Nitrocellulose Analysis by Low Angle Light Scattering

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New Technology in GPC and Viscosities

Topics

- Background
- Brief review of Light Scattering theory
- LALS detector
- NC data by LALS compared to RALS method
- Discussion/Conclusions
- Further work

Principles of Light Scattering Measurements

Light Scattering from Solutions is governed by the Rayleigh Eqn.

$$[1] \qquad \frac{KC}{R_0} = \frac{1}{Mw} + 2A_2C$$

Where R_0 is the Rayleigh Ratio at zero scattering angle,
M_W is the weight-average Molecular Weight,
C is the concentration of the solution,
K is an optical constant,
A_2 is the 2nd virial coefficient.

Note that at low concentration(GPC conditions?) the 2nd term on the right becomes negligible.

$$[1a] \qquad R_0 = KCMw$$

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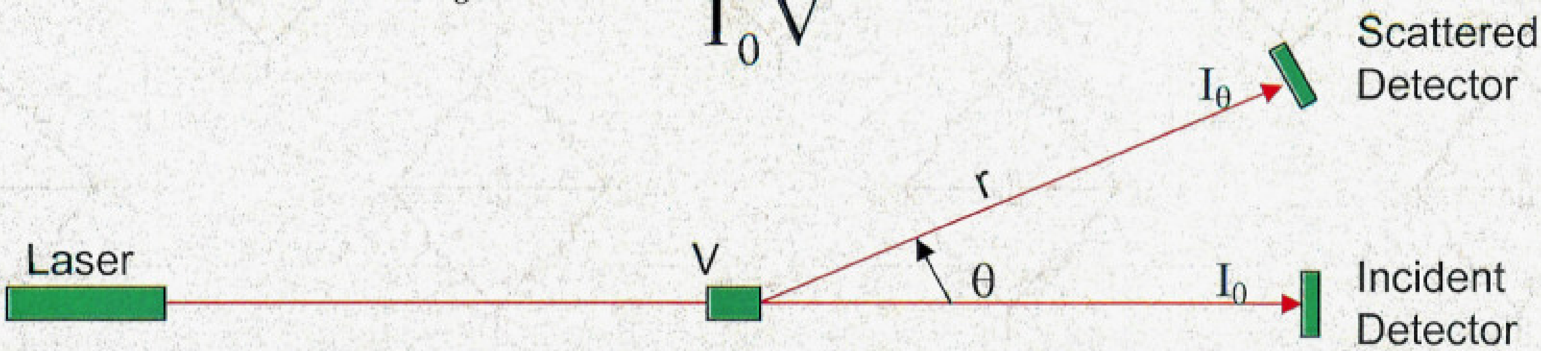
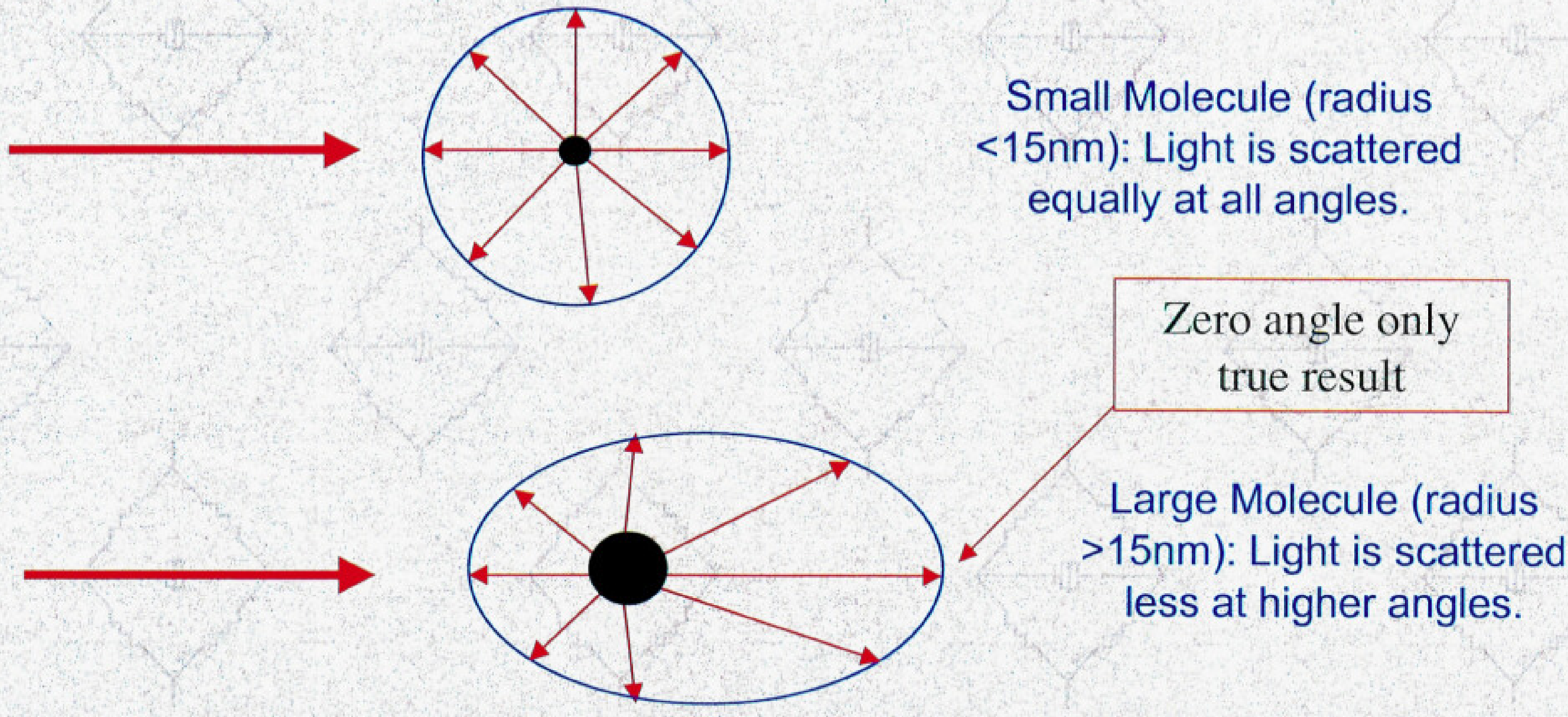
Principles of LS: Rayleigh Ratio

Scattered light cannot be measured at zero angle, of course, so it must be obtained from estimations based on measurement(s) at some higher angle θ. R_θ is defined as the ratio of scattered light intensity per unit volume of the solution to the incident light intensity, normalized.

$$R_\theta = \frac{I_\theta r^2}{I_0 V} \qquad [2\text{-}1]$$



Principles of Light Scattering - Angular Dependence



For larger macromolecules the phenomenon of *intramolecular interference* produces a disymmetry in the scattered light. Destructive interference occurs at backward scattering angles.

Principles of LS: Angular Dependence

If the dimensions of the scattering molecules are much smaller than the wavelength of the incident light, the molecule behaves virtually as a point source of scattered light. The result is a symmetrical scattering pattern and R_θ may be set equal to R_0 without significant error.

$$R_\theta \cong R_0$$

The accuracy of this equation is dependent on θ and on the size of the macromolecule. For $\theta = 90^0$, for example, this is a good approximation for $R_g < 15$ nm, which corresponds roughly to Mw of 150,000 for chain polymers.

