Progress toward reliable NC molecular mass distribution by GPC

Dr E Stubbs
Emma.Stubbs@awe.co.uk
www.awe.co.uk

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Introduction

Nitrocellulose (NC) continues to be an important energetic material at AWE. Characterisation is carried out, in part, using molecular mass distribution (mmd) measurements obtained via GPC, the results of which rely significantly on a number of factors:

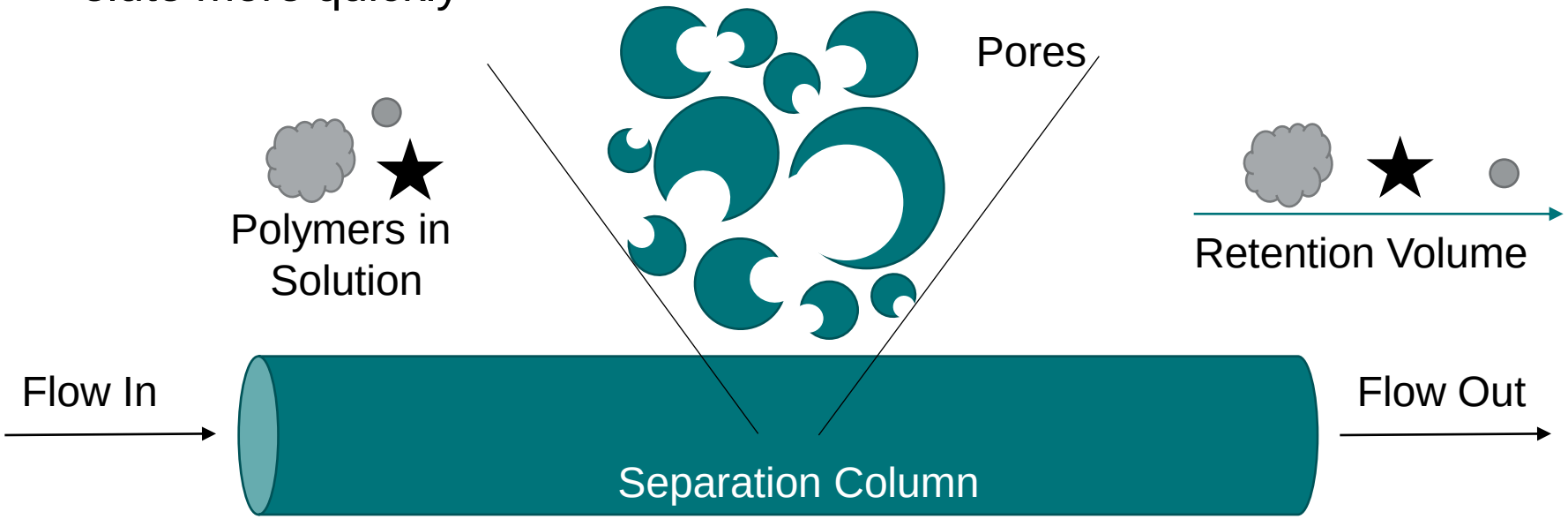
- Procedure used,
- Dissolution of the NC,
- Instrument operation,
- Calibration and data processing.

Previously obtained GPC results have been regarded with caution at AWE, due to the ageing instrumentation and inadequate quality measures.

With a variety of improvements made, reproducible and reliable results are obtained for the determination of NC mmd using GPC.

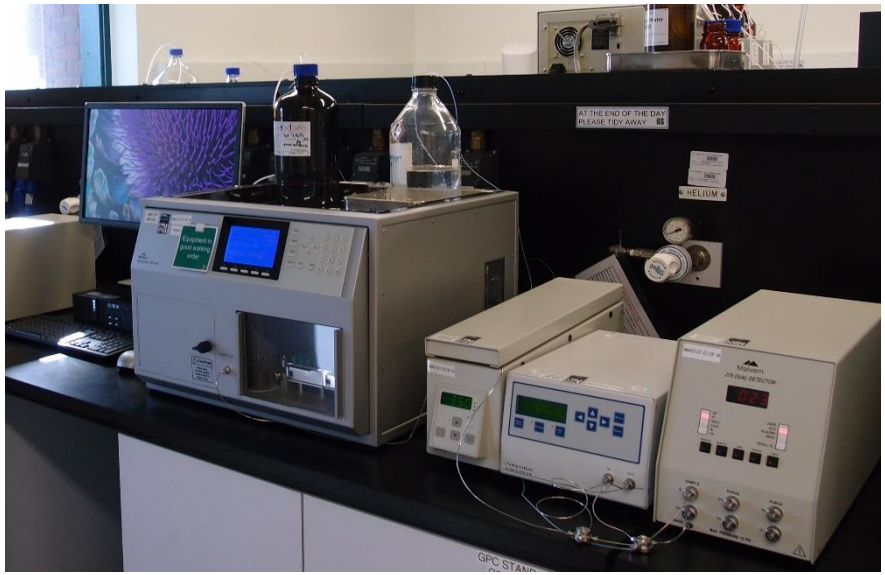
What is GPC?

