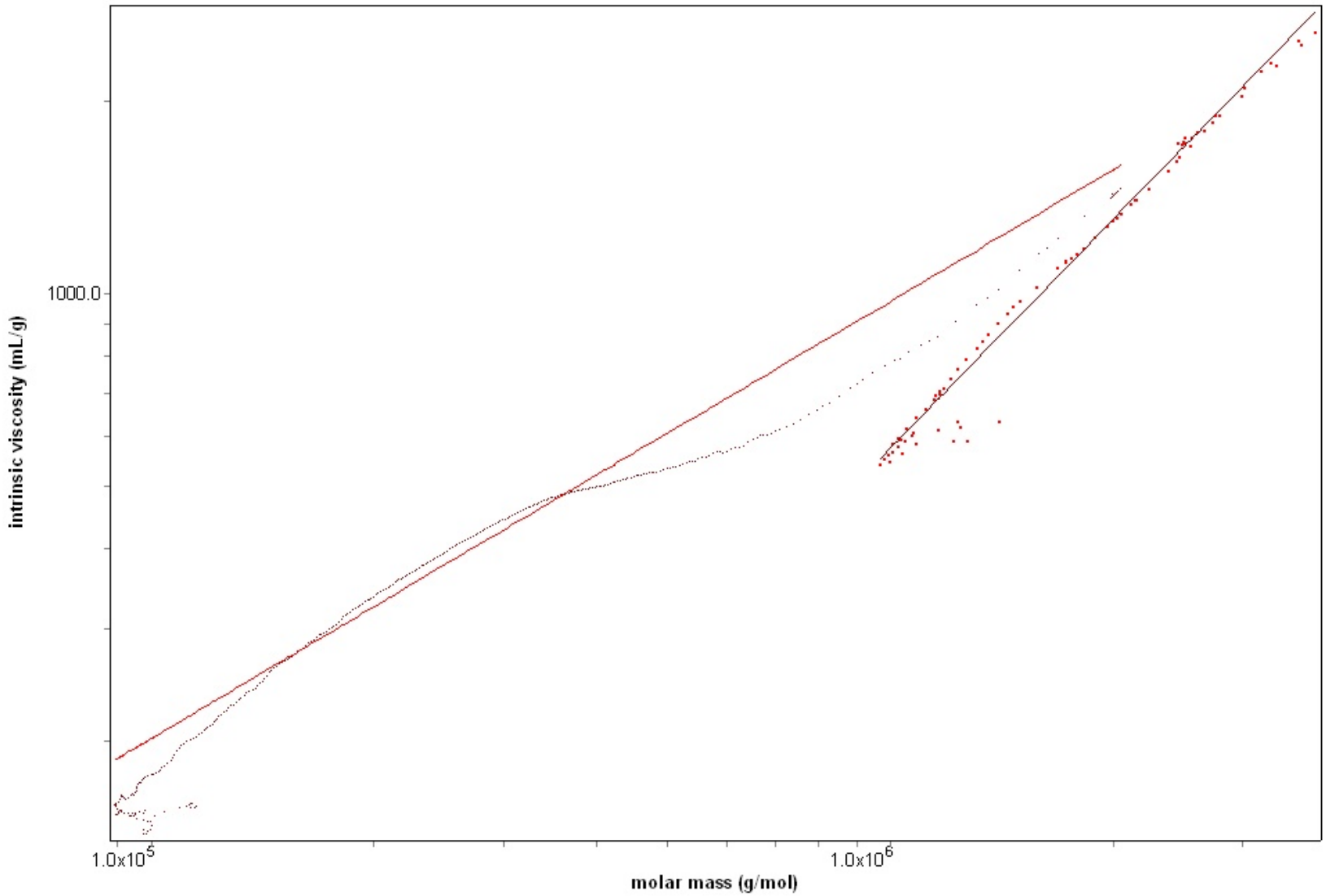


Follows same solvation effect as main peak





Very different Mark-Houwink-Sakurada Plots



Mark-Houwink-Sakurada equation

$$[\eta] = kM_v^a$$

- $[\eta]$ = intrinsic viscosity
- k = constant
- M_v = experimental viscosity average molecular weight
- a = scalar which relates to the "stiffness" of the polymer chains

a = 0 (hard spheres)

a = 1 (semi coils)