Note that for spherical molecules such as proteins, Rg of 15 nm would correspond to Mw of several million!

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Principles of LS: Angular Correction

For large macromolecules exhibiting LS disymmetry, one must estimate R_0 from measurement(s) of R_θ. We can define a *particle scattering function* P_θ to be

$$[8-1] \qquad P_\theta = \frac{R_\theta}{R_0}$$

There are three ways to obtain R_0 or, equivalently, P_θ . These ways correlate with the commercial light scattering instruments.

1. Measure R_θ at very low angles. - LALS
2. Measure R_θ at several angles and extrapolate. - MALS
3. Measure R_θ at 90^0 and calculate P_θ using viscosity data.
   - RALS/Viscometer

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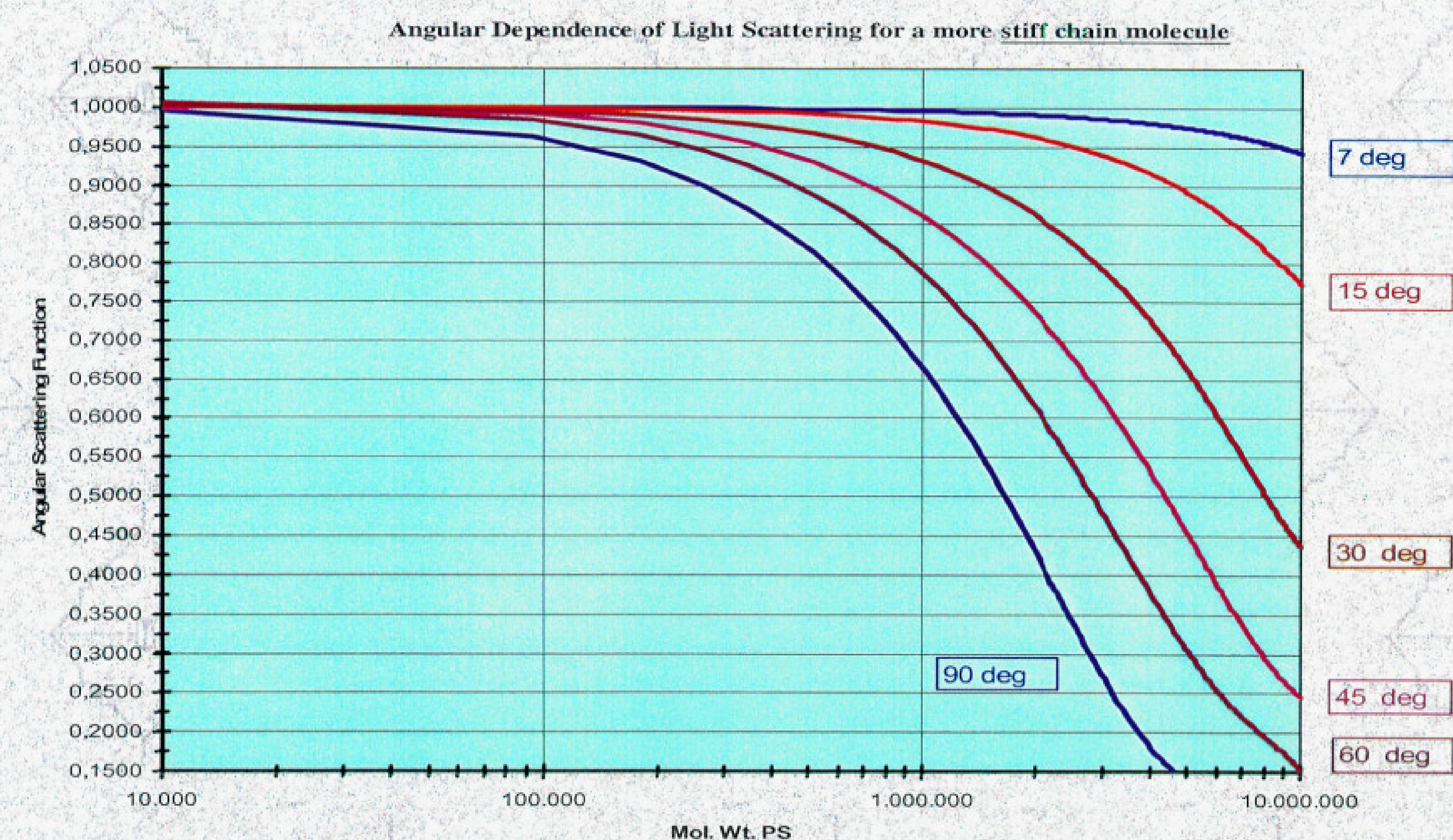
Angular Dependence

Stiffer Chain Molecules (a = 0.8)



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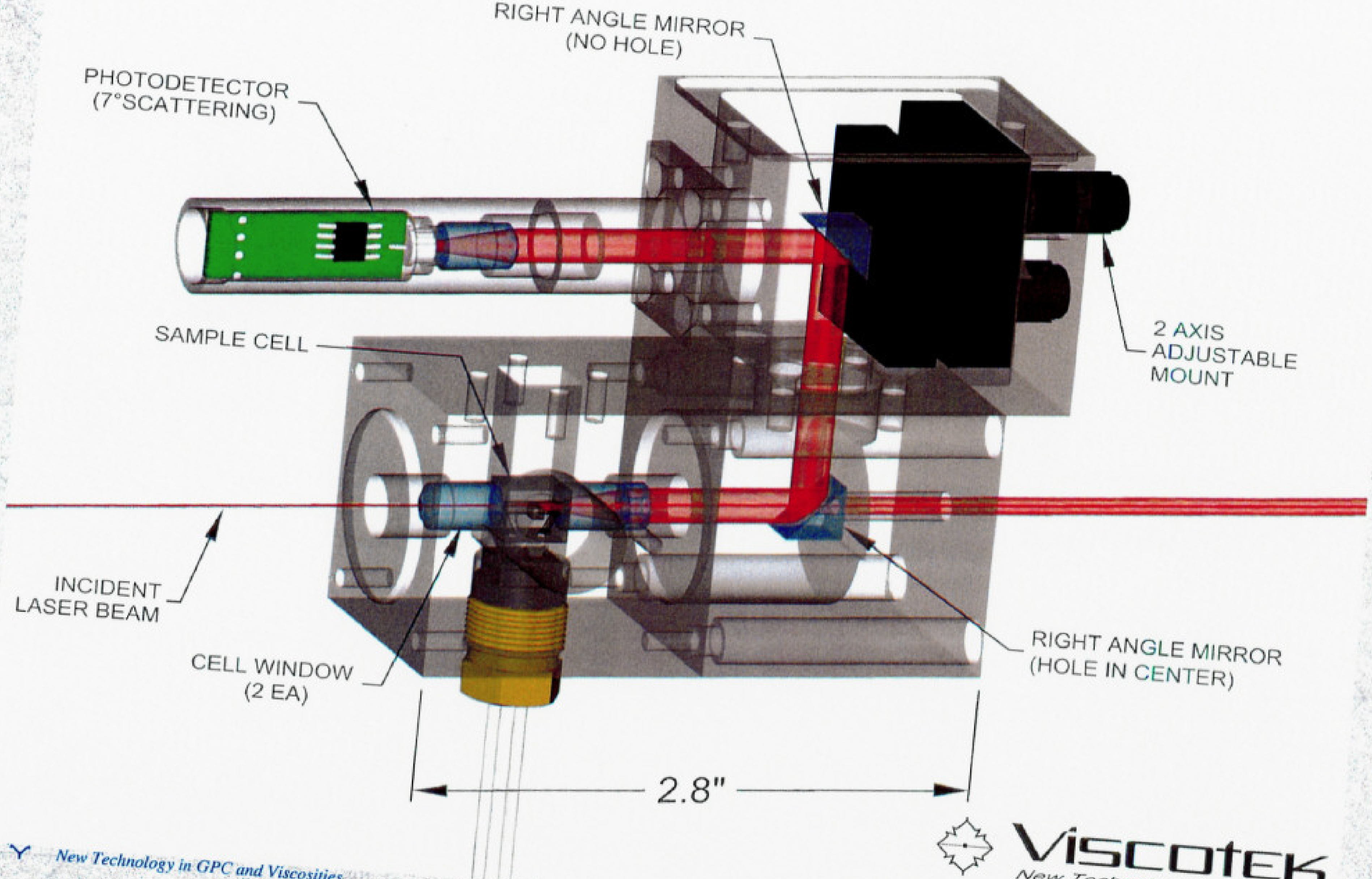
LALLS DETECTOR - CUTAWAY



