

Evaluation of round robin test results for a size exclusion chromatography method for the analysis of nitrocellulose

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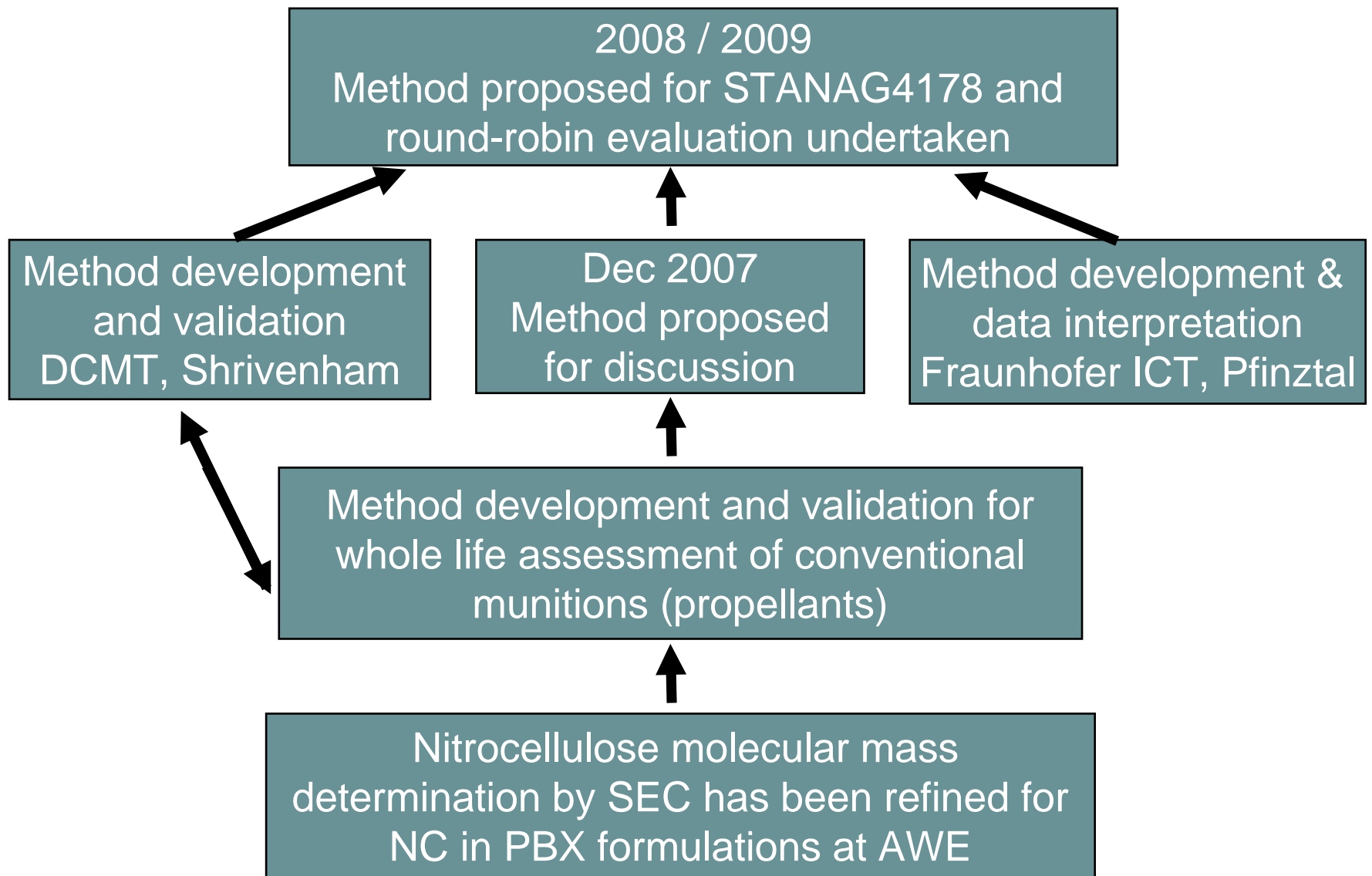
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Background

- Propellants contain high nitrocellulose levels and life is traditionally assessed by stabiliser concentration.
- Mechanical integrity is important – A correlation has been shown between mechanical properties of a nitrocellulose containing PBX and the molar mass distribution.
- Size Exclusion Chromatography (SEC) is a technique that can investigate the molar mass distribution of polymers but has been considered by some as a random number generator.
- A method for the molecular mass determination of nitrocellulose using SEC was proposed for inclusion in STANAG 4178.
- A round-robin inter-laboratory study was undertaken to assess variability of the method





Participants

Organisation	Nation	Detectors
AWE Plc	UK	RI
ATK Radford	USA	RI
Cranfield University	UK	RI
Denel Land Systems	South Africa	RI
Fraunhofer ICT	Germany	RI
General Dynamics	Canada	UV/Vis
Rheinmetall Nitrochemie Wimmis	Switzerland	UV/Vis
PVTT	Finland	UV/Vis
TNO Defence	Netherlands	UV/Vis