- Gel permeation chromatography (GPC) is a technique which separates polymers based on their hydrodynamic volume, where “large” species are less retained than “small” species, hence they elute more quickly



New Instruments

- Previous capability was rapidly becoming out dated, 15 years old instrument, alongside an obsolete instrument >25 years old!
- Installation of new kit not only prevents capability loss but also improved sensitivity of detectors
- Current capability consists of:
  - GPC max autosampler, (Malvern)
  - Column oven,
  - Refractive index detector,
  - MALS detector,
  - Viscometer detector.



Sample Preparation

7 Day Method

Sample	Mw	%RSD
1	627,970	0.66
2	601,040	1.12
3	542,078	0.87

24 Hour Method

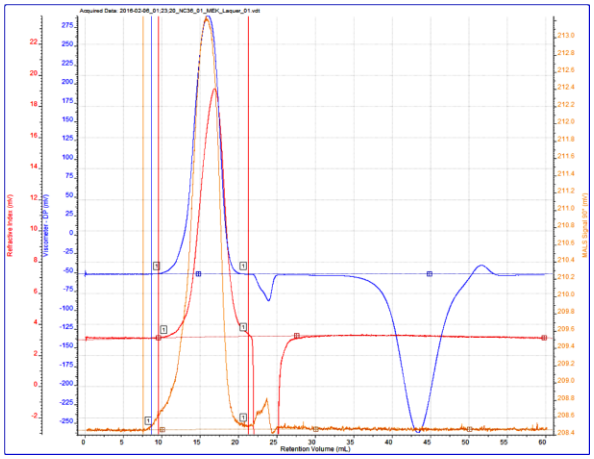
Sample	Mw	%RSD
1	661,835	0.98
2	604,303	1.42
3	552,920	1.92

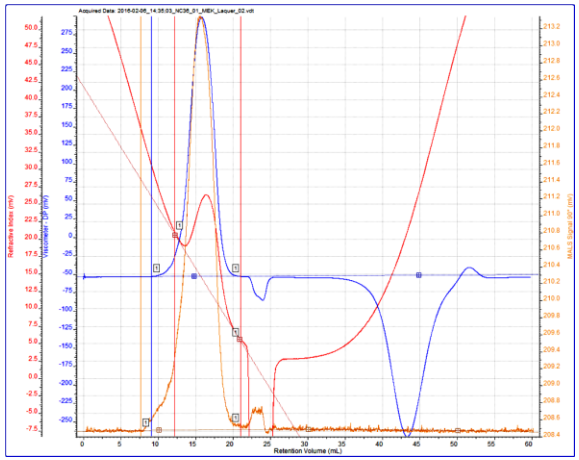
- 3 different NC samples were prepared twice, once using the historic 7 day dissolution method, the other using the improved 24 hour dissolution method.
- Results were obtained using conventional calibration.