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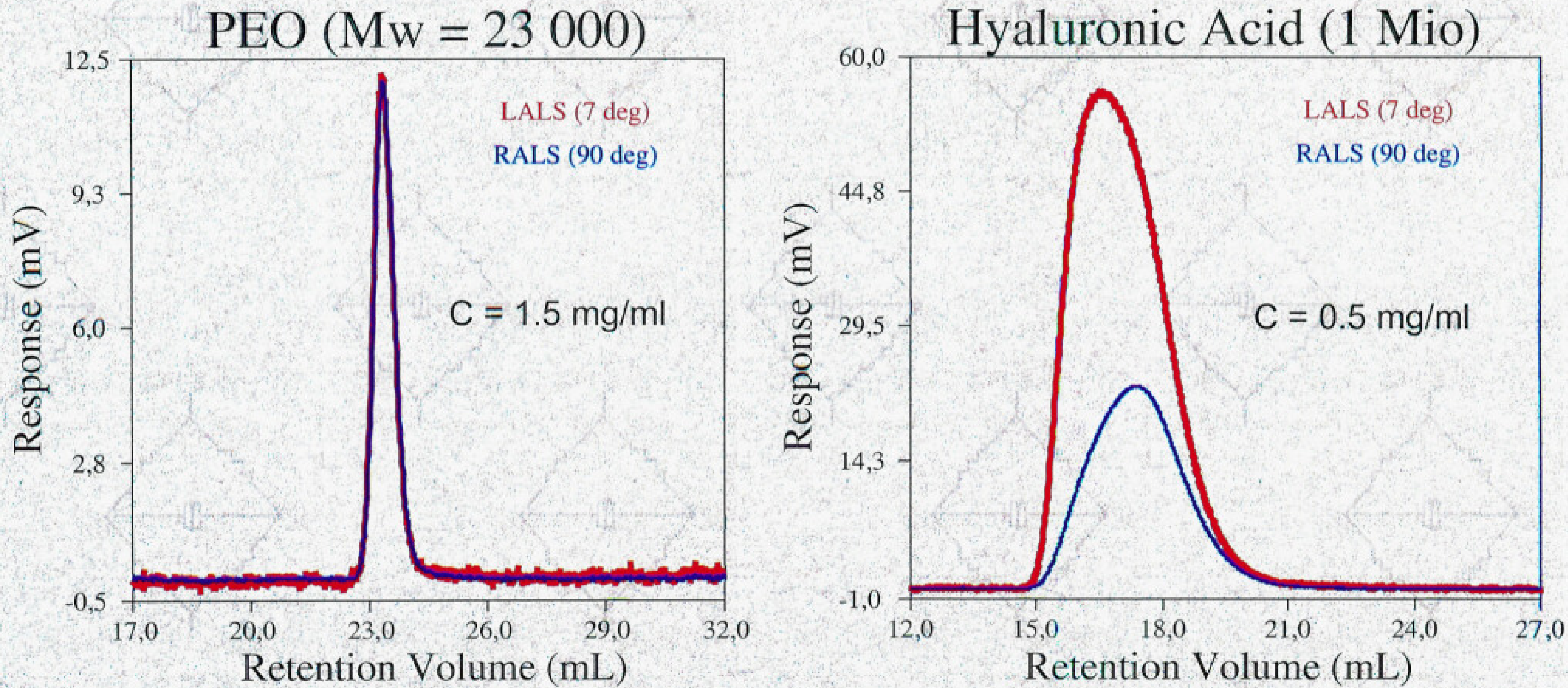
LALS-RALS