Proposed Method

[BHT]	M_n (Dalton) (± 1 s.d.)	M_w (Dalton) (± 1 s.d.)	Polydispersity (± 1 s.d.)
[250ppm]	346200 ± 9050 (2.6%)	669000 ± 10500 (1.6%)	1.933 ± 0.048
[100ppm]	335100 ± 6900 (2.1%)	653500 ± 11500 (1.8%)	1.950 ± 0.034
[0ppm]	329400 ± 3900 (1.2%)	639900 ± 8500 (1.3%)	1.943 ± 0.030

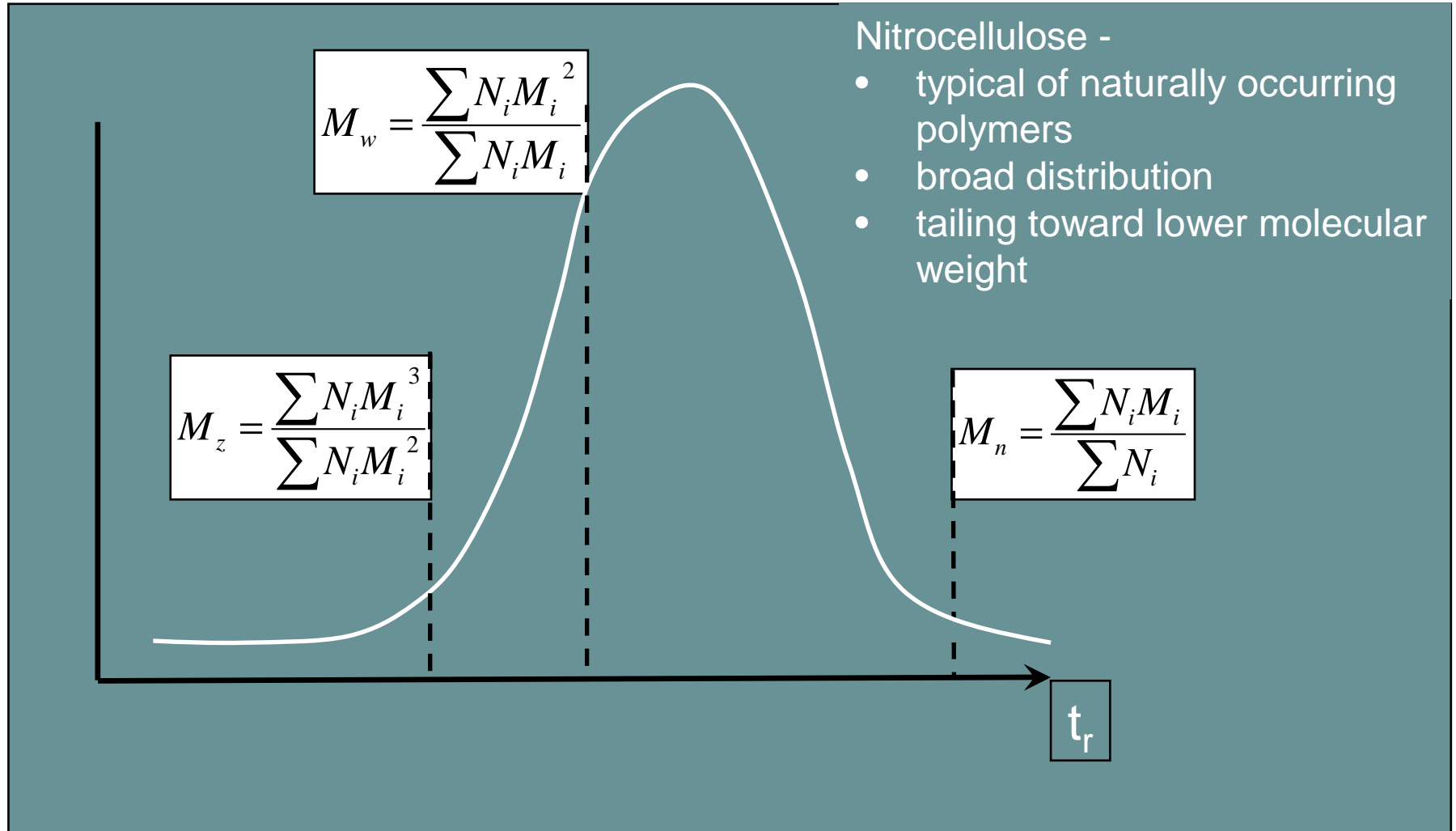
with
(abs)



