Progress toward reliable NC molecular mass distribution by GPC, plus a small introduction to CHN

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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:

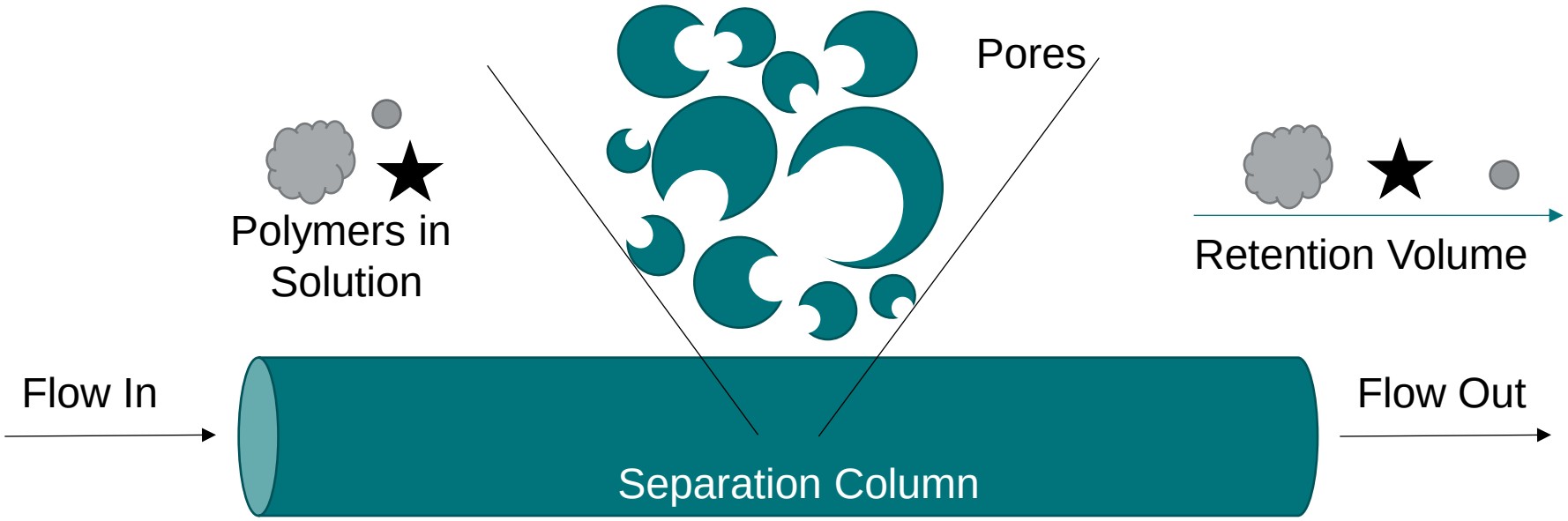
- Procedure used,
- Dissolution of the NC,
- Instrument operation,
- Calibration and data processing.

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.

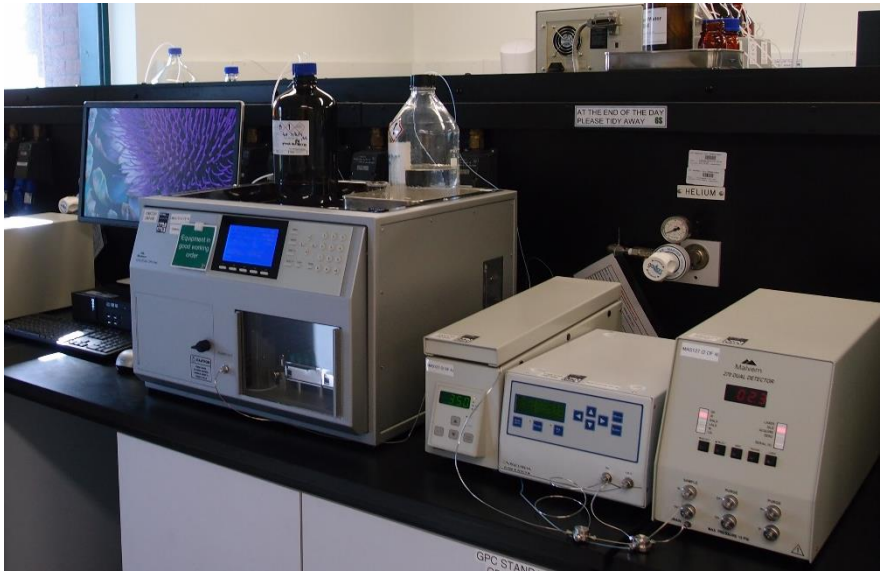
What is GPC?