Chromatography Conditions

- Chromatography conditions are fundamental to good GPC. Without good baselines, and therefore peak integration, reliable, consistent data interpretation becomes impossible!
- The following factors have been found to improve our results:

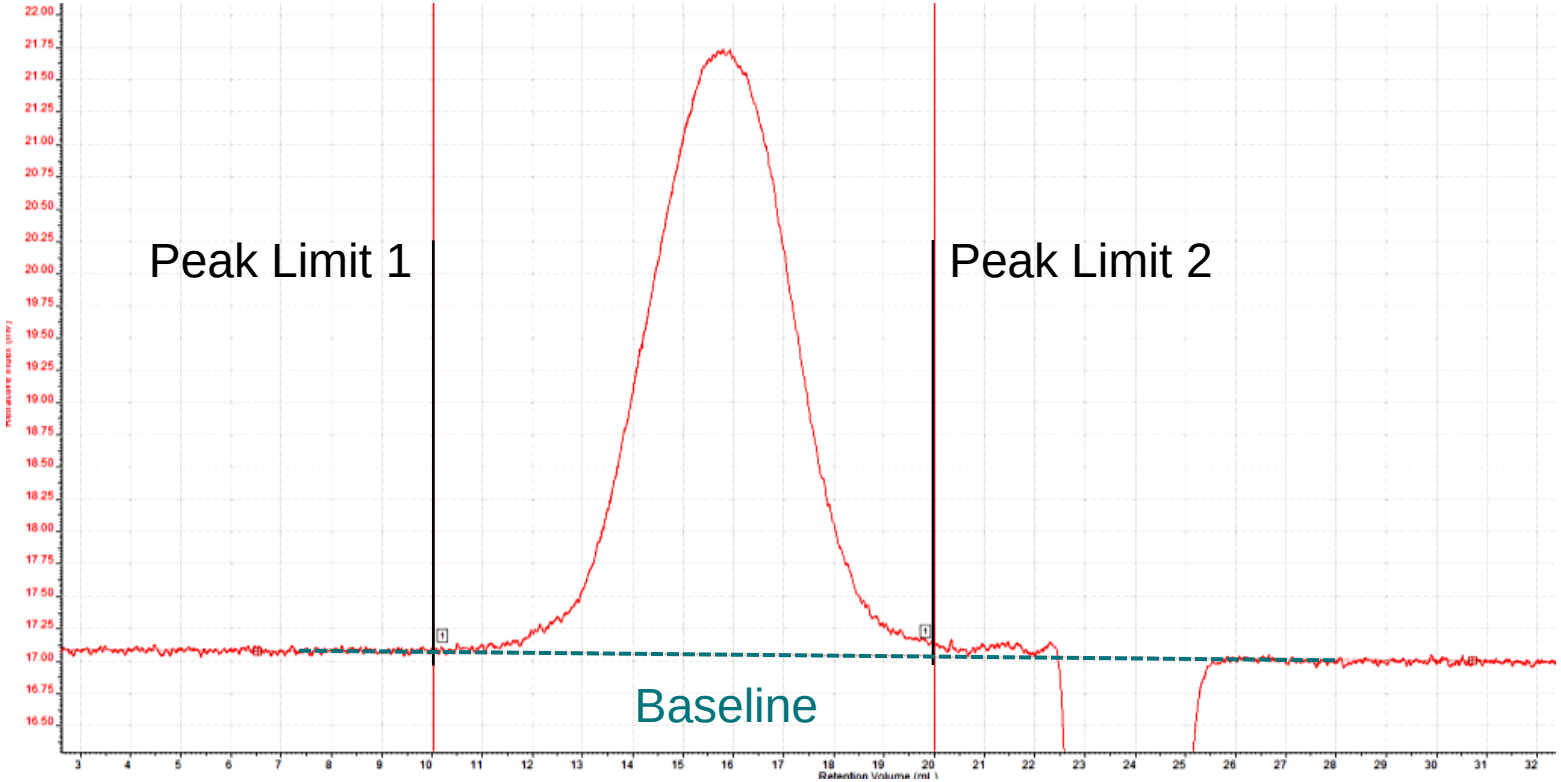
  - Controlled solvent source
  - Well controlled temperature
  - Good Column maintenance
  - Detector purges





