Nitrocellulose Characterisation: Benefits of International Collaboration

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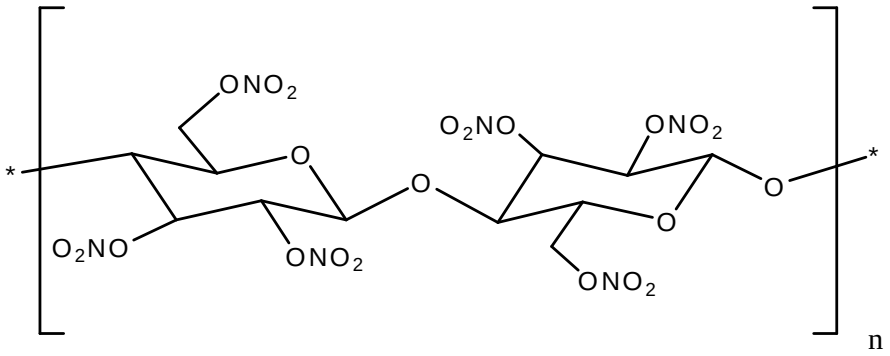
Scope

- Brief review of Nitrocellulose Workshops 1-3
- Summarise achievements
- Introduce the SEC round robin



Previous Workshops

- Meeting 1: February 2001, 19 delegates
  - UK only
  - Viscotek organised & hosted (with AWE input)
  - SEC only
- Topics included:
  - Requirement for robust analysis methods
  - Requirement for knowledge capture
  - SEC data neither repeatable or reproducible
  - Sample dissolution issues noted

Previous Workshops

- Meeting 2: November 2001, 23 delegates
  - UK & Sweden (FOI)
  - AWE organised & hosted event
  - Predominantly SEC and stability

- Topics included:
  - Molecular mass analysis by SEC and ultra-centrifugation
  - Effects of NC source on propellant processing
  - Surveillance of NC-propellants
  - Development of shared SEC experiments

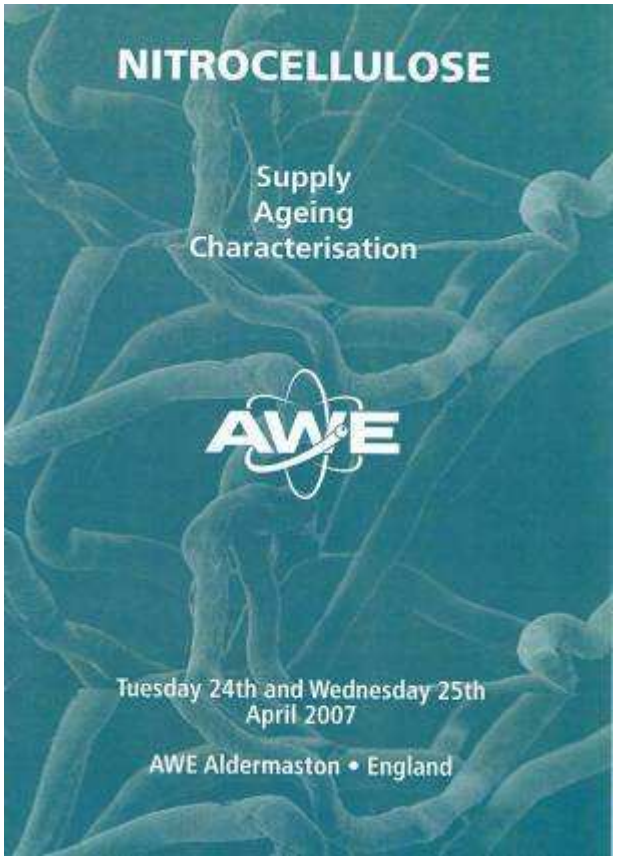
Shared Experiments

- The second meeting yielded a series of shared experiments:
  - Column packing (silica)
  - Eluting solvent (e.g. ethylacetate)
  - Column temperature
  - Sample concentration
  - Optimise dissolution time
  - Hyphenated SEC-FTIR (entire peak is nitrocellullose)
  - Adoption of a ‘standard material’ for an intra-laboratory baseline

Previous Workshops

- Meeting 3: April 2007, 38 delegates
  - Multi-national (9 Nations including USA & RSA)
  - AWE organised & hosted at Aldermaston site
  - Themed: Supply, Ageing, Characterisation