- 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.



Method Parameters

- New triple detector method recently validated - refractive index, viscosity and light scattering detectors
- Two Mixed B columns used
- Blanks, standards and samples all injected in triplicate
- Run flow is 1mL/min and temperature is 35ºC
- Each injection runs for one hour
- Narrow polystyrene (PS105K) used to calibrate method, broad polystyrene (PS245K) then used as check standard
- The RSD% values for triplicate sample injections were deemed to be suitable if Mw <5% and Mn <10%

Sample Preparation

- Concentration normally 2mg/mL

- For nitrocellulose: 0.1g (±0.01g) of dried nitrocellulose, 50mL of stabilised THF added and left on shaker table for 24 hours (±1 hour)

- For HMX formulations: 2g (±0.01g) of sample, 10mL of stabilised THF added and left on shaker table for 24 hours (±1 hour)

Historical Comparison?

- Can we confidently compare data produced by the old method with data produced by the new method?

- Can we create a nitrocellulose library to help with backwards comparisons?

Historical Powder Analysis

- Analysis consisted of four separate runs
- Each run analysed HMX Formulation A
- Data was then compared across the four runs and RSD% values produced
- New light scattering data was plotted against original refractive index data

HMX Formulation Data

Sample ID	Manufacture Date	Mn	Mw	P.D.	
HMX Formulation A	1988	155,000	285,000	1.85	Run 1
HMX Formulation B	1988	152,000	300,000	1.98	
HMX Formulation C	1989	130,000	240,000	1.84	
HMX Formulation D	1989	165,000	297,000	1.80	
HMX Formulation E	1990	129,000	241,000	1.87	
HMX Formulation F	1990	117,000	222,000	1.90	Run 2
HMX Formulation G	1990	138,000	265,000	1.93	
HMX Formulation H	1991	117,000	218,000	1.86	
HMX Formulation I	1991	118,000	225,000	1.91	
HMX Formulation J	1991	119,000	211,000	1.78	Run 3
HMX Formulation K	1992	135,000	260,000	1.93	
HMX Formulation L	1993	128,000	274,000	2.14	
HMX Formulation M	1994	145,000	290,000	2.00	
HMX Formulation N	1994	119,000	237,000	2.01	Run 4
HMX Formulation O	1996	152,000	275,000	1.82	
HMX Formulation P	1997	143,000	285,000	1.99	
HMX Formulation Q	1999	160,000	308,000	1.92	
HMX Formulation R	2004	144,000	288,000	2.01	

