Nitrocellulose Characterisation to Support High Explosive and Propellant Life Assessment

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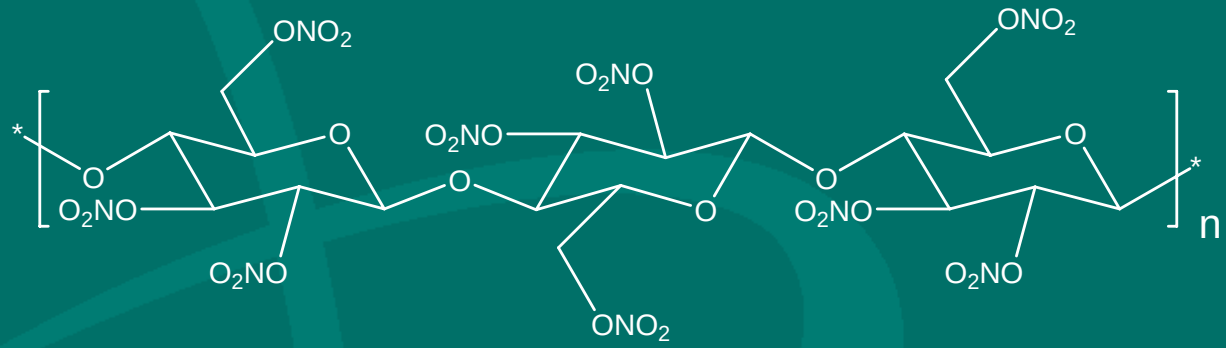
Introduction

- Nitrocellulose is a complex, naturally derived polymer



- Reliable methods for molecular weight determination are not available
- Molecular weight changes will influence properties of formulated products
- We have developed a more robust chromatographic method to improve reproducibility of molecular weight measurements

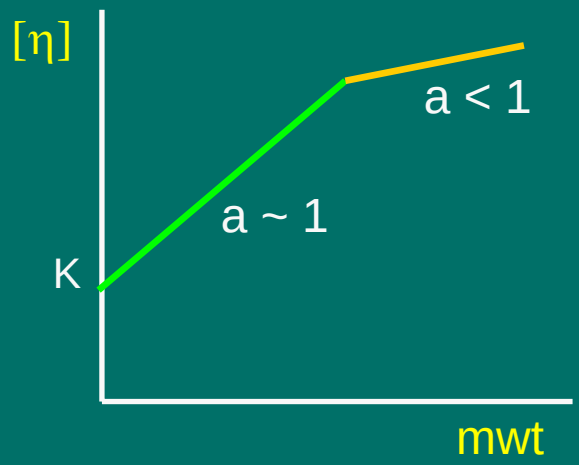
What Information can SEC Provide?

- Fundamental polymer characterisation from one experiment
  - different statistical moments of mwt distribution
    - M_n, M_w, M_z
- Conformational information for the polymer in solution
  - intrinsic viscosity, [η] (i.e.1/ρ)
  - Mark-Houwink K, a values

    a > 1: polymer behaving as a rigid rod

    a < 1: polymer behaving as a gaussian coil

    a << 1: polymer poorly solvated or highly branched
- Hydrodynamic parameters
  - e.g. radius of gyration, R_g