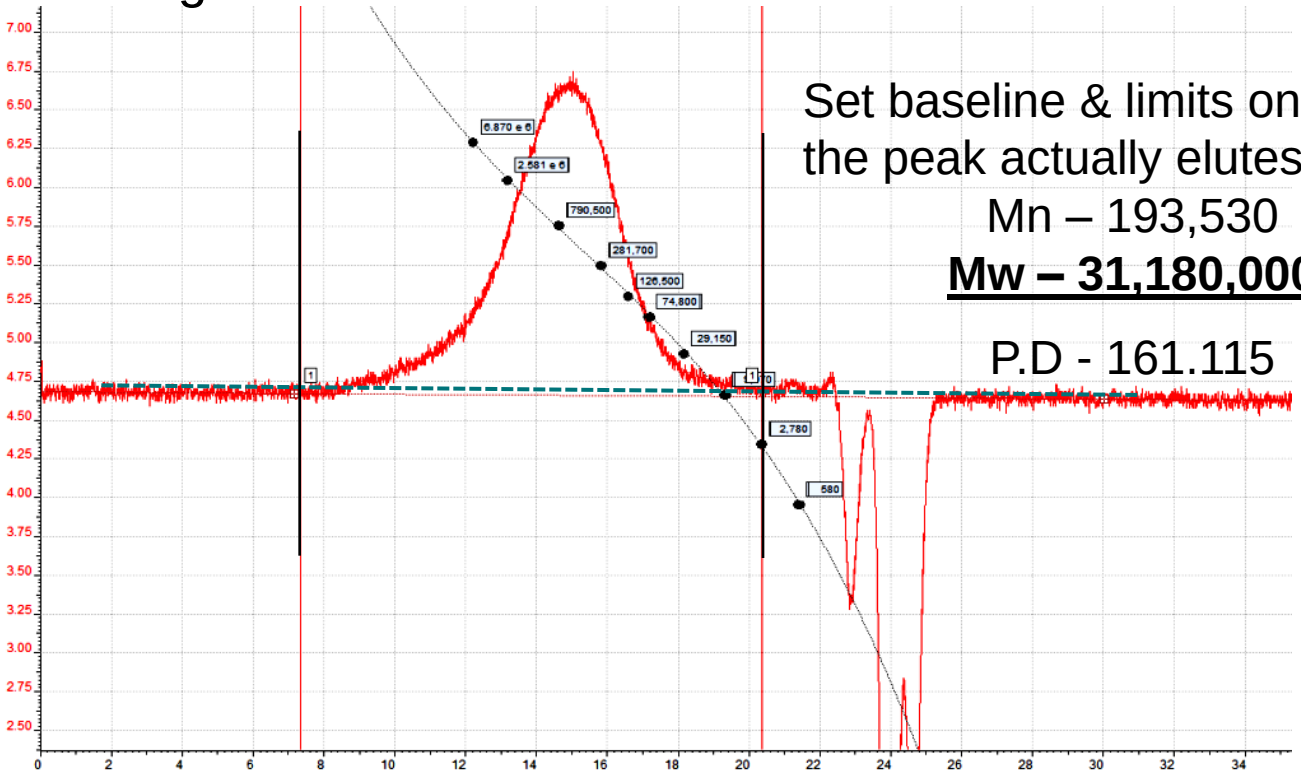
Data Processing

- Where are peak limits and baselines set?



Conventional Calibration

- It was found that for some high Mw NC samples, using a conventional PS calibration curve the front of the peak did not fall within the calibration range of the available standards.