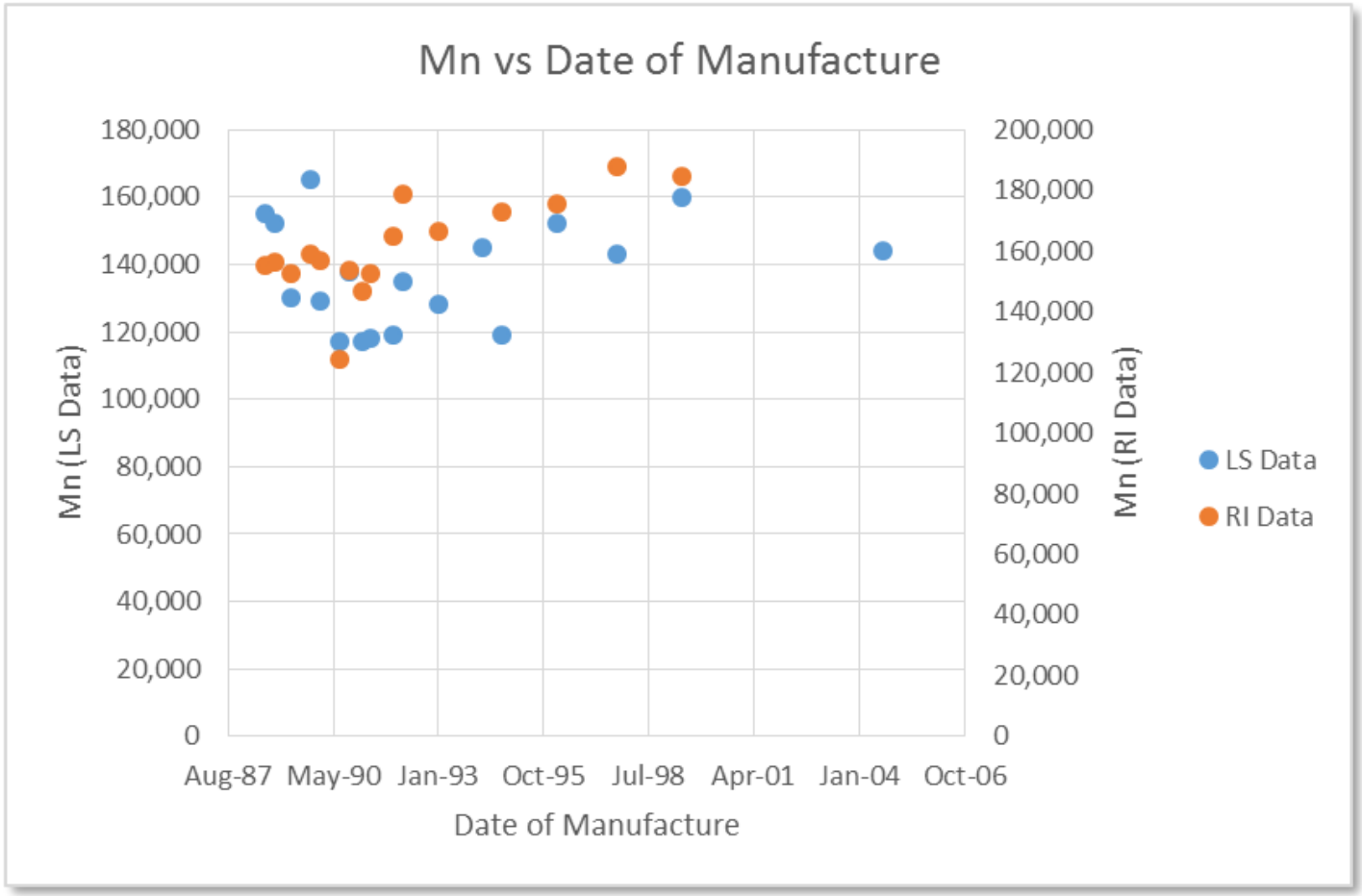
HMX Formulation A Comparison

- Each of the four runs included injections of HMX Formulation A
- These were then compared across the four runs in the table below:

Sample ID	Mn	Mw	P.D.
Run 1	155,000	285,000	1.85
Run 2	148,000	271,000	1.84
Run 3	151,000	288,000	1.91
Run 4	140,000	258,000	1.86

- The comparison of Mw data gives an RSD of <5%, showing a good comparison across all four runs