Important Polymer Properties

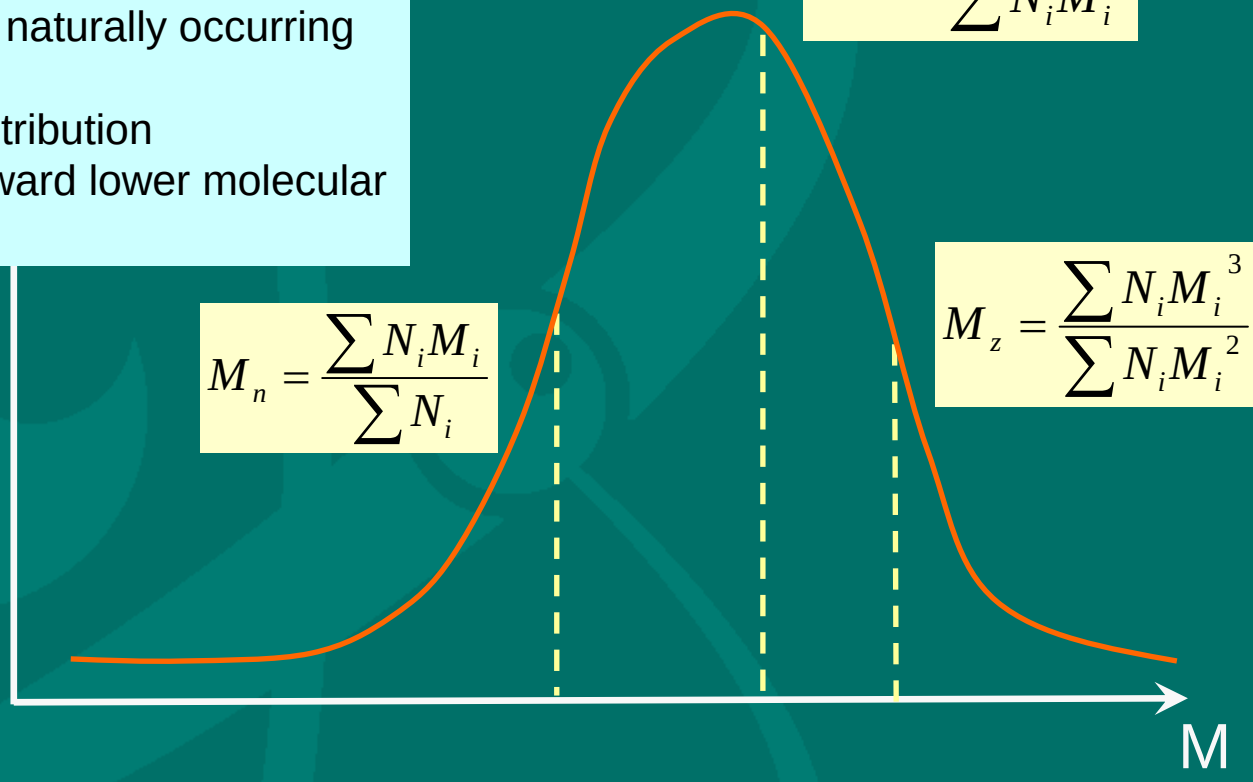
- Statistical moments of a polymer's molecular distribution
  - M_n, M_w, M_z
  - M_n is the 'common sense' average

Nitrocellulose -
- typical of naturally occurring polymers
- broad distribution
- tailing toward lower molecular weight