Set baseline & limits on where the peak actually elutes -

Mn – 193,530

Mw – 31,180,000

P.D - 161.115

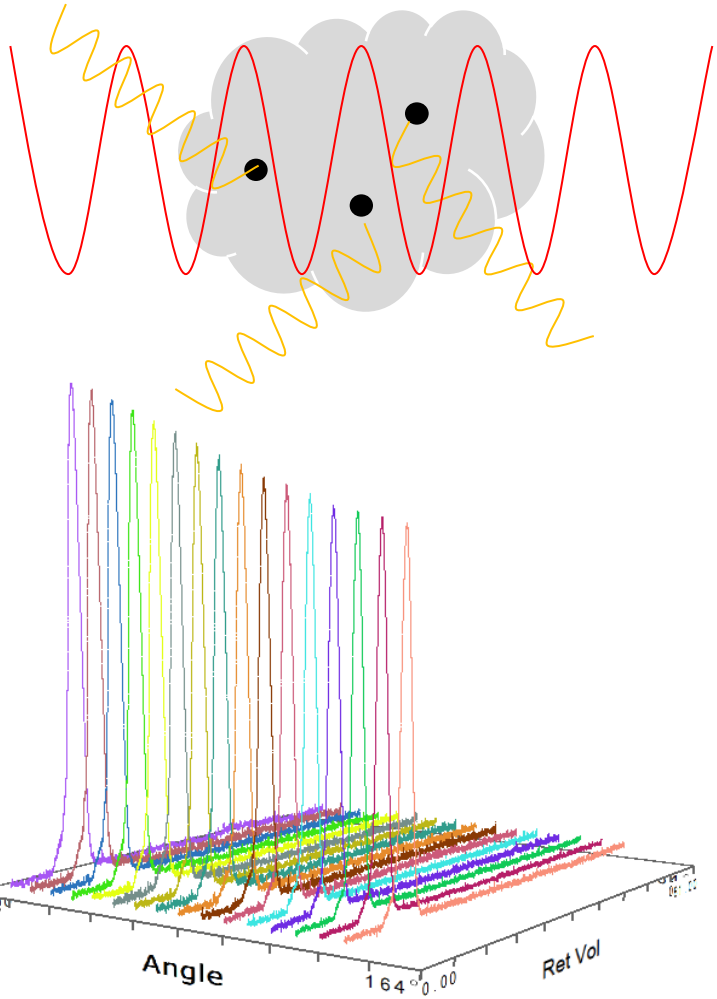
Light Scattering Detectors

- Light scattering detectors work by shining a laser of known λ onto a sample and measuring the scattered light.
- Larger molecules (such as NC) scatter laser light in different directions with different intensities

"Anisotropically"

- The relationship between scattered light and molecular weight is defined by the Rayleigh equation:

$$\frac{KC}{R_\theta} = \left(\frac{1}{Mw} + 2A_2C\right)\frac{1}{P_\theta}$$



Pro's & Con's of Multi Detector Method

Pro's

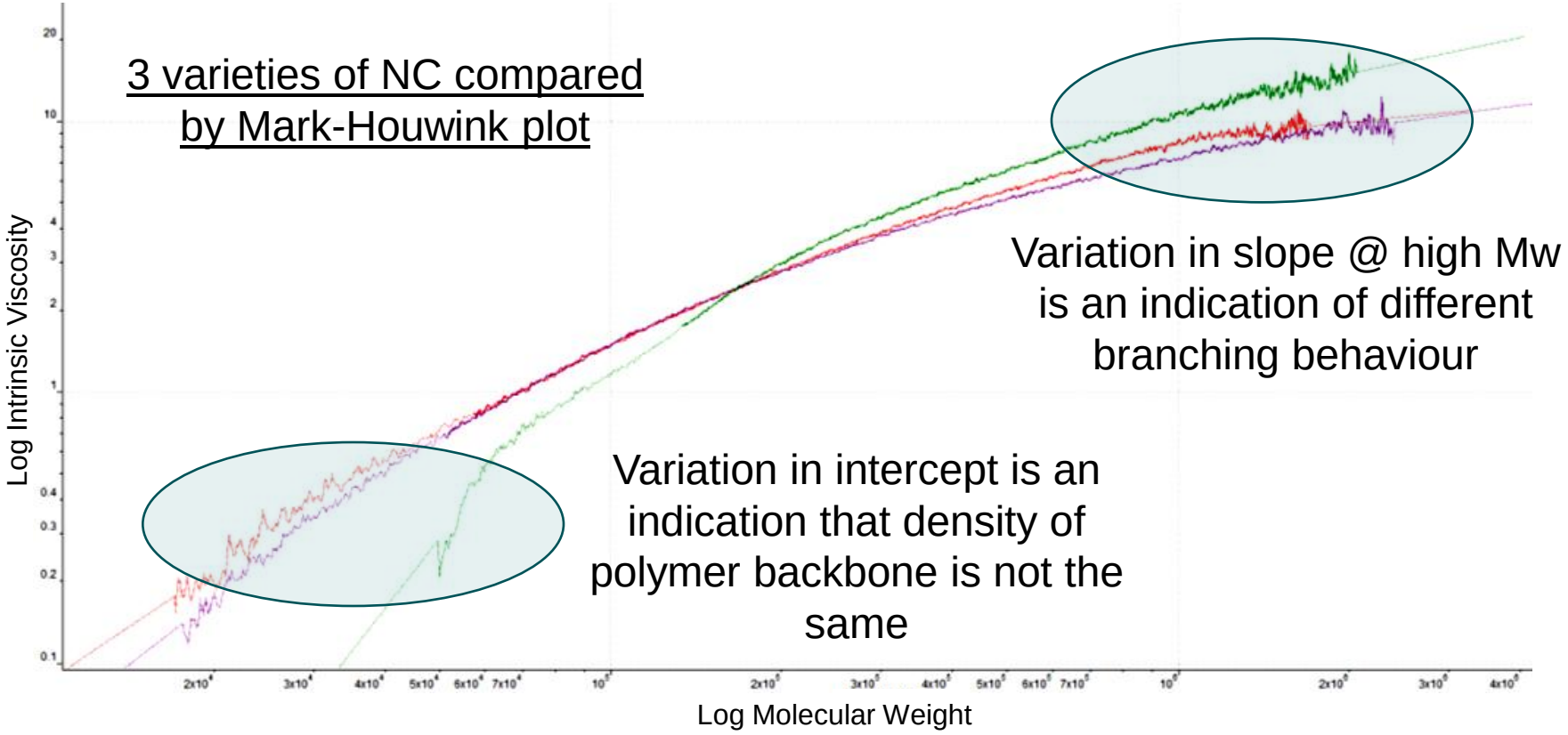
- Doesn't rely on a different polymer for a calibration curve (calibrates detector constants) – Much closer to absolute NC Mw
- Provides additional polymer data such as intrinsic viscosity/branching