Comparing Light Scattering and Refractive Index Data



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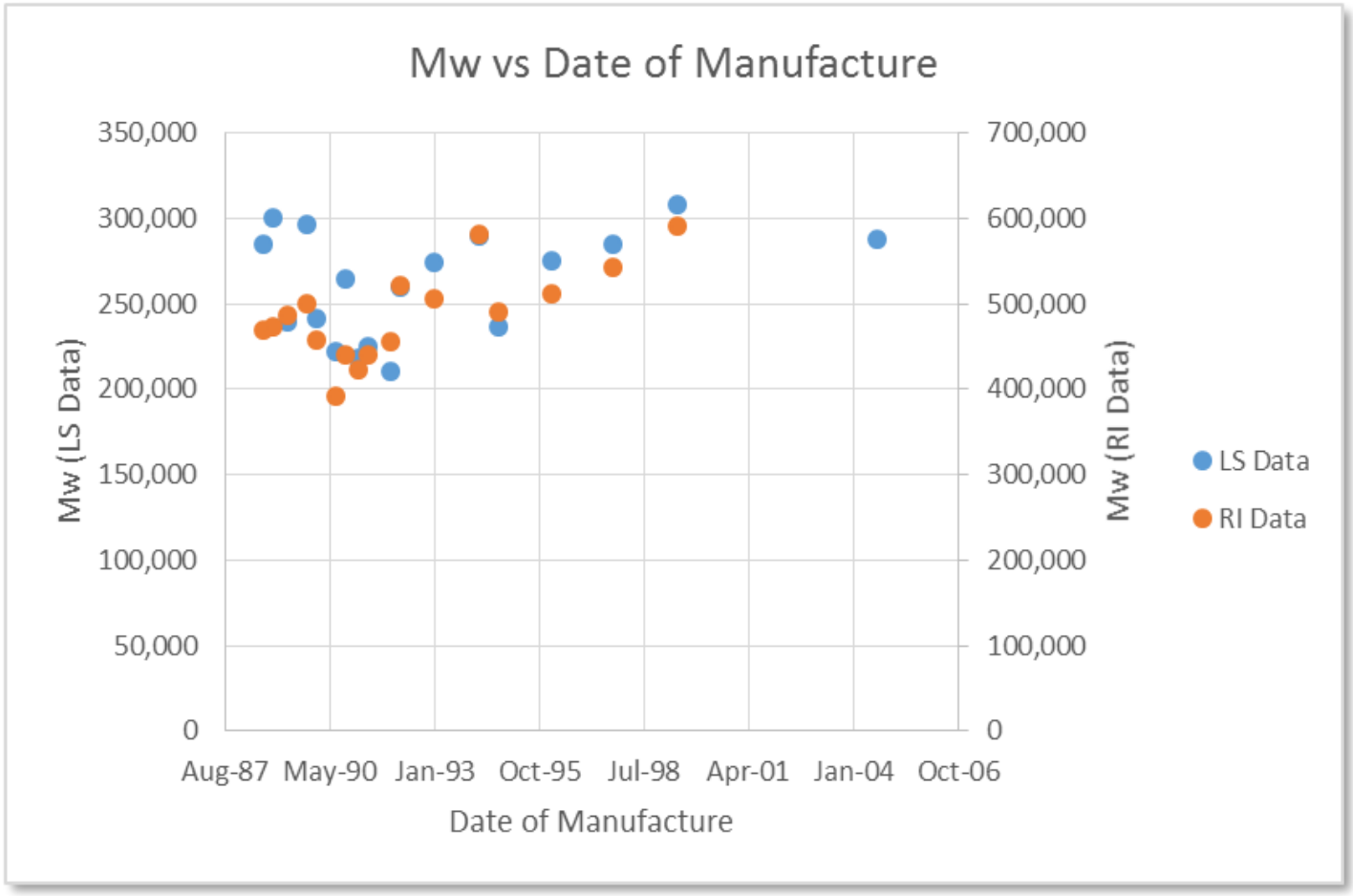

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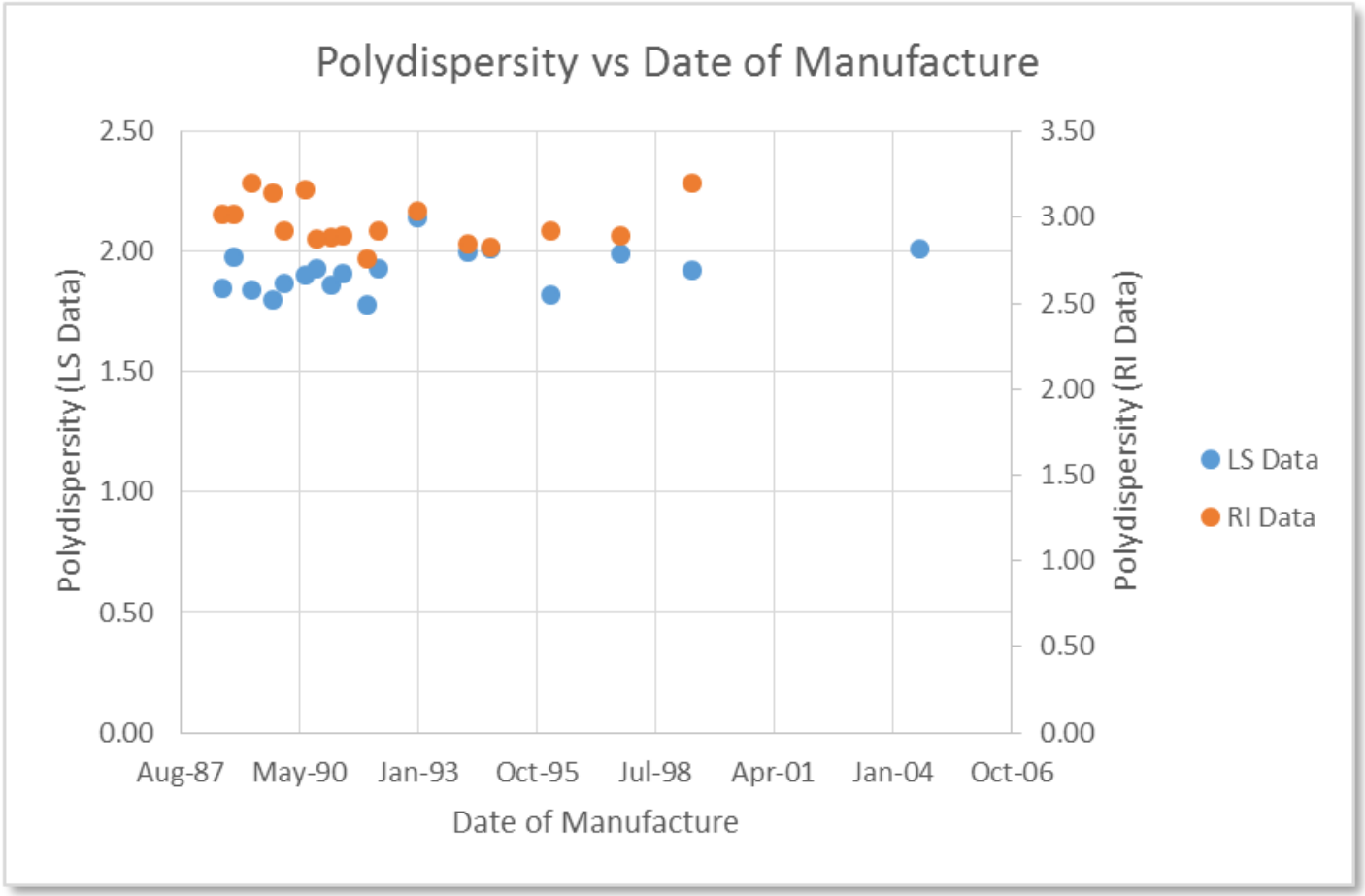