$$M_w = \frac{\sum N_i M_i^{\,2}}{\sum N_i M_i}$$

$$M_n = \frac{\sum N_i M_i}{\sum N_i}$$

$$M_z = \frac{\sum N_i M_i^{\,3}}{\sum N_i M_i^{\,2}}$$



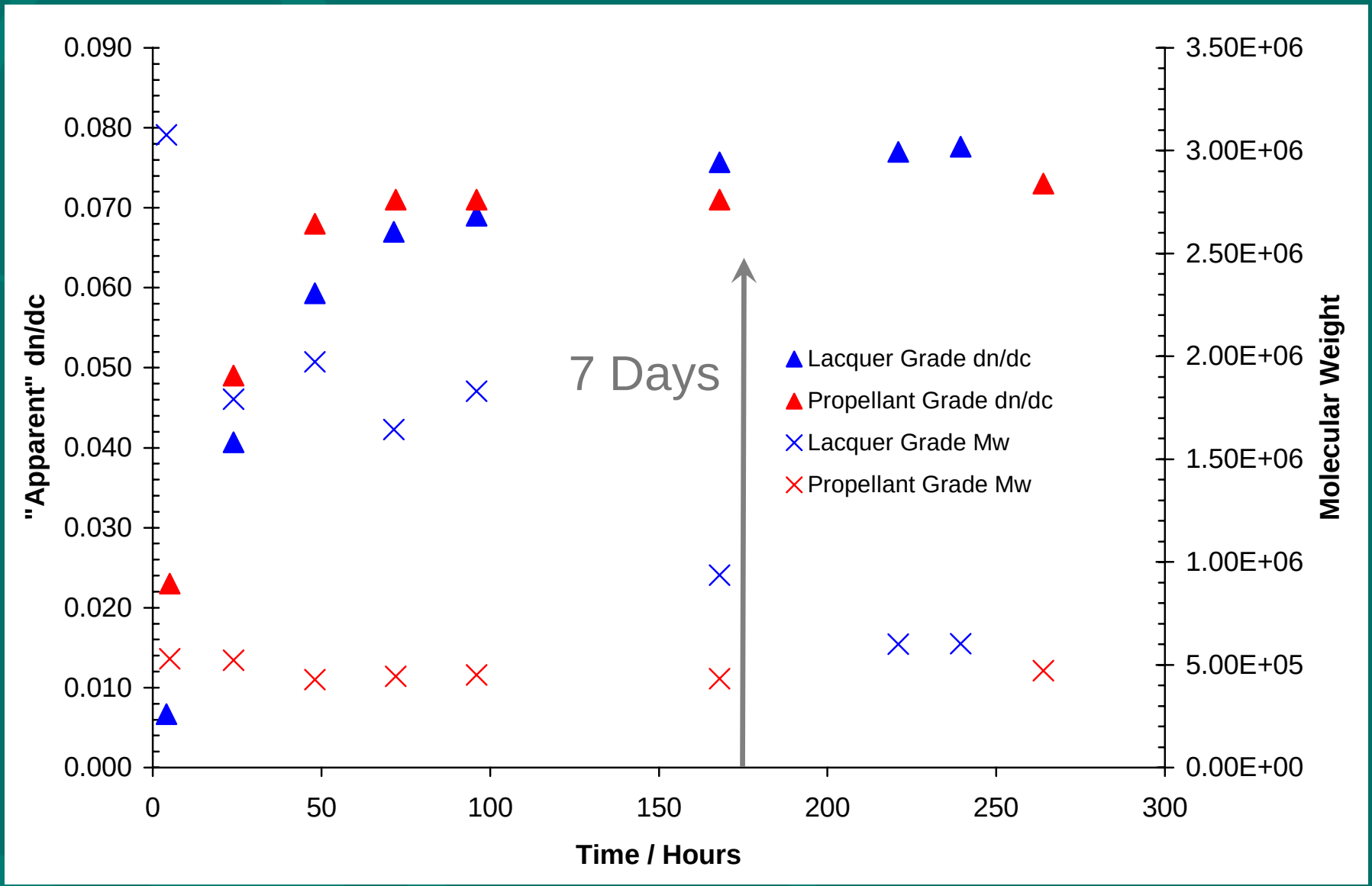
Nitrocellulose Analysis

- Nitrocellulose molecular weight measurement is very challenging
  - High viscosity
  - Natural variability
  - Poor refractive index in common solvents

  } Not suited to SEC

- Results are often difficult to reproduce
- Usefulness of data for (e.g.) kinetics analysis can be severely comprised by variability
- We have succeeded in defining analysis conditions to ‘control’ this variability

Nitrocellulose Dissolution



Different Solvents..?

- Acetone gives complex chromatography
  - Are these effects real?
- Ethyl acetate similar to THF
  - Dissolution more rapid
- Calibration standards not easily available

SEC Experimental Conditions

- Optimised conventional (concentration) detection

Nitrocellulose Concentration	1.5 $mgcm^{-3}$
Dissolution time	7 days at ambient temperature
Mobile Phase	BHT stabilised THF (100 ppm) @ 1 cm^3 min^{-1}
SEC Column(s)	2 x 30 cm PLGel 10 μm Mixed-B styrene-divinyl benzene
Standards	PL Easical A/B Polystyrene
Column Temperature	35 °C