Con's

- System can be expensive to set up
- Results more commonly seen as PS equivalents therefore less comparison opportunities
- Requires known sample concentration (or dn/dc) values

Example of Additional Information

- The Mark-Houwink plot describes the relationship of the intrinsic viscosity of a polymer to molecular weight.



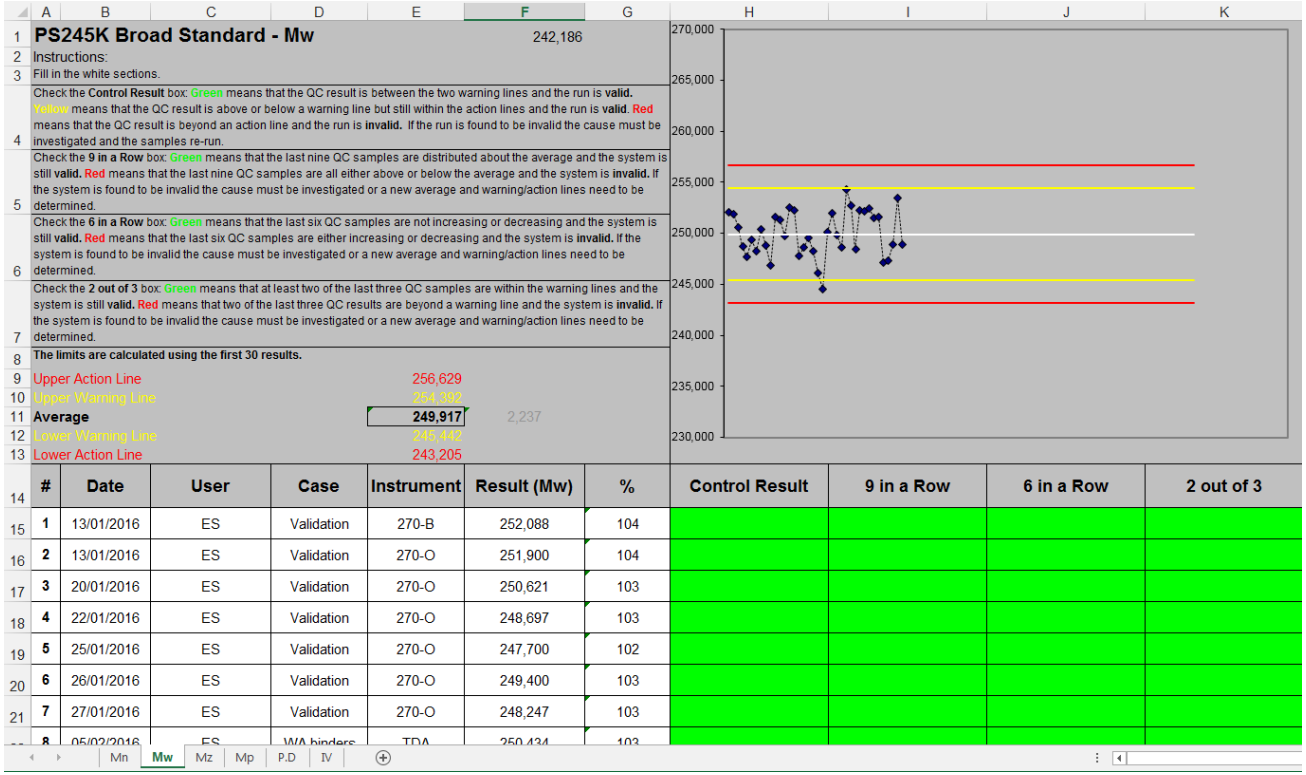
Statistical Results

- Whilst the method currently used is still not finalised, results to date look promising!
- One sample of NC was prepared and injected 9 times
- Molecular weight and intrinsic viscosity showed excellent reproducibility.
- Mn (and therefore PD) were slightly more varied.

	Average	Standard Deviation	%Relative Std. Dev.
Mn	111,906	8416	5.33%
Mw	343,152	2387	0.70%
Polydispersity	3.075	0.217	4.84%
Intrinsic Viscosity	4.666	0.076	1.64%

Quality Control

- A certified reference material (Polystyrene) is always analysed alongside our samples, the results are monitored over time for any significant variation.



PS245K Broad Standard - Mw 242,186

Instructions:

Fill in the white sections.

Check the **Control Result** box: Green means that the QC result is between the two warning lines and the run is **valid.** Yellow means that the QC result is above or below a warning line but still within the action lines and the run is **valid**. Red means that the QC result is beyond an action line and the run is **invalid.** If the run is found to be invalid the cause must be investigated and the samples re-run.

Check the **9 in a Row** box: Green means that the last nine QC samples are distributed about the average and the system is still **valid.** Red means that the last nine QC samples are all either above or below the average and the system is **invalid.** If the system is found to be invalid the cause must be investigated or a new average and warning/action lines need to be determined.