Round Robin Evaluation

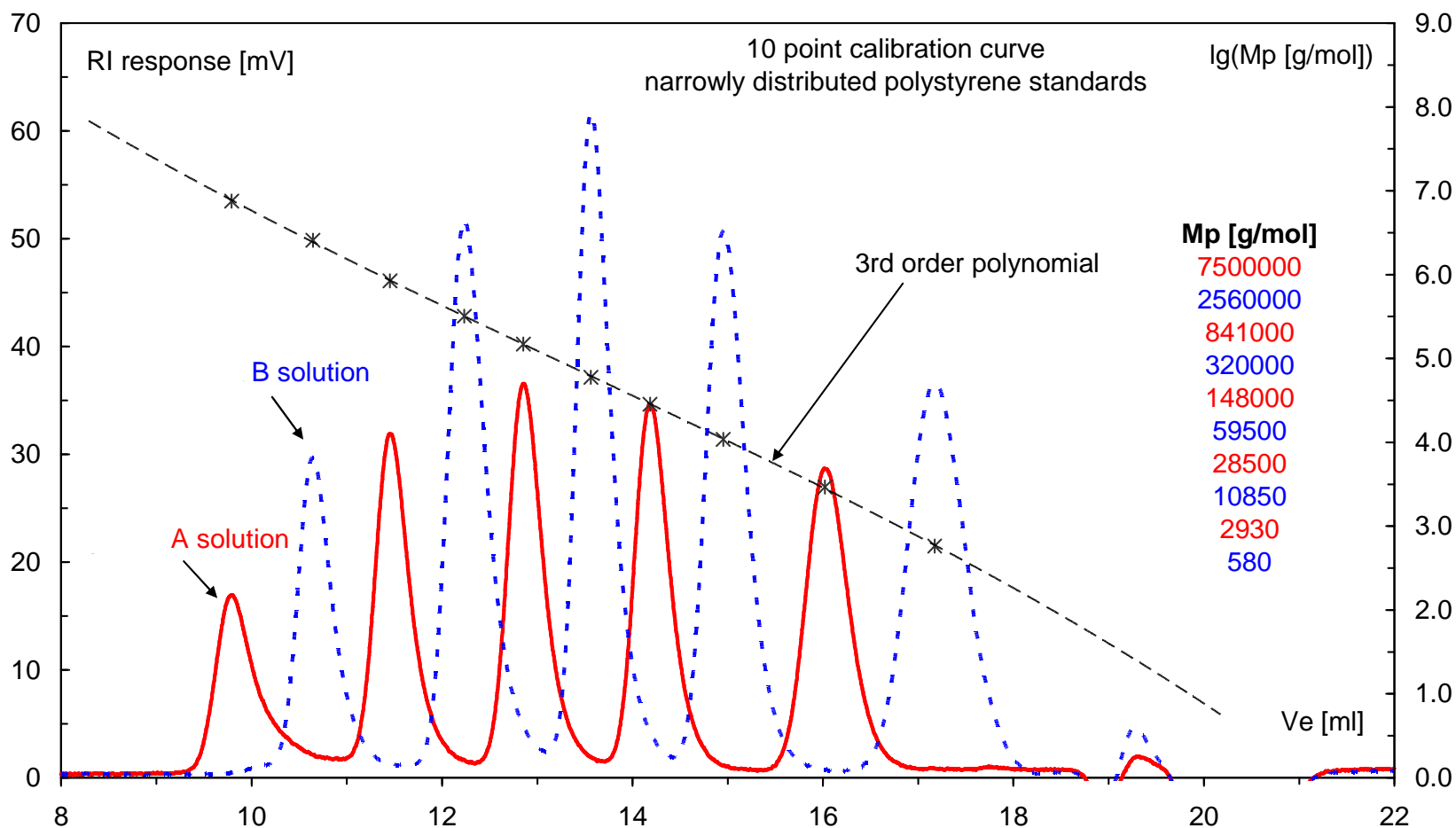
- All Participants received:
 - Two columns manufactured from the same batch of Polystyrene divinyl benzene
 - Polystyrene narrow standards of the same batch
 - Polystyrene NBS706 broad standard
 - Four nitrocellulose samples (water wet) of differing nitrogen content (11.69% to 13.55%)
- All participants asked to report:
 - Drying regime used and sample concentrations
 - Calculated molecular weight distributions for the NBS706 and the nitrocellulose samples