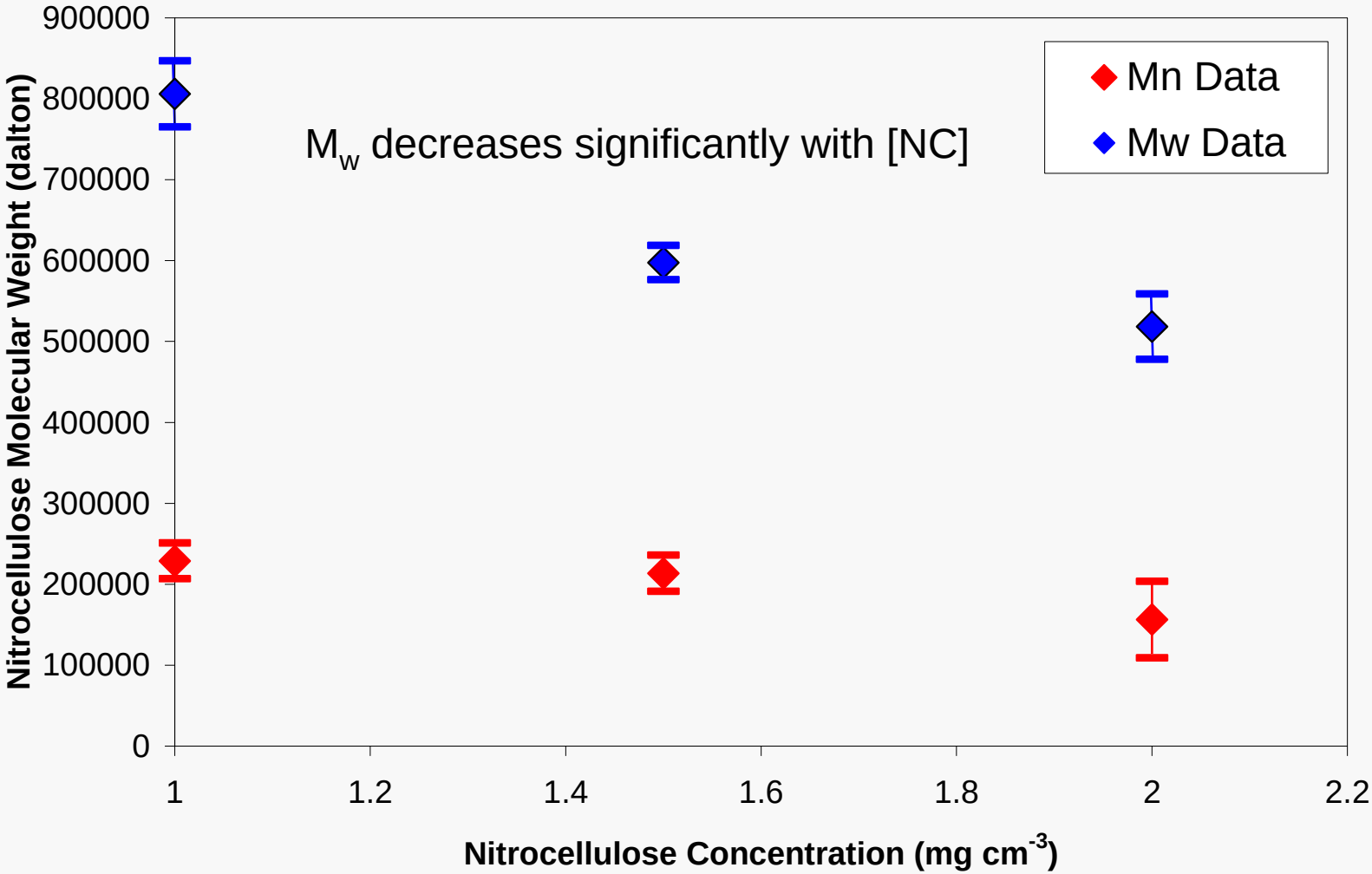
- Method evaluated statistically…

Reproducibility of Results

Sample	M_n (dalton) (± 1 s.d)	M_w (dalton) (± 1 s.d)	M_w/M_n (± 1 s.d)
Propellant Grade (Wimmis 12.6 % N) 1.0 mg cm-3	228800 ± 22100 (± 9.6 %)	806000 ± 40800 (± 5.1 %)	3.575 ± 0.586 (± 16.4 %)
Propellant Grade (Wimmis 12.6 % N) 1.5 mg cm-3	213500 ± 22400 (± 10.5 %)	597500 ± 21100 (± 3.5 %)	2.842 ± 0.443 (± 15.6 %)
Propellant Grade (Wimmis 12.6 % N) 2.0 mg cm-3	156300 ± 47200 (± 30.2 %)	518300 ± 40400 (± 7.8 %)	3.840 ± 1.704 (± 44.4 %)

30 replicate analyses of the *same* nitrocellulose solution

Molecular Weight : Concentration



What Materials Require Characterisation?