Check the **6 in a Row** box: Green means that the last six QC samples are not increasing or decreasing and the system is still **valid.** Red means that the last six QC samples are either increasing or decreasing and the system is **invalid.** If the system is found to be invalid the cause must be investigated or a new average and warning/action lines need to be determined.

Check the **2 out of 3** box: Green means that at least two of the last three QC samples are within the warning lines and the system is still **valid.** Red means that two of the last three QC results are beyond a warning line and the system is **invalid.** If the system is found to be invalid the cause must be investigated or a new average and warning/action lines need to be determined.

The limits are calculated using the first 30 results.

Upper Action Line	256,629
Upper Warning Line	254,292
Average	**249,917** 2,237
Lower Warning Line	245,442
Lower Action Line	243,205

#	Date	User	Case	Instrument	Result (Mw)	%	Control Result	9 in a Row	6 in a Row	2 out of 3
1	13/01/2016	ES	Validation	270-B	252,088	104				
2	13/01/2016	ES	Validation	270-O	251,900	104				
3	20/01/2016	ES	Validation	270-O	250,621	103				
4	22/01/2016	ES	Validation	270-O	248,697	103				
5	25/01/2016	ES	Validation	270-O	247,700	102				
6	26/01/2016	ES	Validation	270-O	249,400	103				
7	27/01/2016	ES	Validation	270-O	248,247	103				
8	05/02/2016	ES	WA binders	TDA	250,434	103				

Looking Forward

- Finalise the method parameters, including:
  - Further improve baselines
  - Settle peak integration limits
  - Test 24 hour prep Vs. 7 day using light scattering
- Once finished carry out a round robin with as many labs as possible *(although multidetector GPC will limit the number of possible participants).*

Summary

- New instrumentation
- Investigated sample preparation
- Explored chromatography conditions
- Examined our data processing practices
- Installed and method developed a multidetector method including viscometer and light scattering detectors
- Instigated an improved quality control system

Thanks to:

- Amy Newman (AWE)
- Paul Deacon (AWE)
- Amy Ross (Malvern)
- Nikki Pockett (AWE)
- Nicola Barnett and Jamie Hill (AWE)