Size Exclusion chromatography

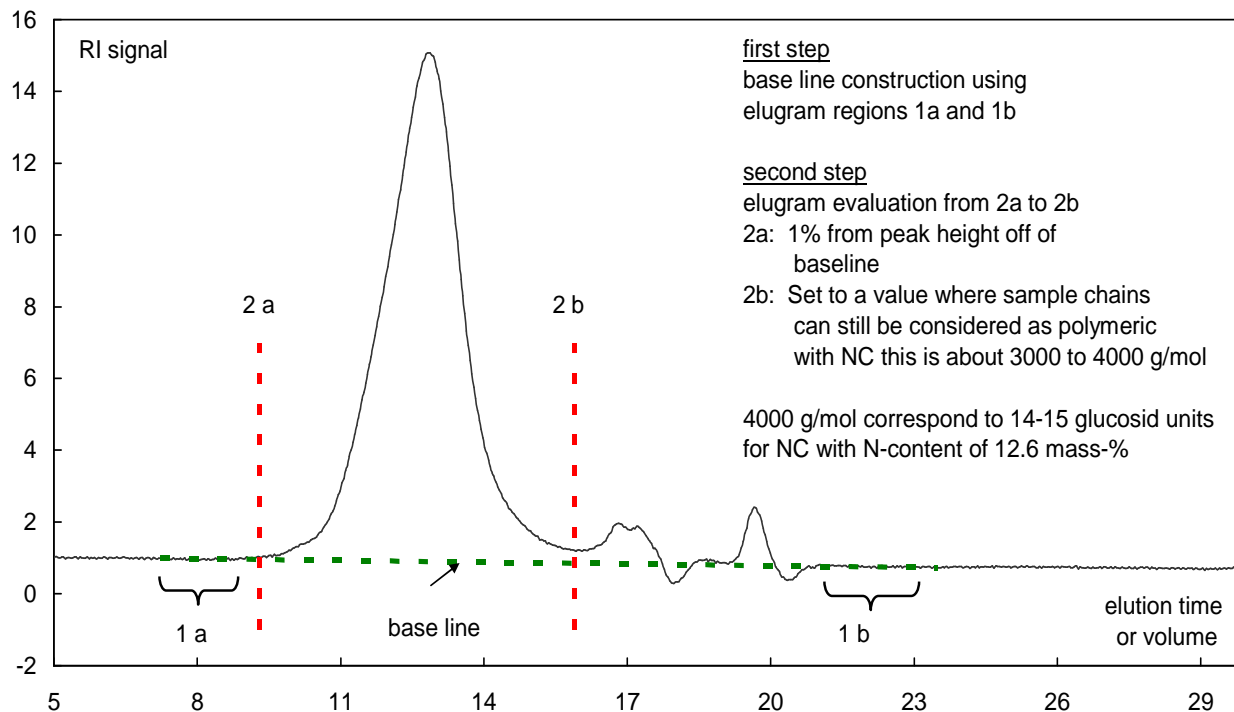




Polystyrene Calibration



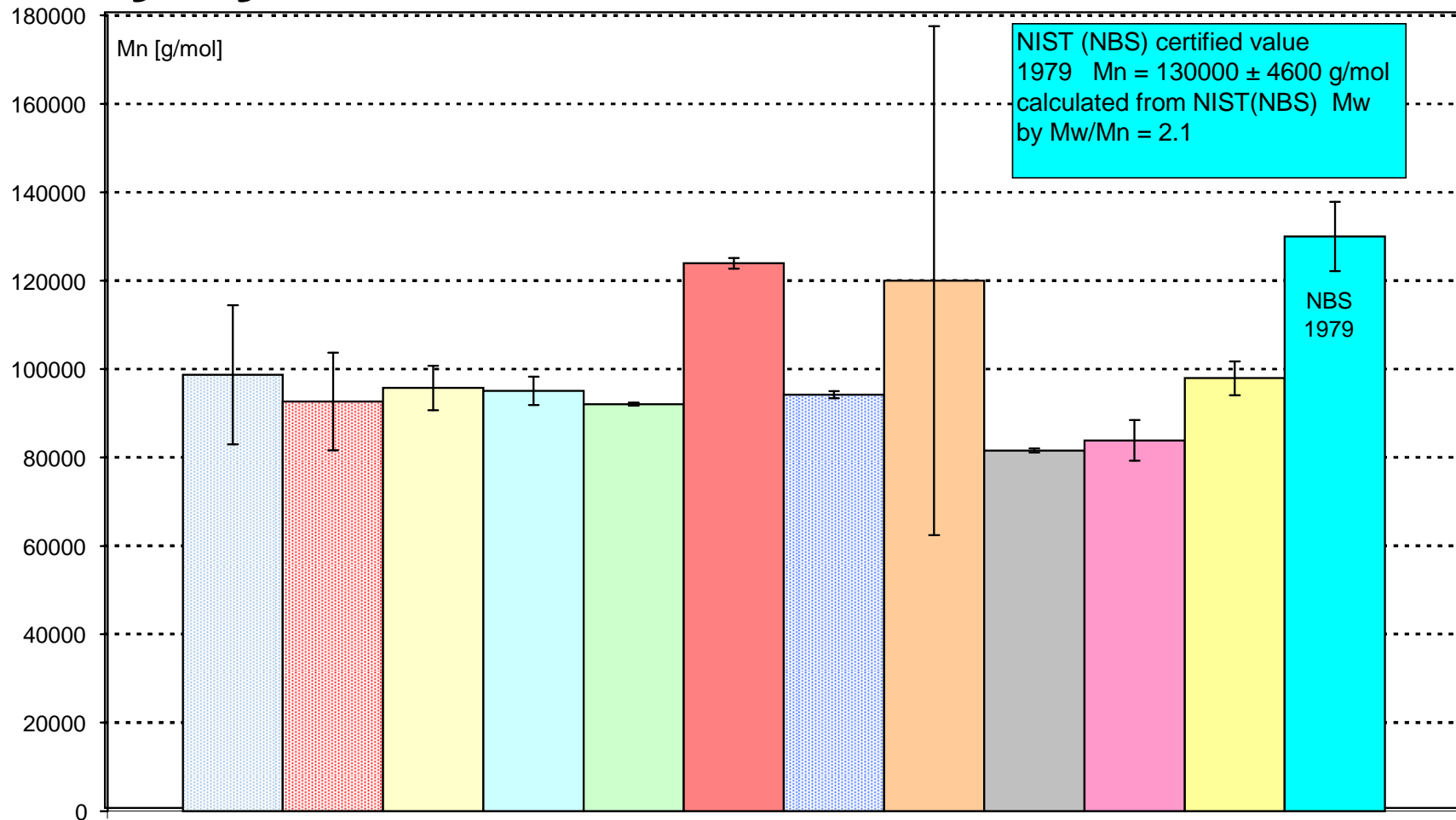
Data Interpretation



Integration limits and base line setting [Ref Pontius H; Dörich M; Bohn M. P69, 39th International Conference of ICT 24-27 June 2008, Karlsruhe, Germany]