- Nitrocellulose based HE, e.g. PBX(A):-
  - 91 % (w/w) HMX as explosive filler (crystals < 100 μm)
  - 9 % (w/w) gelatinous visco-elastic binder

Binder {
- 1 % (w/w) high viscosity lacquer grade nitrocellulose
- 8 % (w/w) aromatic nitroplasticiser
- 0.02 % (w/w) stabiliser (ethylcentralite)

PBX(A)

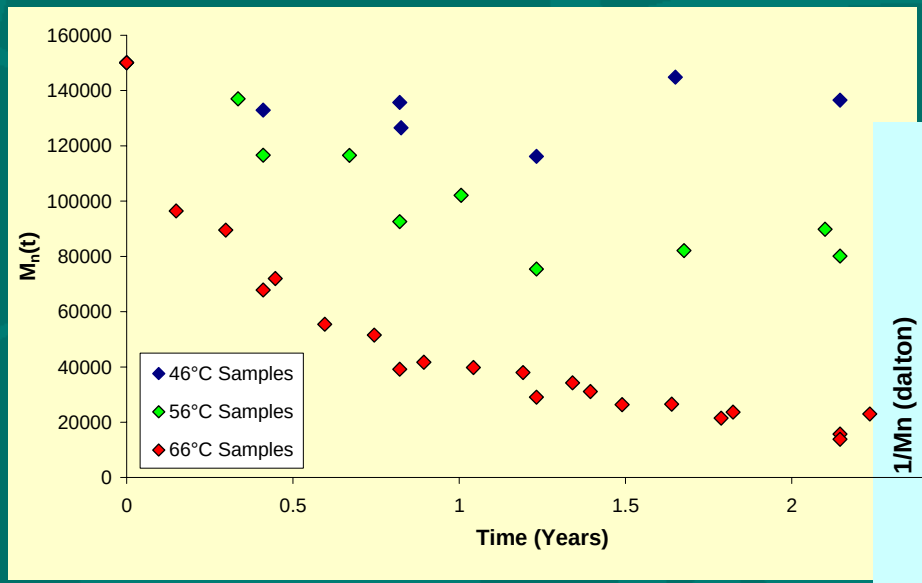
- Nitrocellulose based propellants
  - Double base propellant
  - Triple base gun propellant

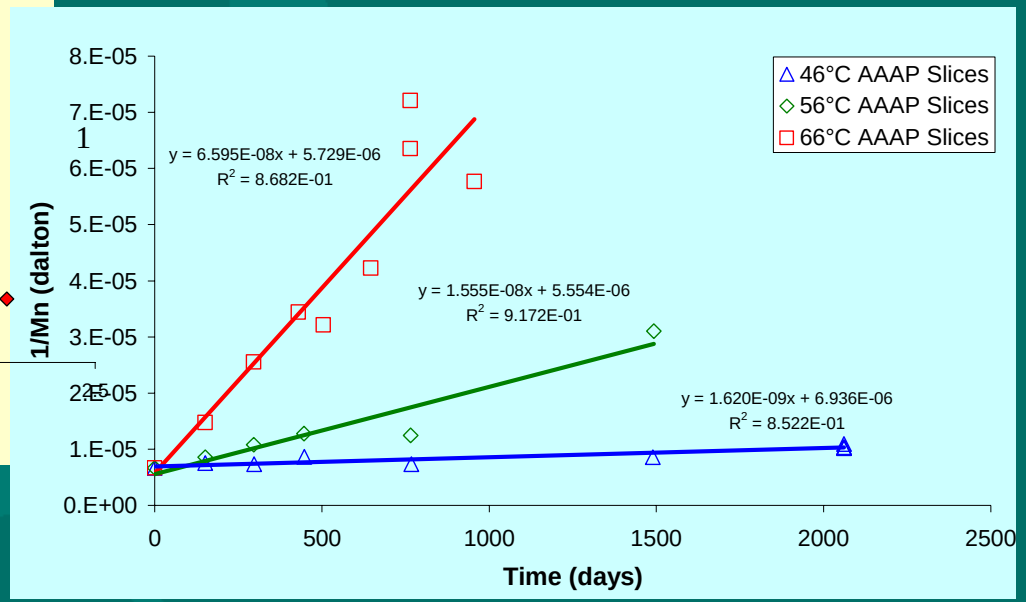
- Other nitrocellulose products
  - Inks, lacquers, paints, specialist coatings