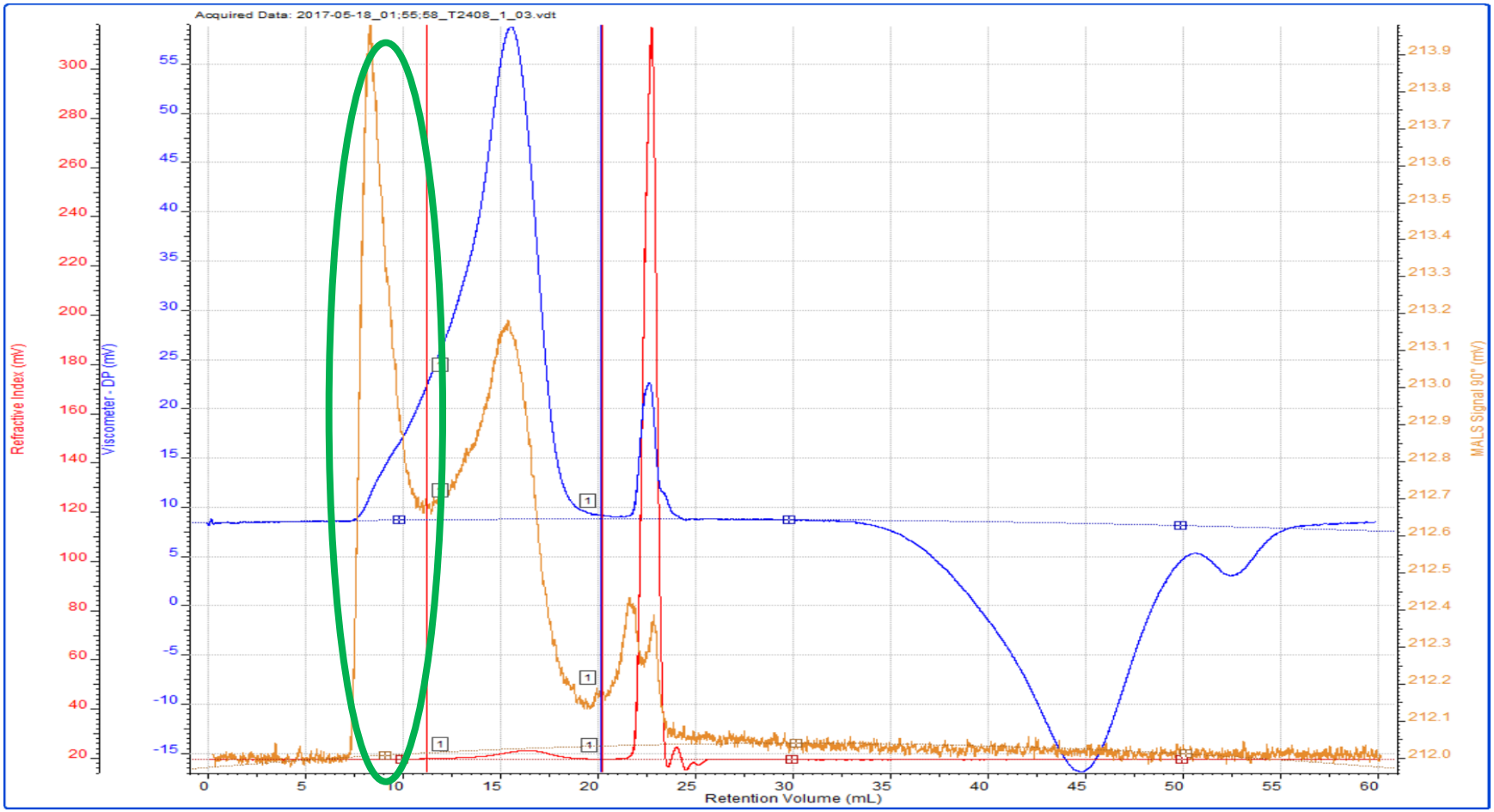
Success!