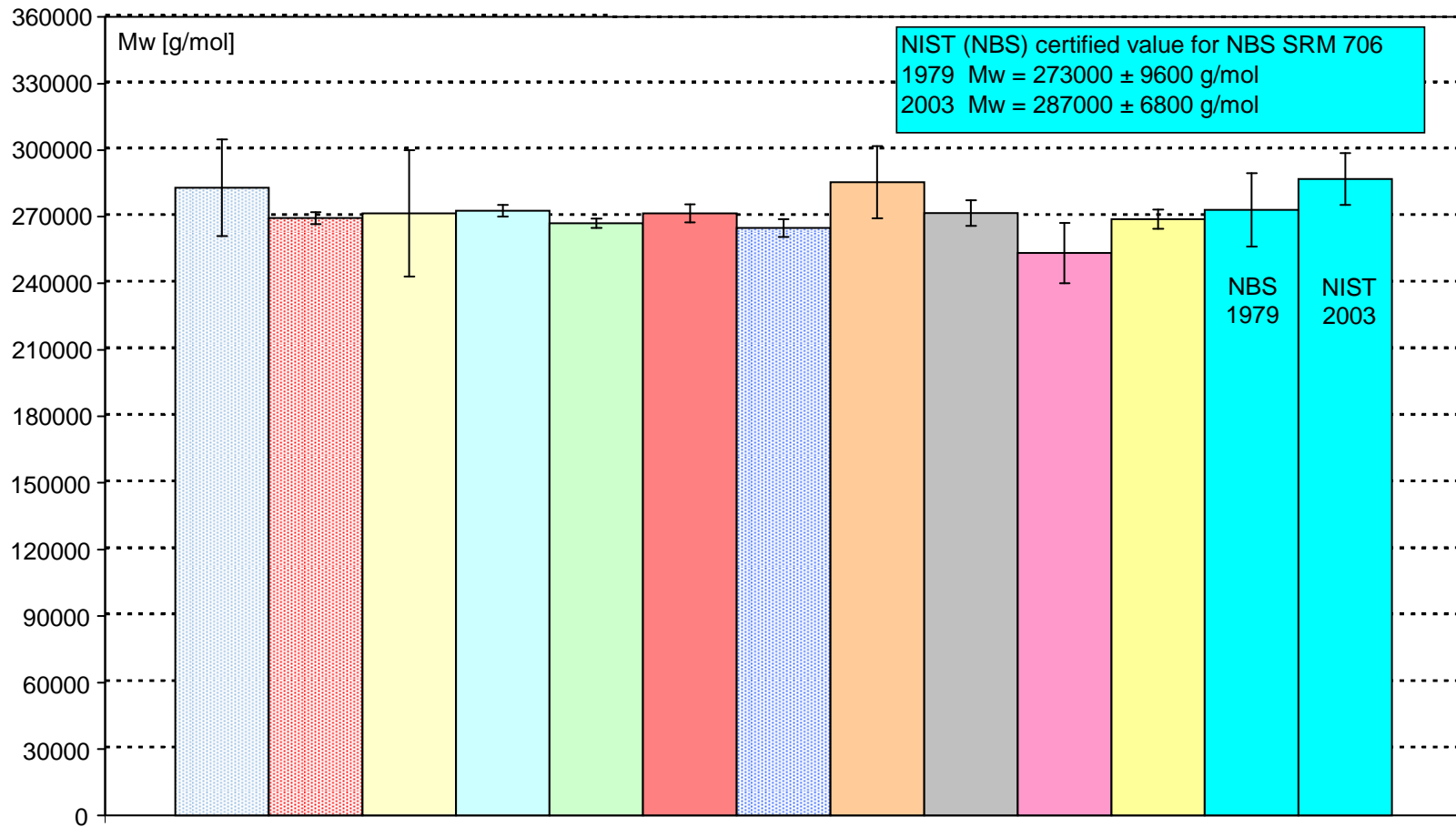


Polystyrene Standard NBS706 Mn





Polystyrene Standard NBS706 Mw



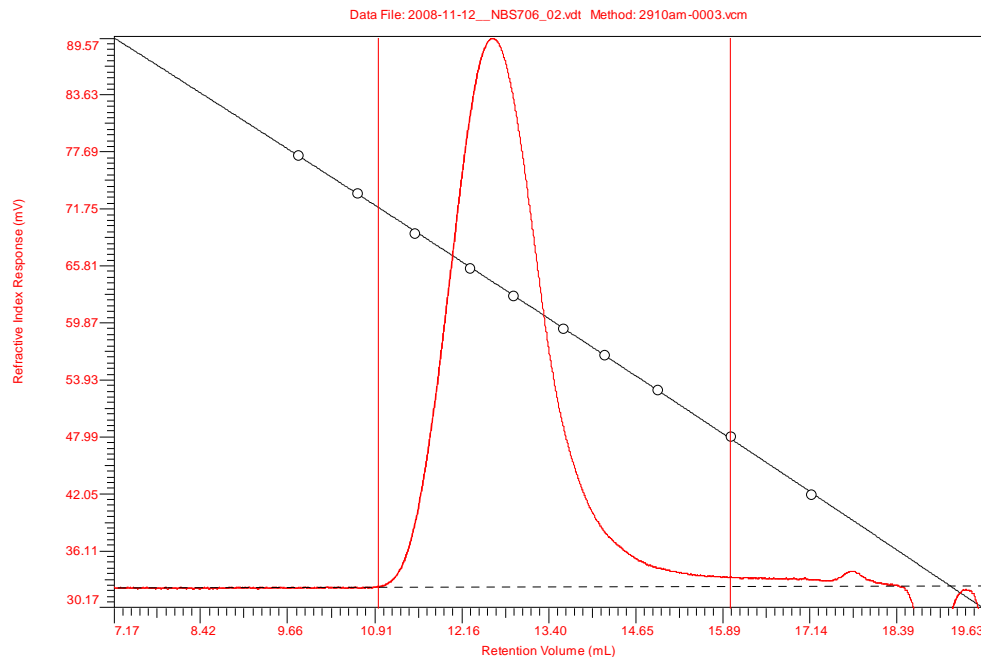


NBS706 Data

Laboratory	Mn		Mw	
	Mean	Relative SD at 95% Conf	Mean	Relative SD at 95% Conf
1	98700	15.9	283070	7.7
2	92660	11.9	269380	1.0
3	95740	5.3	271500	10.5
4	95060	3.4	272660	0.9
5	92050	0.4	266993	0.8
6	123940	1.0	271500	1.5
7	94210	0.9	264850	1.5