Response for Small and Large Molecules



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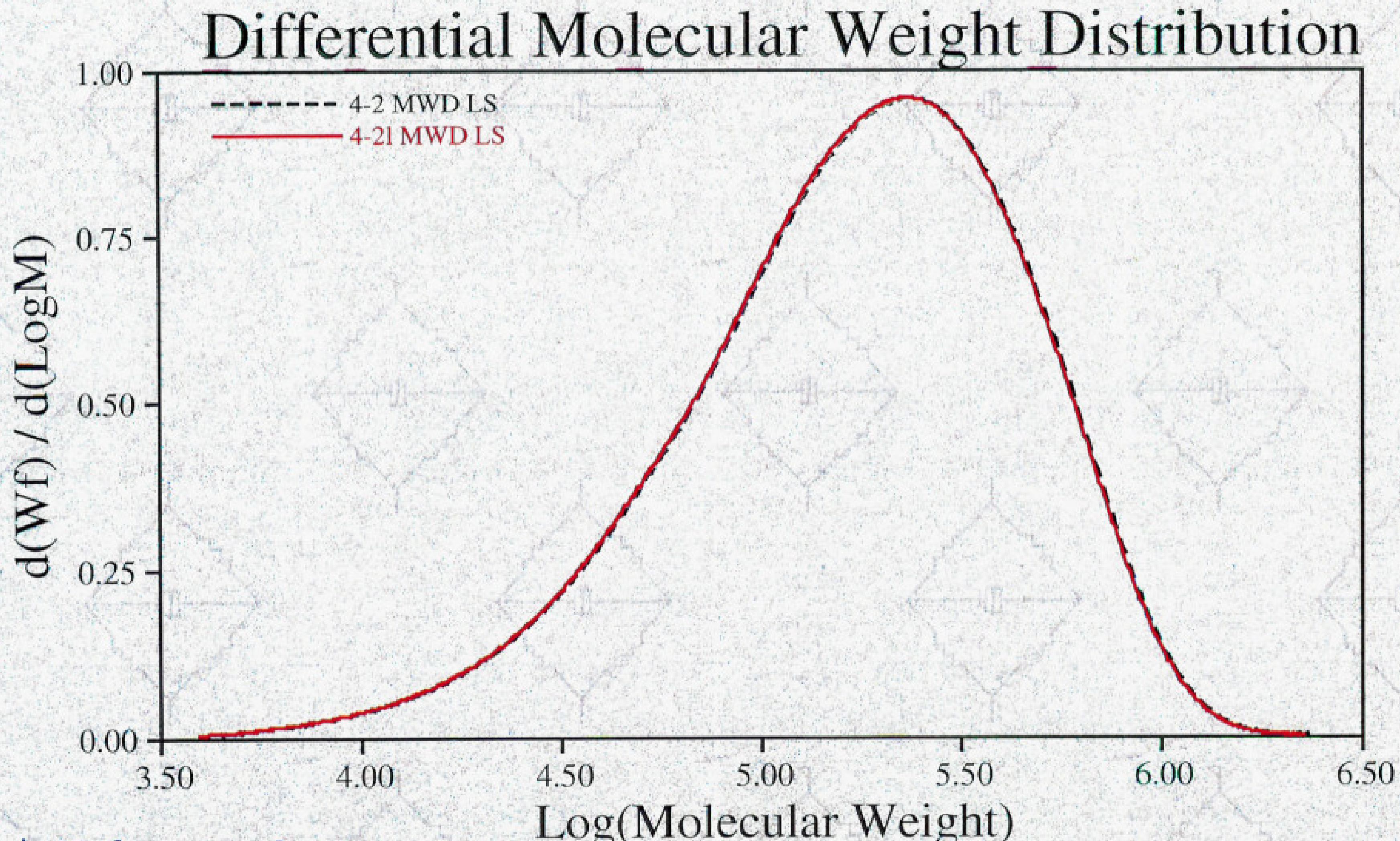
Experimental

- Calibrate system with Narrow PS
- Check calibration with broad PS standard
- Run 4 nitrocellulose solutions supplied by Alan Macdonald from AWE
- Calculate data by both LALS and RALS/Visc

PS Standard by RALS & LALS



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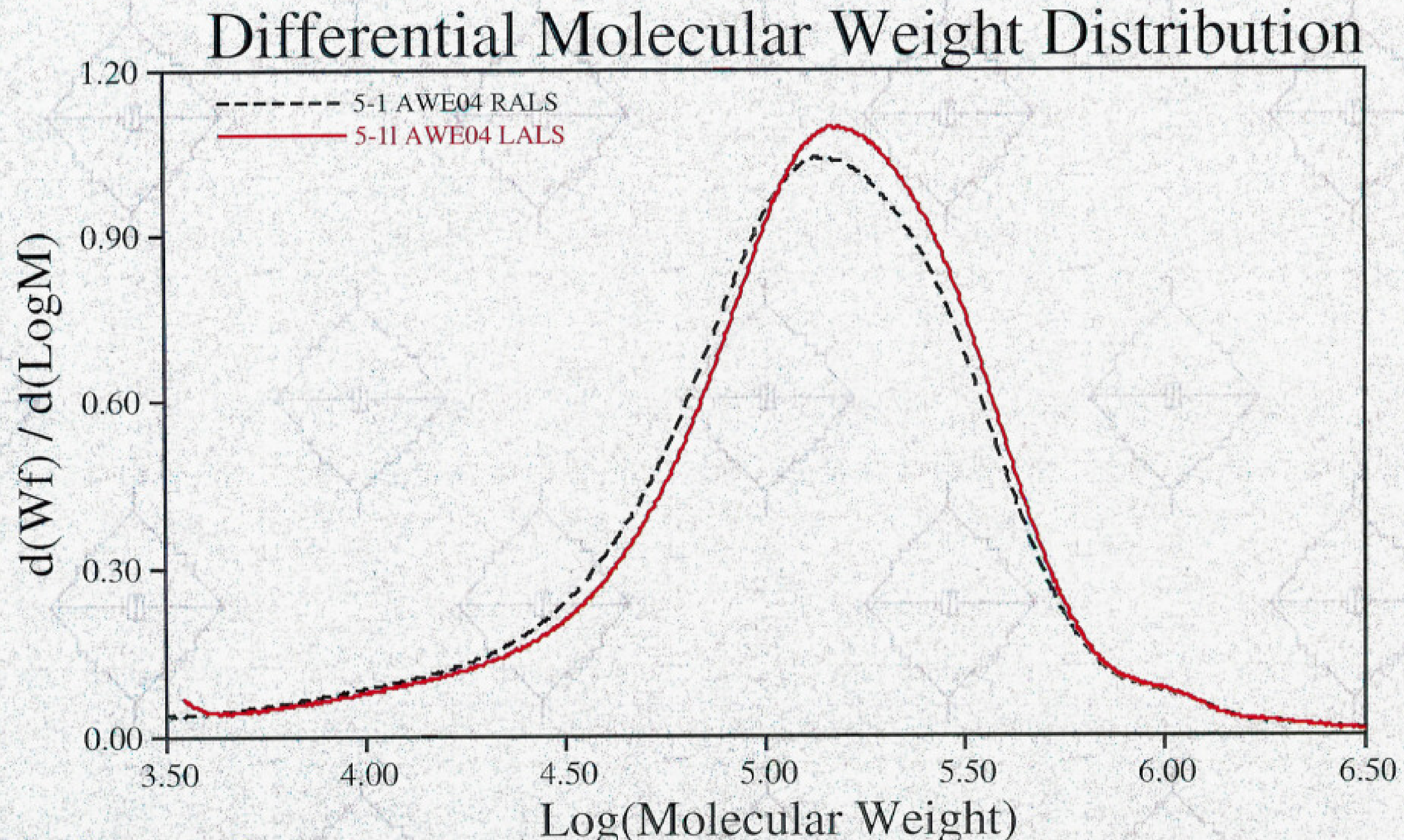
AWE Sample 04