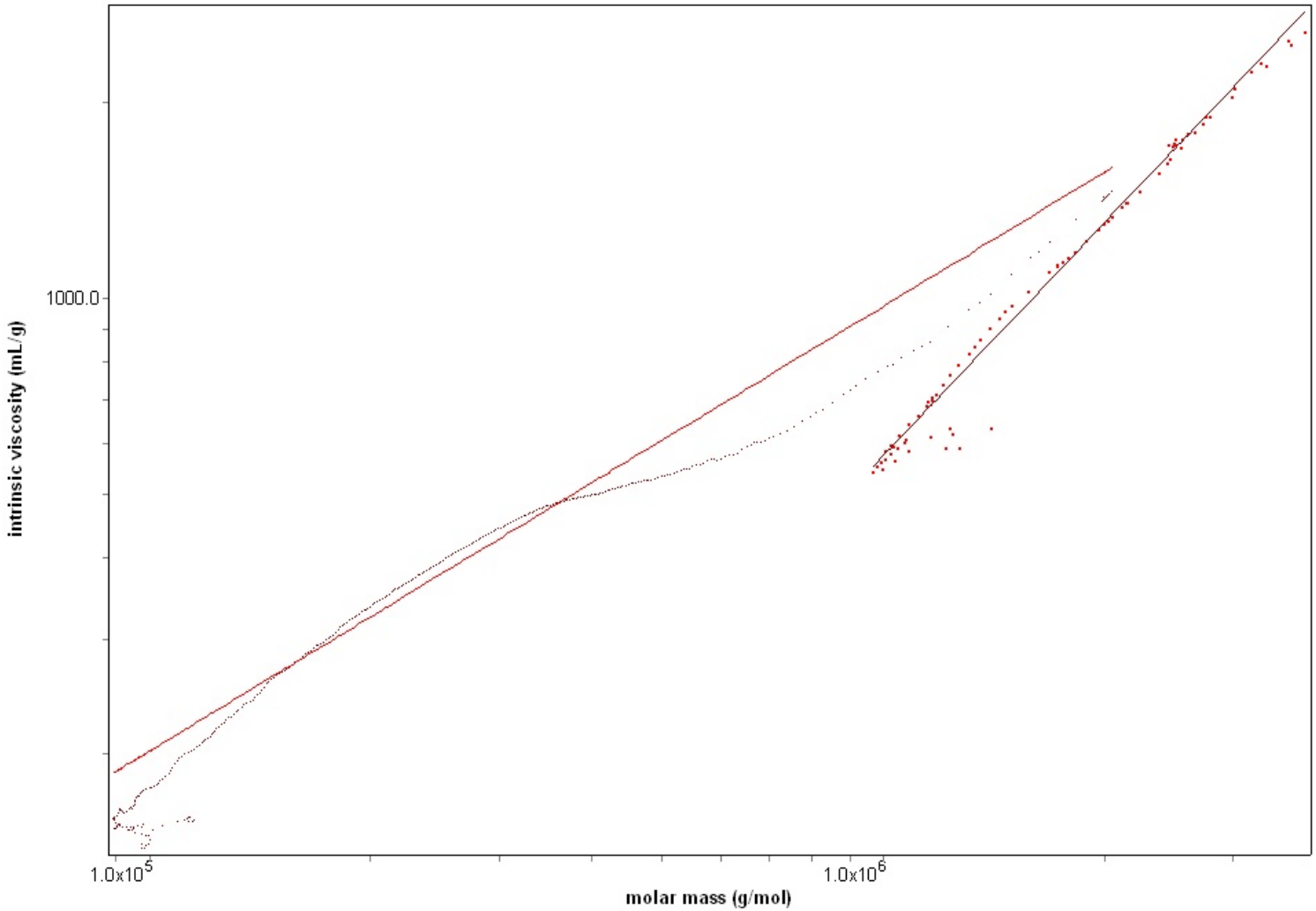
a = 2 (rigid rods)