8*	120020	48.1	285500	5.7
9	81580	0.6	271590	2.2
10*	83900	5.5	253640	5.4
11	97900	3.9	268910	1.6
* Average of two injections				
Mean	97500 (93490)	27.9 (13.0)	270730 (270960)	6.9 (6.0)



NBS706 Data Evaluation



- Outliers in Mn data identified by Grubbs Test

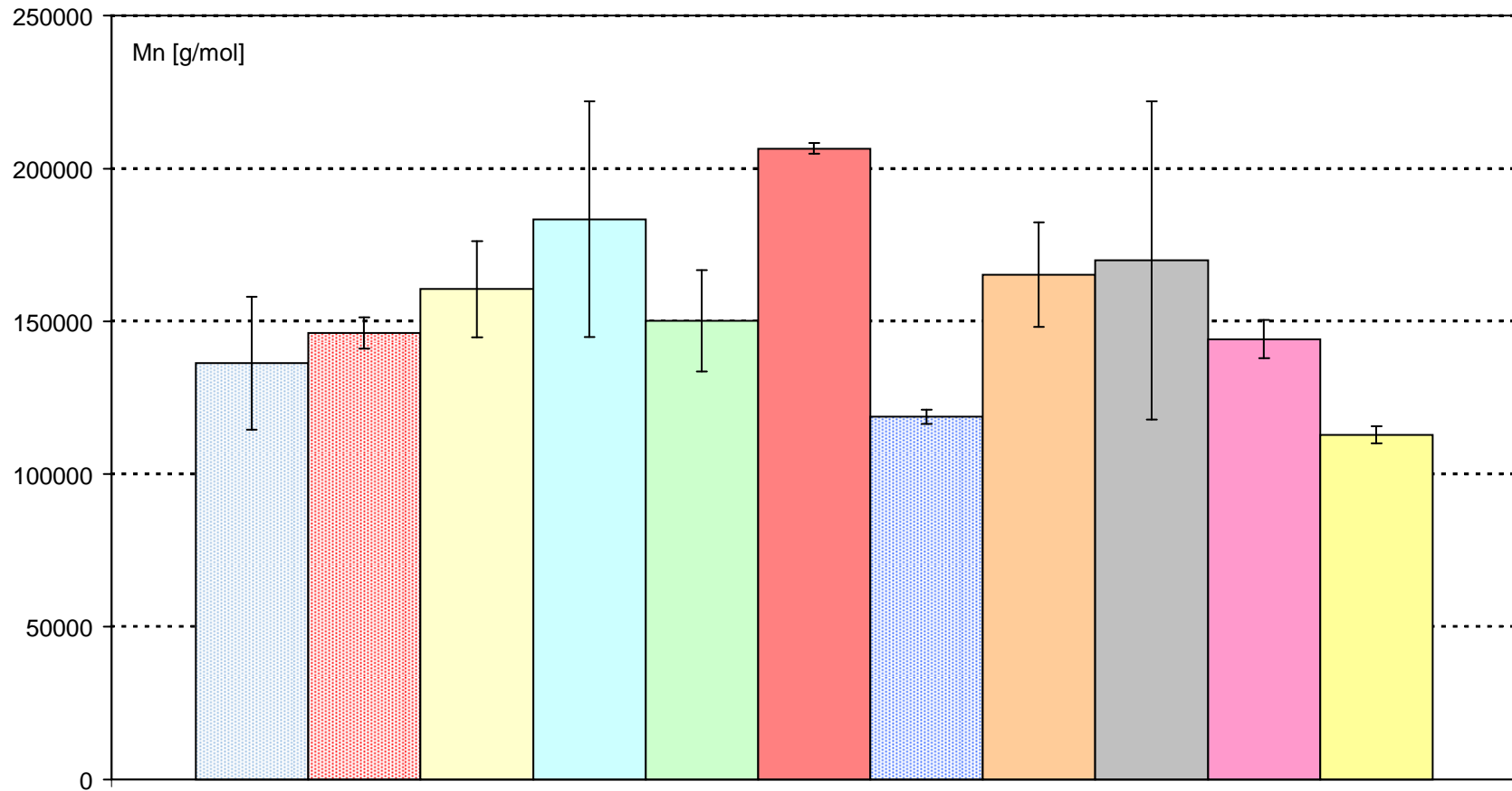
- ANOVA analysis:
Fcrit = 2.55

Mn Fcalc = 5.61 Not same family
Mw Fcalc = 2.59 Same family ?