Meeting 3


NITROCELLULOSE
Supply
Ageing
Characterisation
Tuesday 24th and Wednesday 25th
April 2007
AWE Aldermaston • England

Meeting 3 Overview

- 3 sessions, each with an invited speaker
  - Neil Turner, DOSG
  - Ruth Sopranetti, Nitrochemie Wimmis
  - Manfred Bohn, Fraunhofer ICT
- 15 presentations were given
- Electronic proceedings issued & recorded with British Library*
- The concept of an SEC round robin was raised at the closing discussion

* C. Leppard; Nitrocellulose: Supply, Ageing, Characterisation; Conf. Proc.; 2007

Meeting 3 – Example Topics

- Issues Surrounding Qualification and Certification of munitions with Nitrocellulose*
  - *Neil Turner, Defence Ordnance Safety Group, UK*
- Survey of Standard Nitrocellulose Testing Methods and the Abel Heat Test*
  - *Ruth Sopranetti, Nitrochemie Wimmis, CH*
- Nitrocellulose-based Energetic Materials - Stability, Decomposition, and Ageing*
  - *Dr Manfred A. Bohn, Fraunhofer-Institut für Chemische Technologie (ICT), Germany*

- Rocket Propellant Characteristics as Influenced by Cellulose Type and Source
  - *Martin Sloan, Roxel Rocket Motors, UK*
- Nitrocellulose Characterisation to Support High Explosive and Propellant Life Assessment
  - *Dr Paul Deacon, AWE, UK*
- Characterisation of Plasticised Nitrocellulose using Pulsed Field Gradient (PFG) NMR and Rheology
  - *Jessica Gwyther, Bristol University, UK*
- Kinetics of Nitrocellulose Ageing
  - *Dr Alan Burnham, Lawrence Livermore National Laboratory, USA*

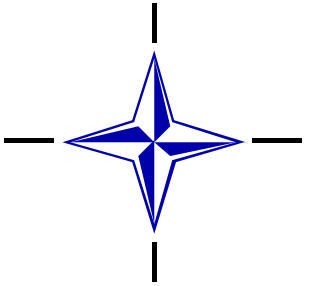
* Invited Speaker

Current Workshop

Current Workshop

- Meeting 4
  - Multi-national
  - Organised by Cranfield University
  - Supported by AWE and DOSG (UK MoD)
- Various themes:
  - SEC analysis (including update on round robin)
  - Development of STANAG 4178 (Ed. 2)
  - Chemical and physical characterisation
  - Ageing and stability

SEC Progress since 2007



- NATO STANAG 4178 (Ed. 2) currently undergoing ratification
  - “Test Procedures for Assessing the Quality of Deliveries of Nitrocellulose from One NATO Nation to Another”
- Ed. 2 includes an SEC method
  - Small sub-group formed to finalise experimental details
- Non-mandatory test intended to aid overall characterisation of nitrocellulose

SEC Discussion & Working Group (DWG)

- Formed to finalise SEC method in STANAG 4178 (Ed. 2)
  - Nitrochemie, AWE, ICT, TNO (CH, UK, D, N)
- Several meetings
  - February 2008, Nitrochemie
  - February 2009, Shrivenham
  - April 2009, Nitrochemie
  - May 2008/2009, Presentations to NATO AC/326 SG/1 CNG
- Several publications from the DWG
  - ICT conference 2008; P68, P69, P70
  - ICT conference 2009; P80, P81

STANAG 4178 (Ed. 2) SEC Method

- Use a recognised drying method
  - e.g. 60 ℃ for 2 hours
- Prepare solutions in HPLC-grade THF
  - 1.5 mg cm^{-3}
  - BHT < 250 ppm
  - 7-days pseudo-static or 30 minutes rapid stirring
- 10 μm mixed porosity columns PS-DVB at 35 ℃
  - Calibrate with narrow polystyrene standards
- Concentration detector (RI, UV-Vis)