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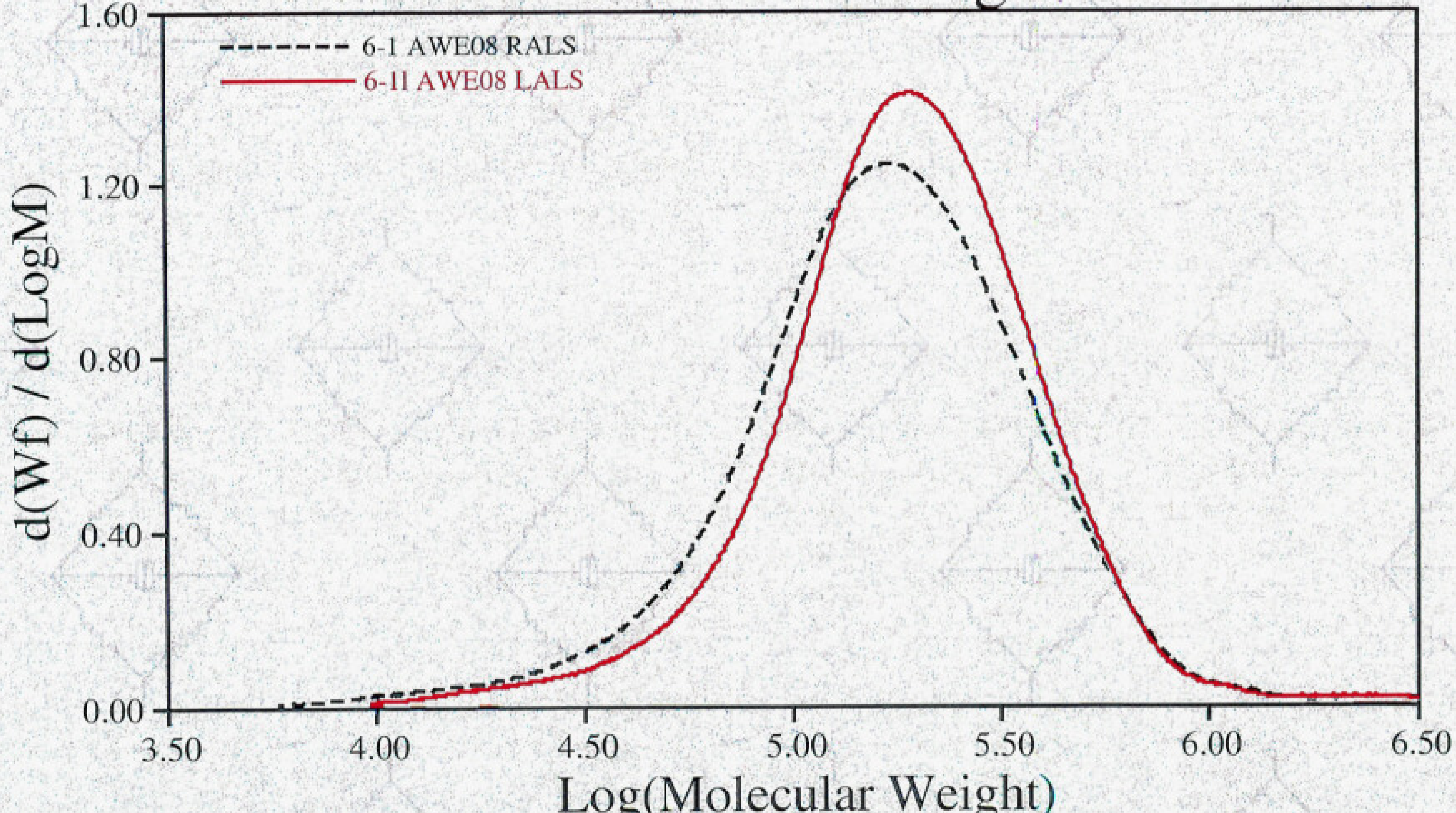
AWE Sample 08

Differential Molecular Weight Distribution



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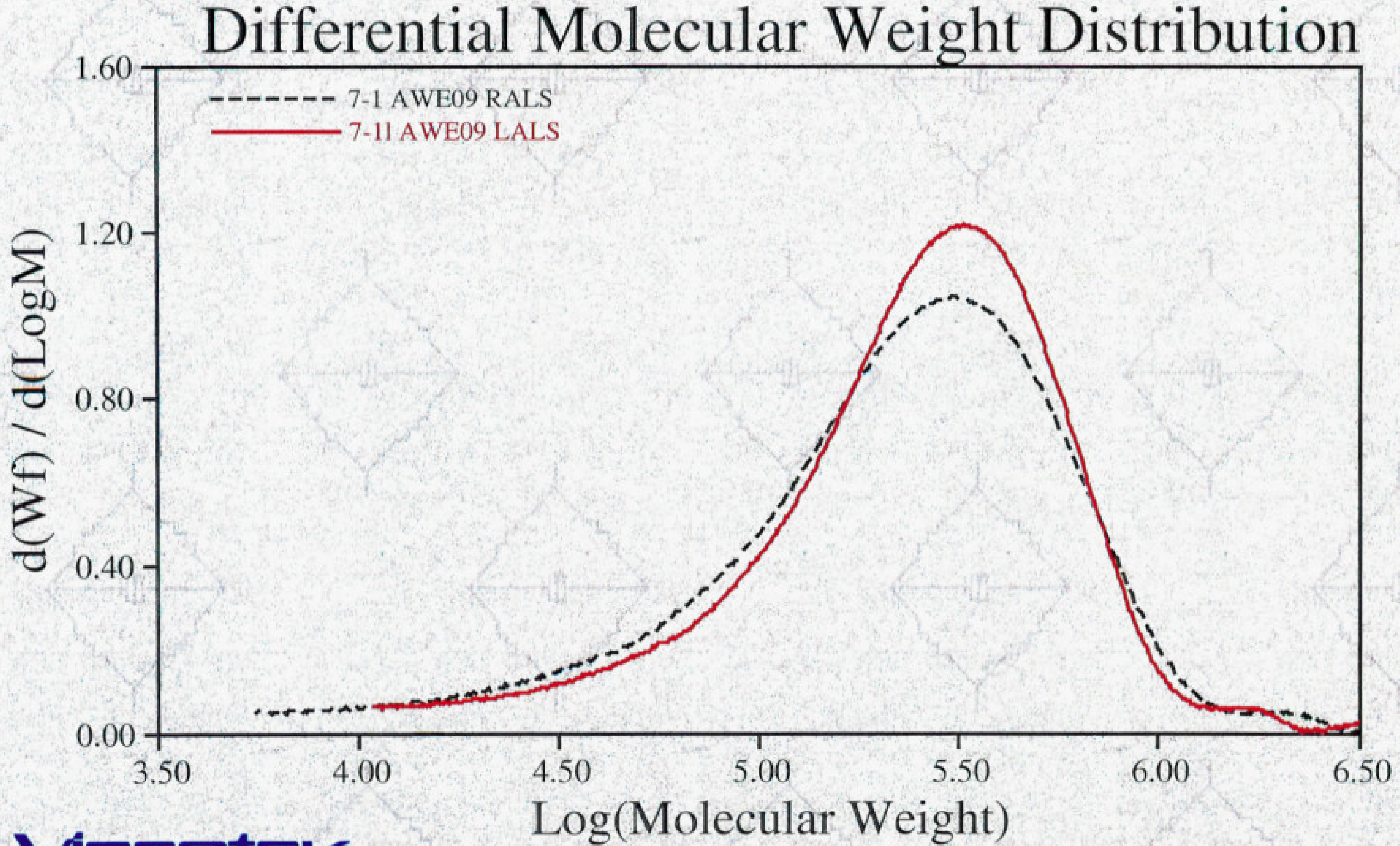
AWE Sample 09