- Integration at PS 2930 daltons
- Consistent but includes large area of tail so influences Mn data
- Conclusion: confidence in Mw determinations for well characterised polymers

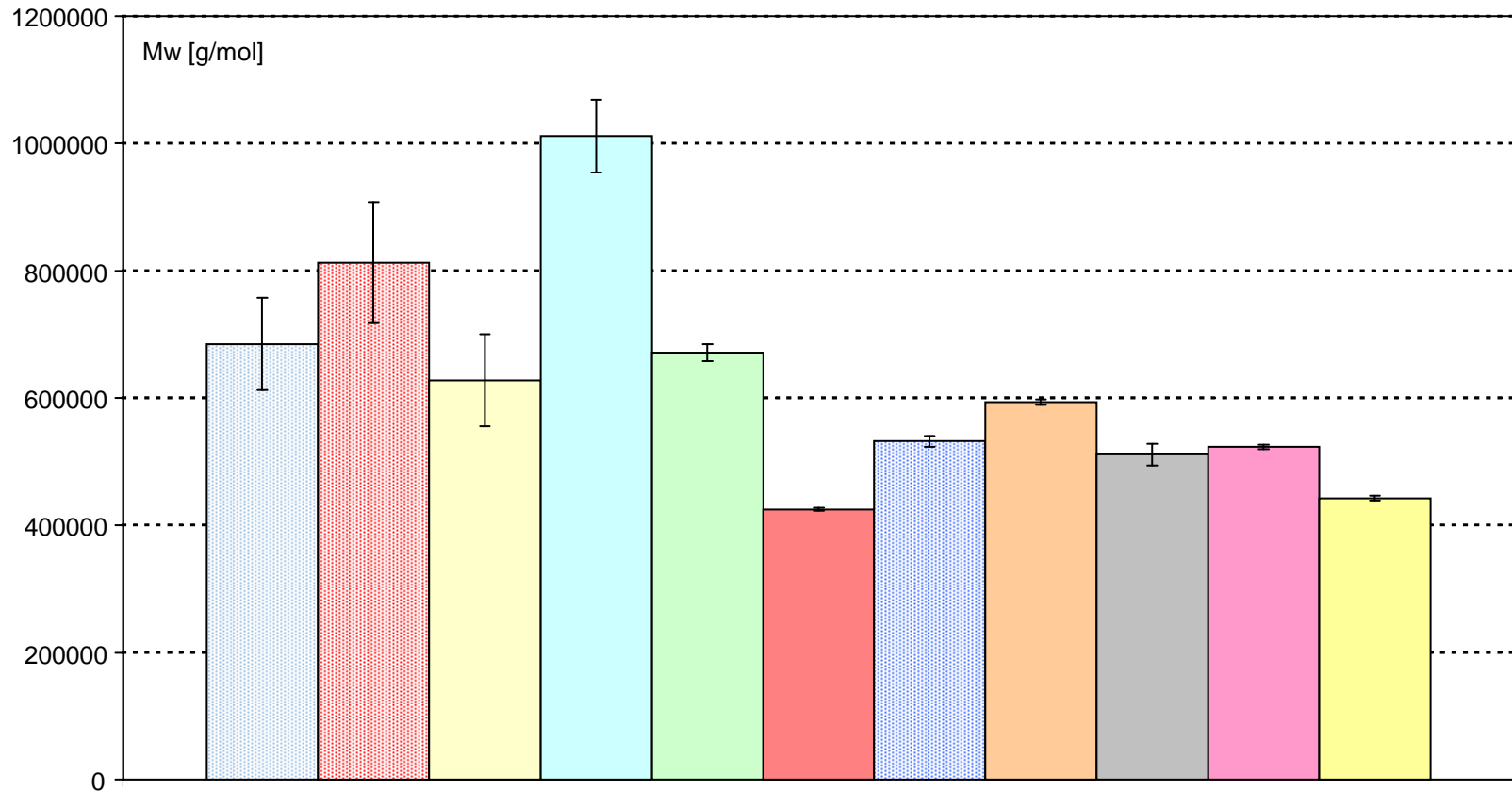


Nitrocellulose Mn Data (12.15% N)





Nitrocellulose Mw Data (12.15% N)





Nitrocellulose Data (12.15% N)