Excellent SEC Repeatability

Experiment	M_n (dalton) (± 1 σ)	M_w (dalton) (± 1 σ)	Polydispersity (± 1 σ)
1 *(20 injections)*	195,200 4,200 (2.2 %)	651,100 10,900 (1.7 %)	3.34 0.09
2 *(20 injections)*	194,500 4,200 (6.2 %)	653,700 12,600 (1.9 %)	3.37 0.17
3 *(20 injections)*	205,100 7,500 (3.7 %)	676,300 6,900 (1.0 %)	3.30 0.11
4 *(20 injections)*	190,800 9,800 (5.1 %)	625,400 6,800 (1.1 %)	3.29 0.18
5 *(20 injections)*	200,600 7,400 (3.7 %)	649,200 19,200 (3.0 %)	3.24 0.07
Average *(of 100 injections)*	197,300 ± 9,800 **(5.0 %)**	651,100 ± 20,200 **(3.1 %)**	3.31 ± 0.13 **(4.1 %)**

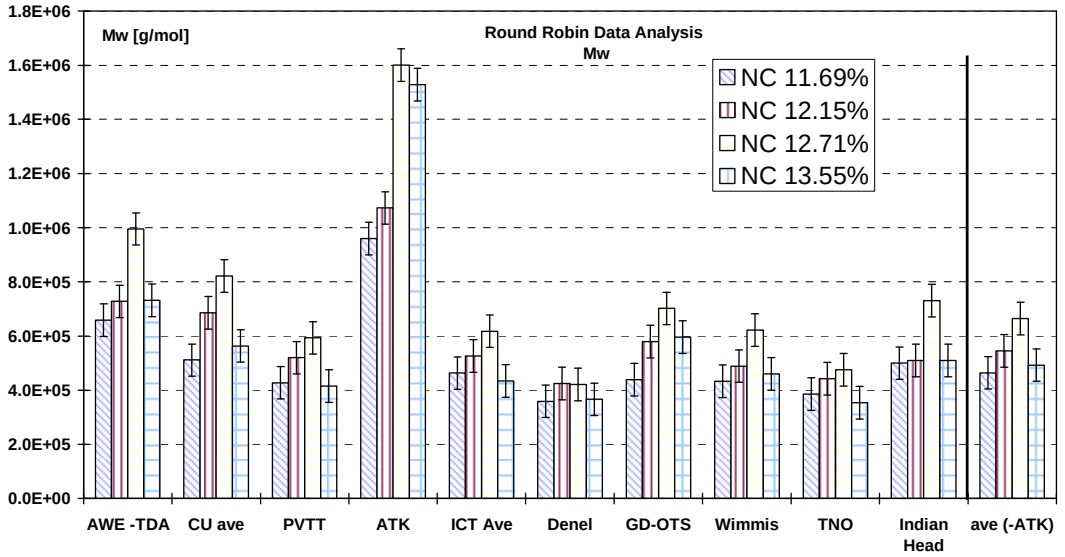
SEC Round Robin

- A truly international collaborative effort
  - 10 organisations, 9 Nations
- SEC columns & polystyrene standards provided by AWE
- 4 nitrocellulose samples provided by Nitrochemie
  - Identities not disclosed to facilitate ‘blind test’
  - All results returned promptly – thank you!
- Coordinated by Cranfield University
- Update at 40th Conf. Fraunhofer ICT in 2009#

P. Deacon *et al*; Proc. 40th Int. Conf. Fraunhofer ICT; P81 - 1 to 14; 2009

SEC Round Robin

- Nitrocellulose samples were ranked in the same order by each laboratory
- For both M_n and M_w
  - 12.71 % nitrogen >
  - 12.15 % nitrogen >
  - 13.55 % nitrogen ~
  - 11.69 % nitrogen



What Have we Achieved so Far?

- People were working in isolation
- An international group of experts are now working together
- Nitrocellulose SEC analysis – a challenging area – has progressed well
  - Incorporated into STANAG 4178 (Ed. 2)
  - The SEC round robin has been completed
  - Parameters that must be controlled are now better understood (e.g. drying conditions, dissolution time)

What can we Still Achieve?

- Nitrocellulose variability
  - Cotton vs. wood pulp, bleached vs. unbleached etc
  - Security of supply
- Nitrocellulose stability
  - Still much to learn
  - Mechanisms, dependence on local environment
- SEC analysis of nitrocellulose-based formulations
  - Propellants, high explosives
- Experts combined knowledge to tackle these – and other – issues (leverage)