- Pre Peak a= 1.2
- Main Peak a= 0.68

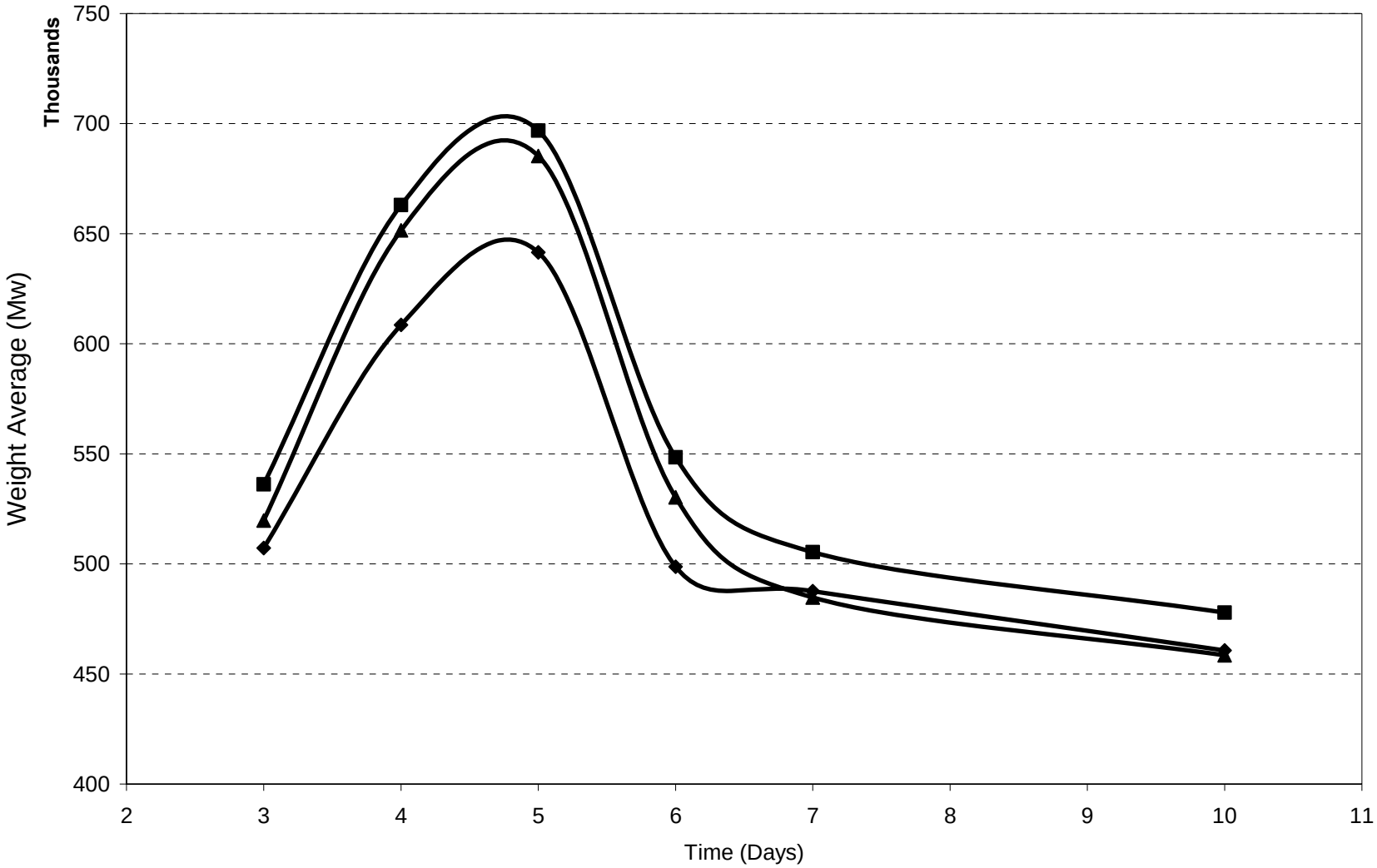
a = 0 (hard spheres)

a = 1 (semi coils)

a = 2 (rigid rods)



Solvation Effects & MHS plots



Current Reproducibility (AWE & Cranfield Uni)

Instrument	Mn (daltons)	p.d.
Waters (auto)	202000	3.0
Viscotek 250 (auto)	214000	3.3
Viscotek 250 (manual)	192000	3.7
Viscotek TDA (Auto)	179000	4.8
Viscotek TDA (manual)	172000	4.8
Wyatt (manual)	210000	1.3
Average *Mn* = 195000 (±10%)		

Summary 2001

- **<u>Suggested Further experimentation</u>**

- MHS Plots
  - Solvation effects/Pre-peak
- Temperature effects
  - Higher Temperature Decreases % Pre-peak
- Varying the solvent
  - Different amounts of Stabiliser (BHT) effects Solvation & Pre-peaks

Standard GPC conditions

- Sample concentration of **0.15% (w/v) in THF** (GPC grade, stabilised with 250ppm BHT), with periodic shaking 7 days. **Injection Volume 100µl**.
- Mobile phase of stabilised **(250ppm BHT) THF (1 ml/min)**
- Three Polymer Labs PLgel **10µl Mixed Phase B** (300x7.5mm) columns & a pre column. **Column temperature 35°C**
- A Viscotek (VE 1121) GPC solvent pump, Kontron (DEG-104) degasser and a Waters 717plus auto sampler.
- Triple detector system (SEC3):
  - Light Scattering: Wyatt Technology DAWN® HELEOS™
  - Viscometer: Wyatt Technology ViscoStar™
  - Refractive Index: Waters 2410
- A 10 point PS EasiCal calibration (*Mp*) range 580-7,500,000 daltons.

Acknowledgements

- AWE – *Deacon, Macdonald, Garman*
- TES-DOSG – *Baker, Turner*
- ROXEL – *Sloan, Fossey*
- Cranfield University – *Bellerby, Moniruzzaman, Reid, Perez*