Laboratory	Mn		Mw	
	Mean	Relative SD at 95% Conf	Mean	Relative SD at 95% Conf
1	158040	15.9	757637	10.6
2	151260	3.5	812680	11.7
3	176370	9.9	699720	11.5
4	222050	21.1	1068780	5.6
5	166720	11.0	684490	2.0
6	208310	0.9	427160	0.6
7	121070	2.0	540810	1.6
8	182350	10.3	597480	0.7
9	221920	30.6	511150	3.4
10	144140	4.3	523140	5.4
11	112840	2.5	442657	0.9
Mean	153990	32.0	621420	46.8



Nitrocellulose Data Evaluation

ANOVA analysis of 11 data sets : $F_{crit} = 2.30$

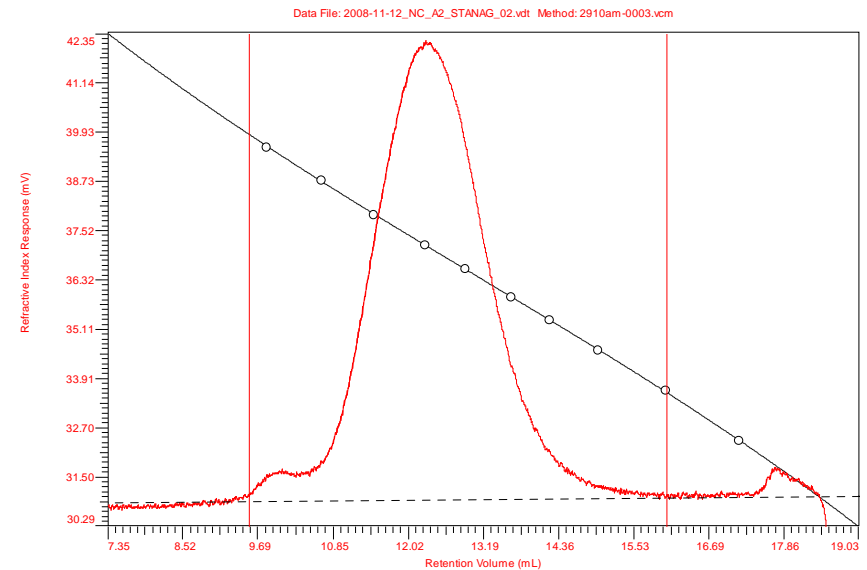
NC	F _{calc}	
	M _n	M _w
11.69% N	28.26	79.87
12.15% N	15.80	5.93
12.71% N	1.16	10.44
13.55%N	21.03	65.46

- Only one case where the data (M_n) can be considered to be the same family at 95% confidence
- NBS706 data suggest variability is not related to the SEC systems
- High variability
 - Natural variability of the sample
 - Sample preparation



Nitrocellulose Data Evaluation

NC	Mn		Mw	
	Mean	Relative SD at 95% Conf	Mean	Relative SD at 95% Conf
11.69% N	126910	32.3	515570	47.7
	121000	24.9	479090	31.7
12.15% N	153990	32.0	621420	46.6
	153990	32.0	582390	34.7
12.71% N	166830	42.8	780800	89.3
	164780	41.9	694880	47.3
13.55% N	121450	36.4	589300	74.4
	121440	36.4	520230	41.0



- Pre-peak affected two data sets – high Mw
- Same SEC instrument
 - sensitive RI detector



Variability

- Sample preparation thought to be main area of variability
- Drying regime:
 - Initially left to Lab preference
 - Thermal load applied during drying variable. Some degradation possible.
 - Consistency is now believed to be important
- *Pontius et al; P80 40th International Conference of ICT (2009)*

Organisation	Drying method
AWE Plc	samples on filter paper, 80°C for 2 h
ATK Radford	samples in cardboard tray, - 75°C for 3 h
Cranfield Univ.	65°C for 2 h under vacuum over silica gel left overnight under vacuum
Denel	65°C for 4 h under vacuum Stored in a vacuum desiccator
Fraunhofer ICT	40°C for 24 h under vacuum over P ₂ O ₅ dried to constant mass
General Dyn.	70°C for 6 h under vacuum dried to ~ 0.2 mass-% water content
Nitrochemie	dried in hot air blower at 60°C for 1 h 100 °C for 0.5 h
PVTT	dried in desiccator for 2 h at ambient temp. 60°C for 2 h
TNO Defence	65°C for 24 h water content 0.2 – 0.4 mass-%



Refined Method

- Sample drying at 60°C for 2 hours
- Samples prepared at 1.5mgcm⁻³ in THF stabilised with <250ppm BHT
- Dissolution time: 30 minutes at 37°C - 39°C with stirring
- Polystyrene calibration standards across the whole nitrocellulose distribution. Broad polystyrene instrument performance check standard
- Mobile phase flow rate: 1cm³min⁻¹
- Triplicate sample injection per vial of 100µl
- Columns: Two 10µ, 30 x 7.5cm mixed porosity polystyrene divinyl benzene maintained at 35°C



Conclusions

- Good multinational support and commitment
- NBS706 Mw data demonstrates lab to lab reproducibility
- Nitrocellulose data has large variability
 - Nitrocellulose sample prep regimes need to be standardised (drying in particular)
- 7 day dissolution not ideal for manufacturers
 - An alternative fast dissolution method proposed with no impact on data
 - Sample in - data out; 1 working day
- Refined method accepted for STANAG4178



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