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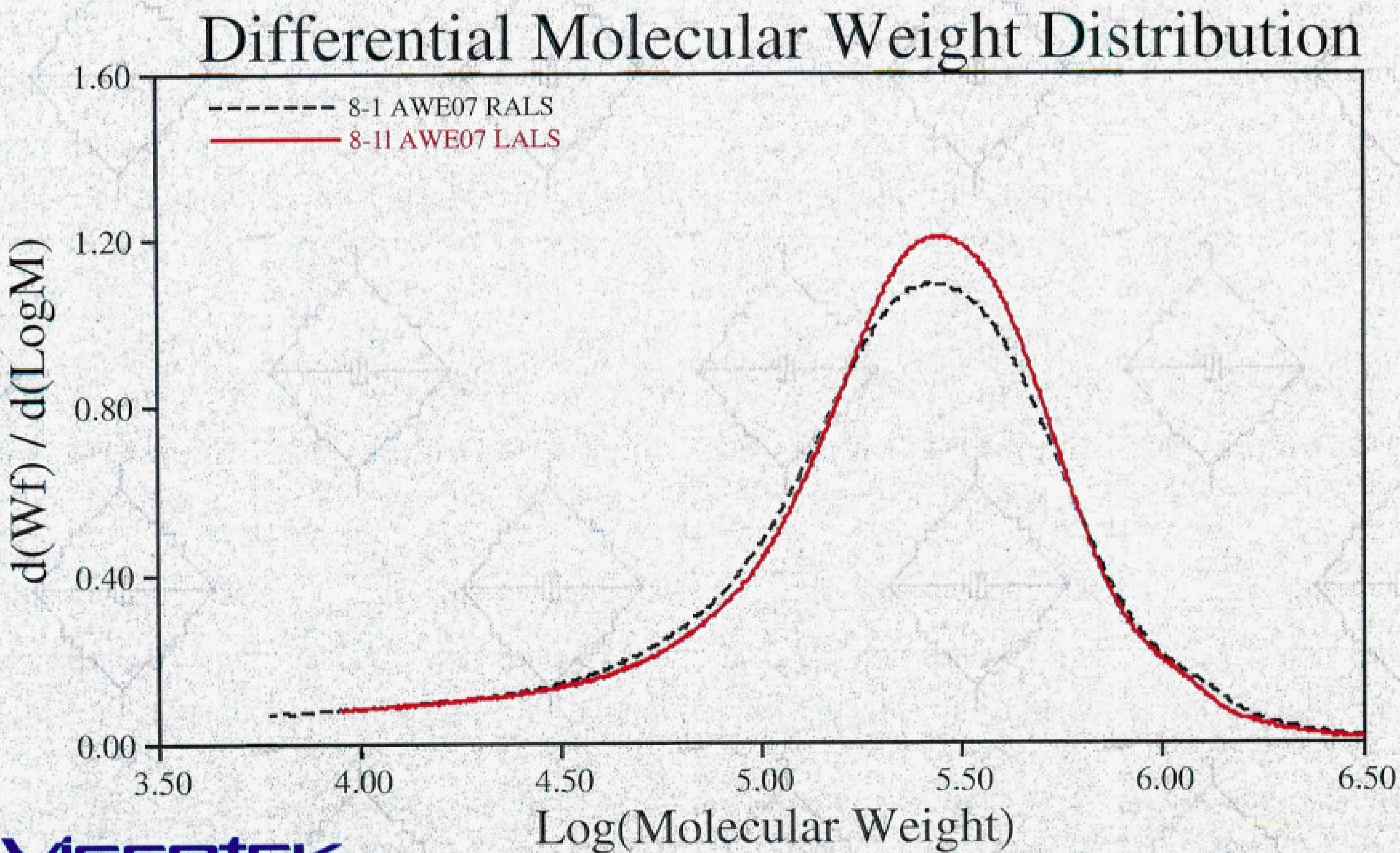
AWE Sample 07



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Analysis Summary (Triple Detector)

File	Sample	Mw	Mn	PD	IVw	Rg (nm)	alpha	log K	dn/dc	Conc	% Rec.	Cal
4-2	PS 250K Broad - RALS	254,500	96,720	2.63	0.8138	18.17	0.717	-3.933	0.185	1.510	0.000	nc_rals
4-2L	PS 250K Broad - LALS	250,300	95,030	2.63	0.8127	18.07	0.716	-3.923	0.185	1.510	0.000	nc_lals
5-1	AWE 04	200,600	56,170	3.57	3.542	26.49	0.914	-4.282	0.085	2.028	0.000	nc_rals
5-1L	AWE 04	208,800	67,130	3.11	3.555	27.01	0.959	-4.545	0.085	2.028	0.000	nc_lals
6-1	AWE 08	238,500	112,000	2.13	8.235	38.12	0.839	-3.570	0.121	1.764	0.000	nc_rals
6-1L	AWE 08	246,200	137,000	1.80	8.255	38.98	0.945	-4.172	0.121	1.764	0.000	nc_lals
7-1	AWE 09	443,800	102,200	4.34	5.881	39.01	0.809	-3.748	0.088	0.760	0.000	nc_rals
7-1L	AWE 09	417,600	141,400	2.95	6.136	39.57	0.952	-4.551	0.088	0.760	0.000	nc_lals
8-1	AWE 07	334,300	95,910	3.49	3.793	32.46	0.864	-4.169	0.073	1.576	0.000	nc_rals
8-1L	AWE 07	328,500	118,200	2.78	3.825	32.59	0.954	-4.674	0.073	1.576	0.000	nc_lals