Arrhenius Kinetics Analysis

- Thermal acceleration causes nitrocellulose molecular weight decrease
  - Ageing data acquired from 7 years multidisciplinary effort !

$$\frac{1}{M_n(t)} = \frac{1}{M_n(0)} + kt$$

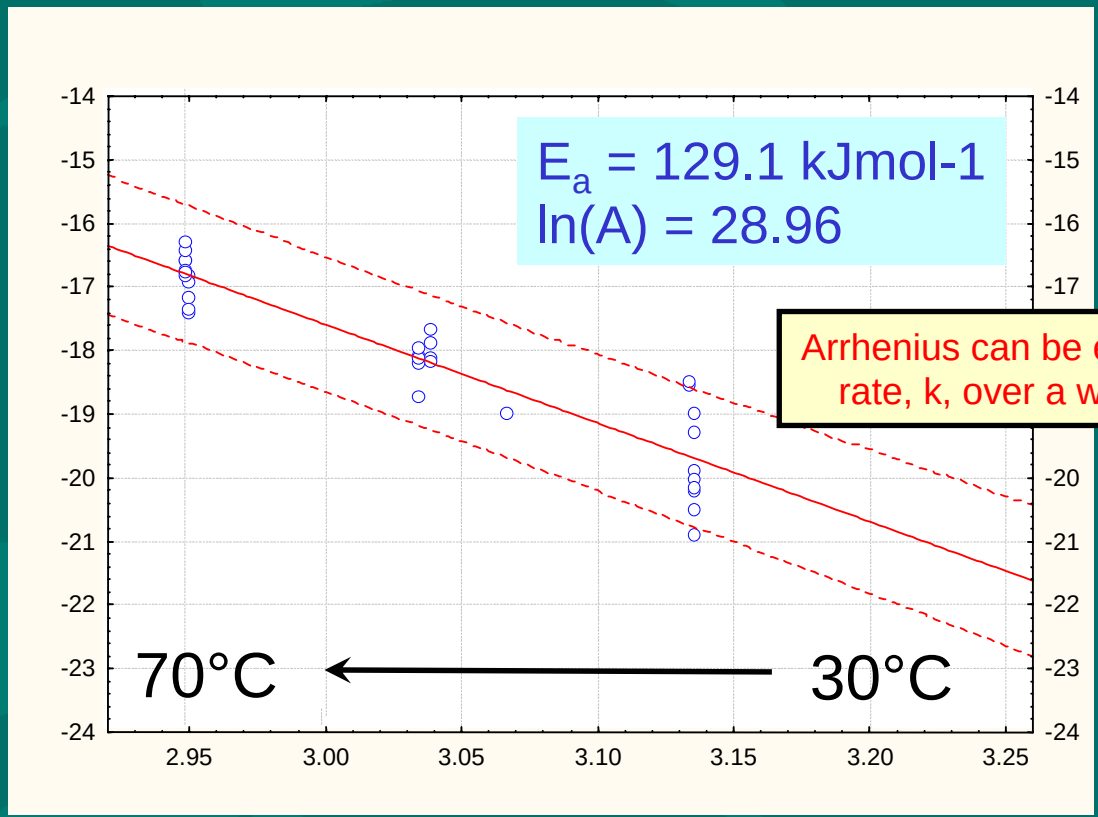




- Arrhenius kinetics used to parameterise nitrocellulose chain scission

Kinetics of Nitrocellulose Degradation

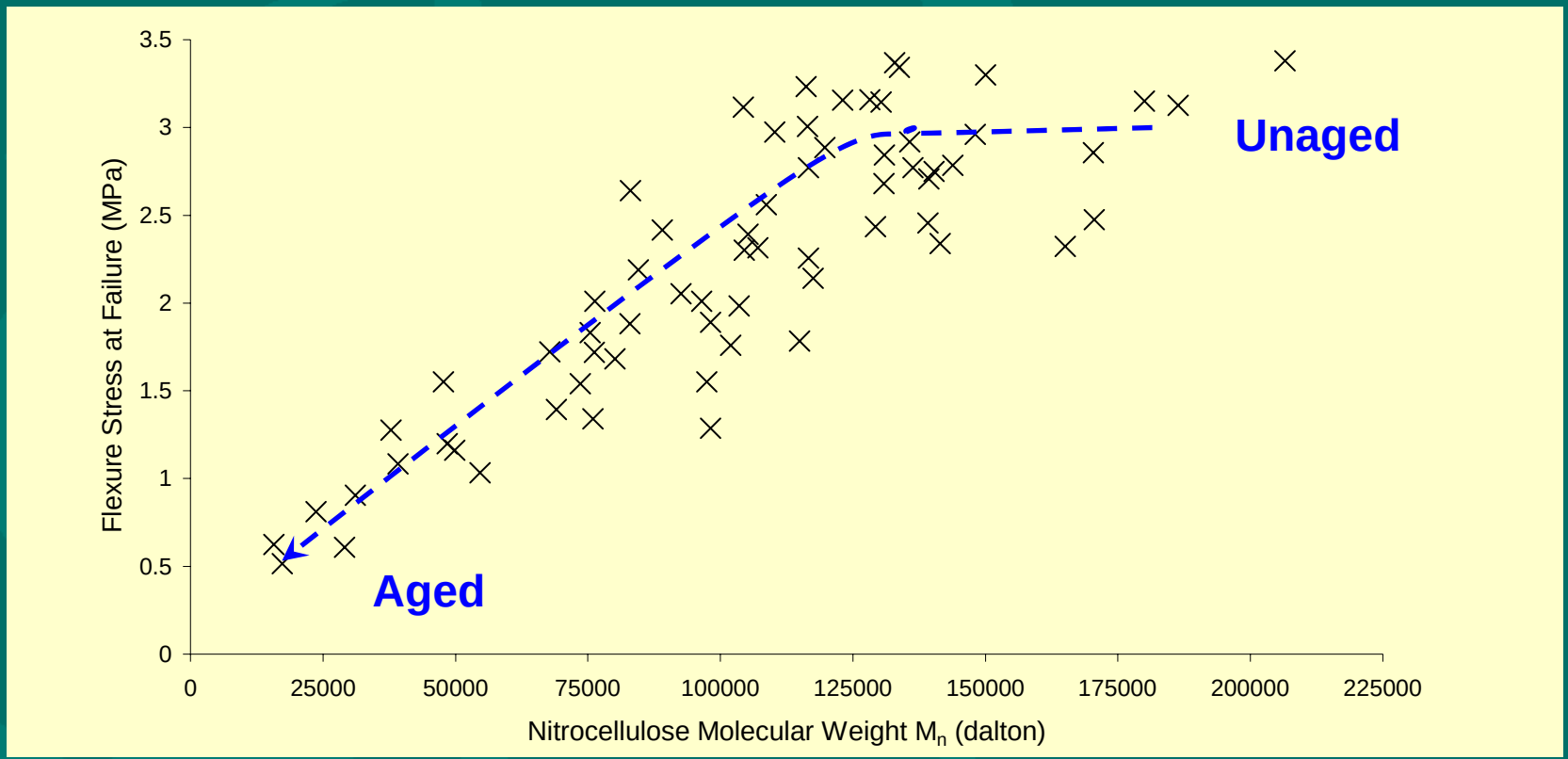
- Point-by-point technique used to stabilise calculated values of E_a, A, extrapolated ln(k)
- Arrhenius regression predicts ln(k) over a wide temperature range (with ± 95% limits)



Arrhenius can be extrapolated to calculate rate, k, over a wide temperature range

What is the Significance?

- PBX(A) moulding powder is isostatically pressed to high density (~ 98 % TMD)
  - pristine, unaged material remains brittle and weak
- Time further weakens PBX(A) due to reduction in nitrocellulose molecular weight



Collaboration with DCMT

- We are working in collaboration with DCMT, Cranfield University
- SEC methods are being used to characterise nitrocellulose extracted from DB and TB propellants
  - Unaged
  - Aged
- Phil Gill presentation “ Whole Life Assessment of Nitrocellulose in Rocket and Gun propellants”
  - Wednesday morning…

Conclusions

- Nitrocellulose analysis remains a challenge
- We have evaluated an SEC method for molecular weight determination
- The results of this analysis have successfully been used to characterise a high explosive
  - Arrhenius kinetics analysis performed
- The method is transferable to DB and TB propellants

Acknowledgements

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