- Proved the method works well for this type of formulation
- Proved comparisons can be made between old and new data
- Started a nitrocellulose molecular weight library – need to continue

Future Work

- ‘New’ problem: Front shoulder seen on nitrocellulose peak – increases molecular weight values
- Gets worse as formulations are aged
- Try analysing samples using a four-column method, this should enable us to separate the peaks

Shoulder Peak Example



Summary

- New instrumentation
- New method has been validated
- Needed to show we could compare new data with historical data
- Have shown that new method shows same data trends as original data
- Started a nitrocellulose molecular weight library to enable backwards comparison of any new and future data produced
- Need to investigate the extra peak

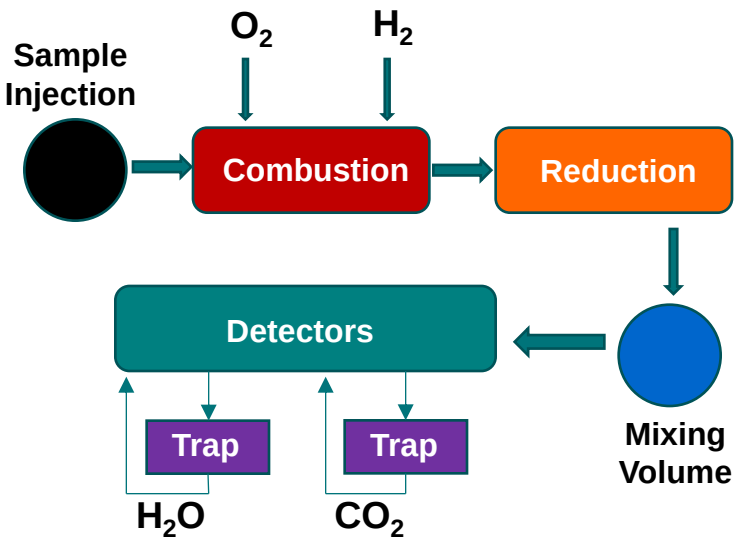
Introduction to CHN analysis

- Elemental analysis (CHN) determines the percentage ratios of carbon, hydrogen and nitrogen in a material
- This is especially useful as a surveillance technique for nitrocellulose
- The nitrogen content will lower as the nitrocellulose decomposes until it will be so low, it no longer performs as needed
- It can also be used to help with ‘shelf-life’ testing

What is CHN?

- Approximately 2mg of sample is weighed into tin capsules
- The instrument uses combustion to oxidise the sample under high temperature/high oxygen conditions
- The products pass through specialised reagents to remove interferences and produce simple combustion gases (CO_2, H_2O, N_2 or NO/NO_2)
- The gases are then passed over pure copper wire to remove excess oxygen and to reduce the nitrogen oxides to N_2
- The gases then enter a mixing chamber to ensure a homogenous mixture at constant temperature and pressure
- The mixture passes through a series of high-precision thermal conductivity detectors, each containing a pair of thermal conductivity cells. Between the first two cells is a water trap. The differential signal between the cells is proportional to the water concentration, which is a function of the amount of hydrogen in the original sample
- Between the next two cells is a carbon dioxide trap for measuring carbon, finally nitrogen is measured against a helium reference

What is CHN?



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