GPC TDA300 - Triple mode column GMHxl 2x solvent THF

Viscotek Europe Ltd _Triple Detector GPC analysis_ _Jul 12, 2001_

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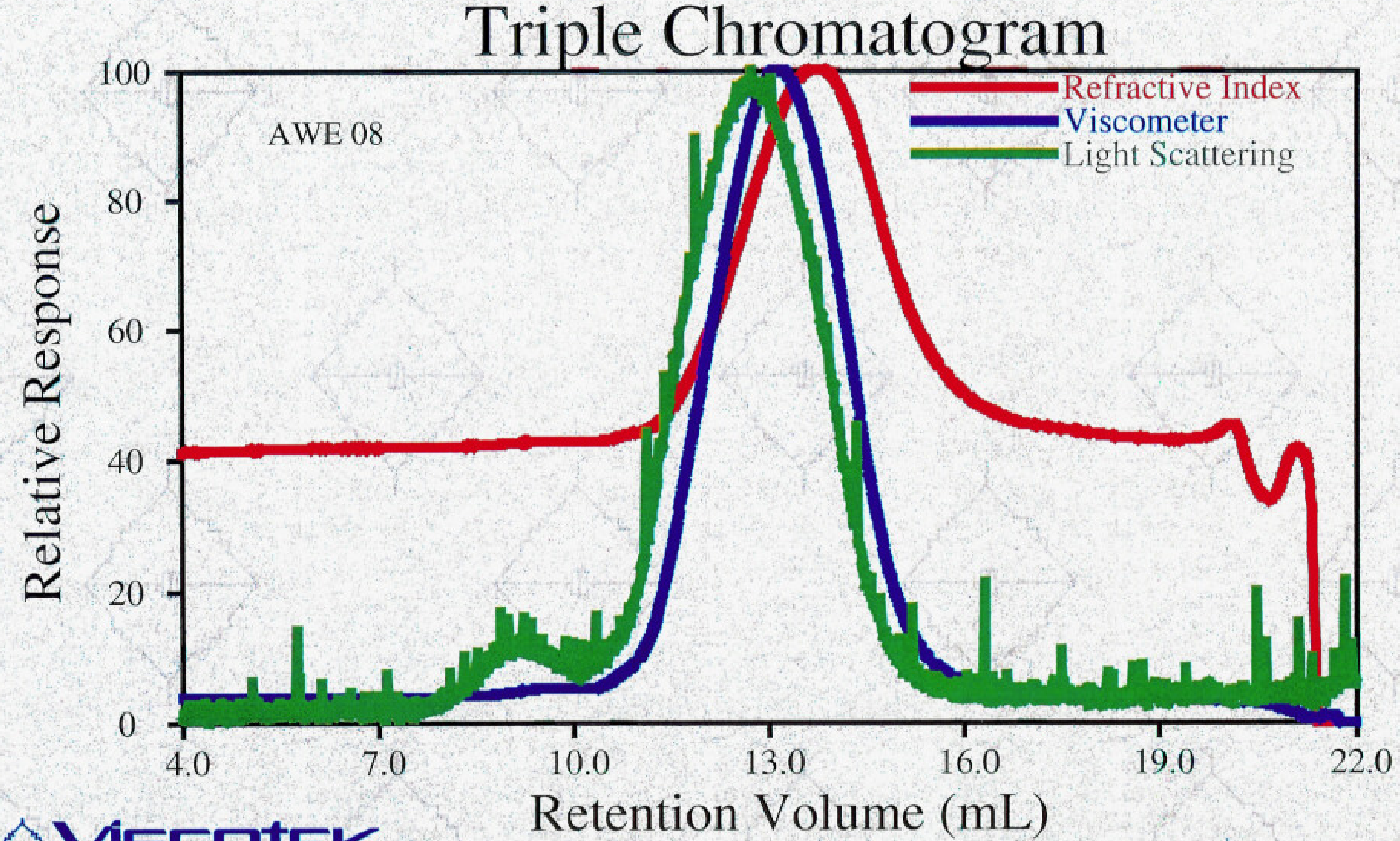
AWE08, LALS data



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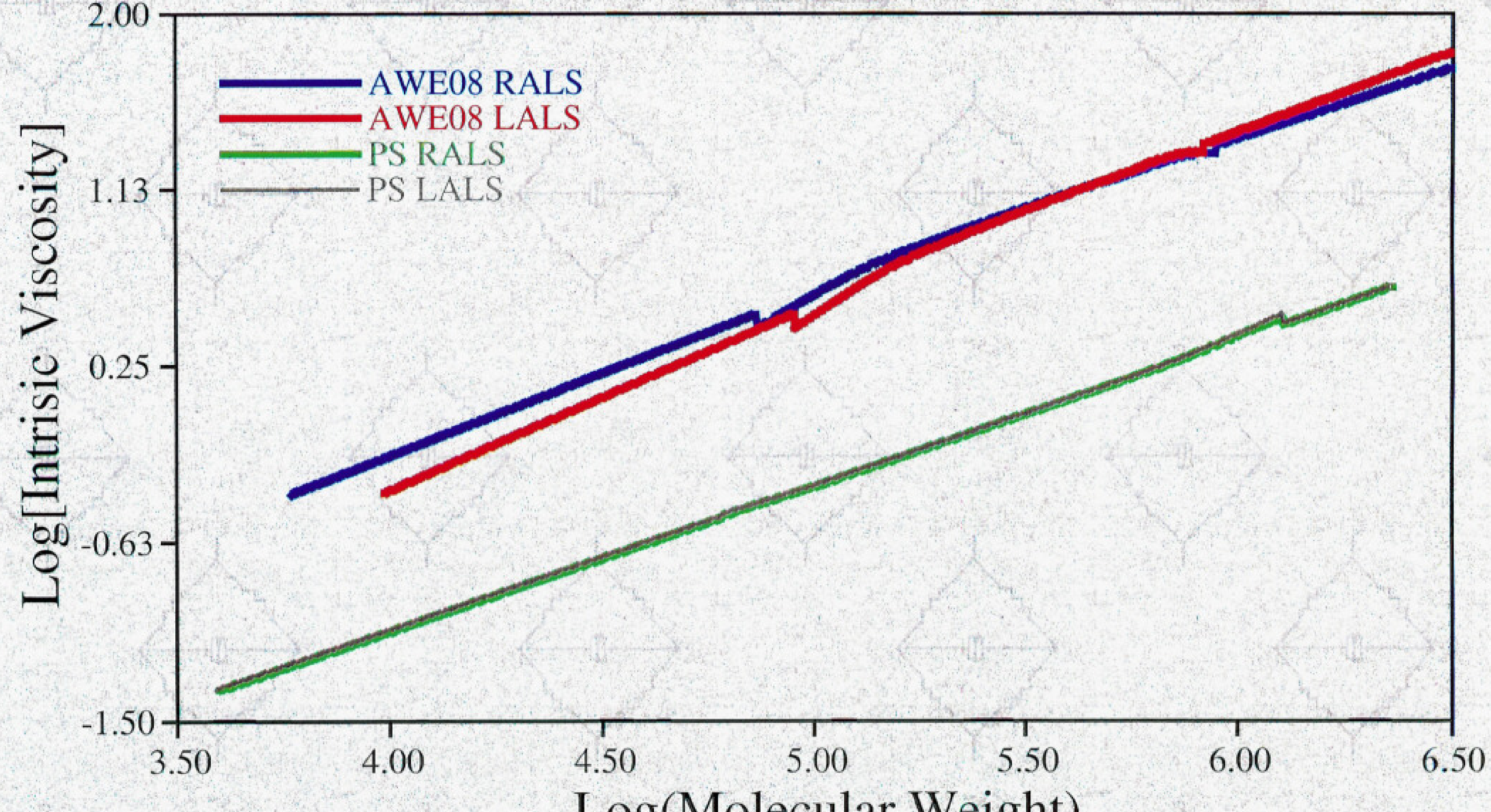
Mark-Houwink Plot



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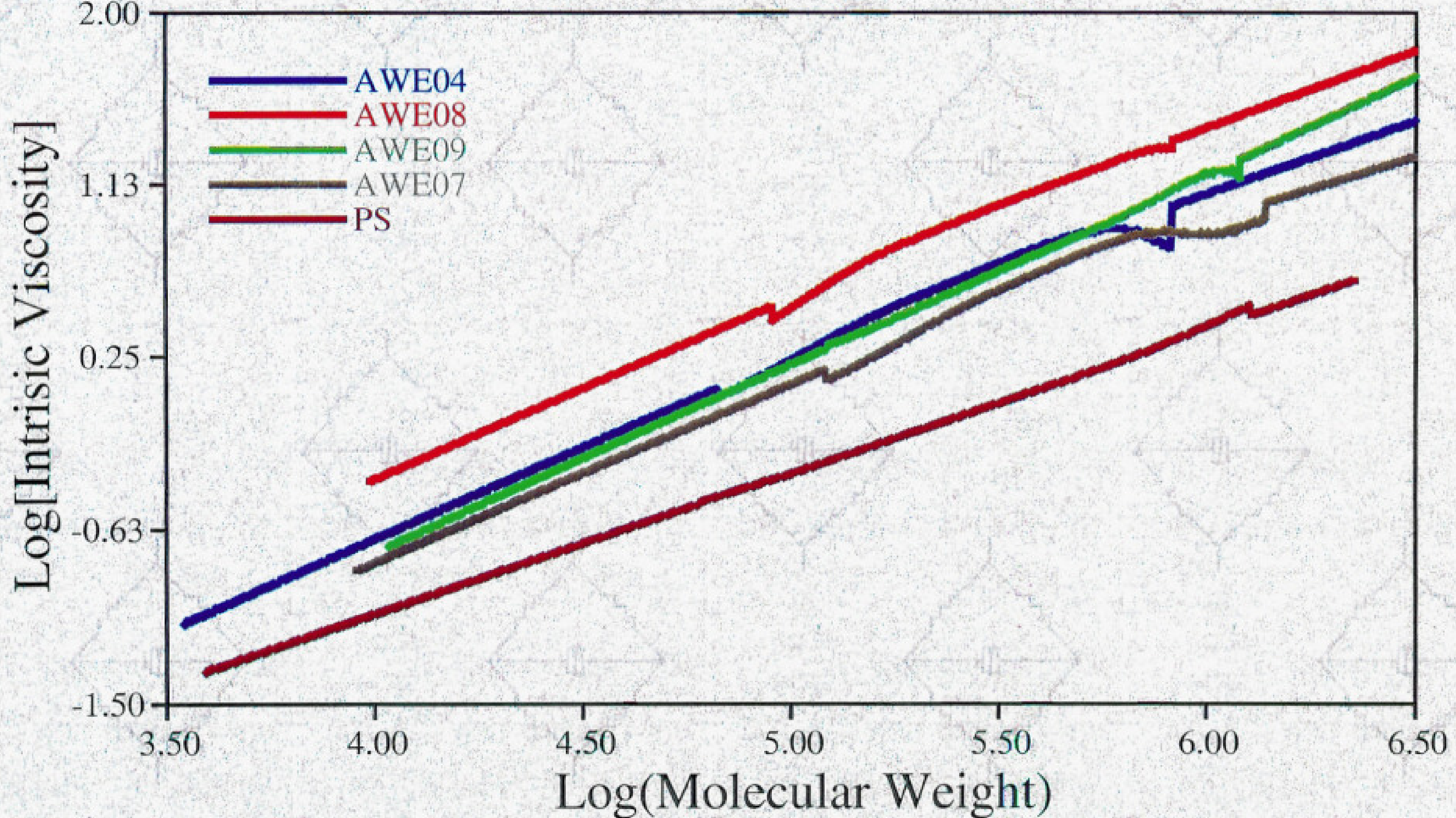
Mark-Houwink Plot



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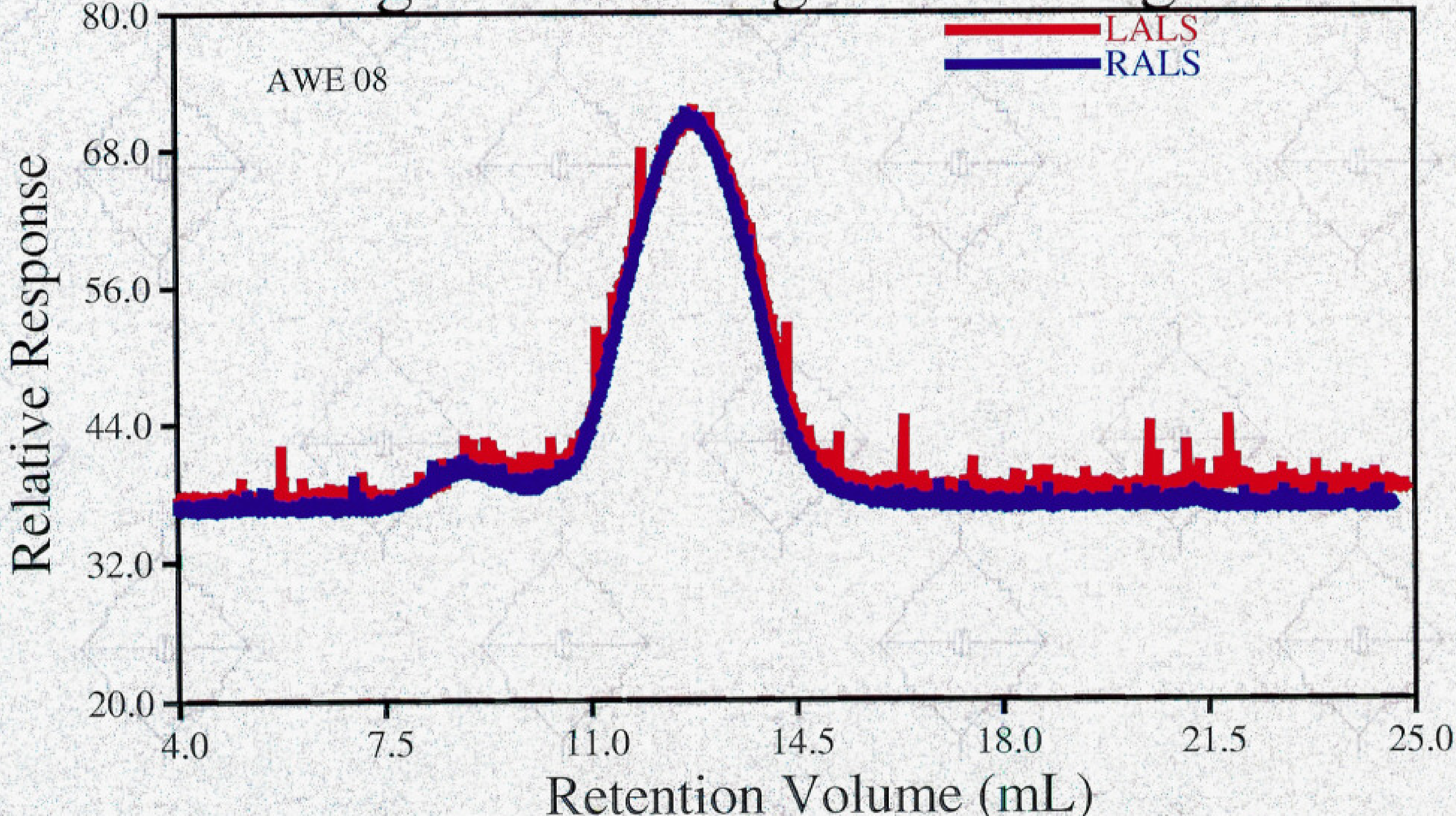
Light Scattering Chromatograms



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Conclusions

- LALS data broadly confirms RALS data.
- Some small differences in molecular weight but mainly <5%
- LALS raises further questions about ‘pre-peak’

Further work

- More structured study:
  - Analysis of ‘fresh’ solutions
  - Analysis with time
- Focus on ‘pre-peak’
  - Measure MW separately by LALS
  - dn/dc?

Thanks!

- Nicola Marheineke
- Alan Macdonald
- Max Haney