Bacterial Cellulose - Analysis and Nitration








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Introduction

- **Nitrocellulose (NC) is a key ingredient in energetic material formulations for rocket and gun propellants, pyrotechnics and explosives**

- **NC is made by nitration of cellulose**
  - cellulose produced in plants is prone to natural variations due to primary source (cotton or wood), local climate, available nutrients and seasonal changes
  - variations result in inconsistent nitrocellulose properties, which can cause severe problems in munitions manufacture, reduced life and in-service failures

- **Objective**
  - develop a consistent form of NC that is reproducible over many years, without reliance on uncertain supply chains and the variance in naturally produced cellulose

- **Investigated solution**
  - bacterial cellulose – consistent, long nano sized fibrils
  - potentially high levels of material consistency with security and continuity of supply

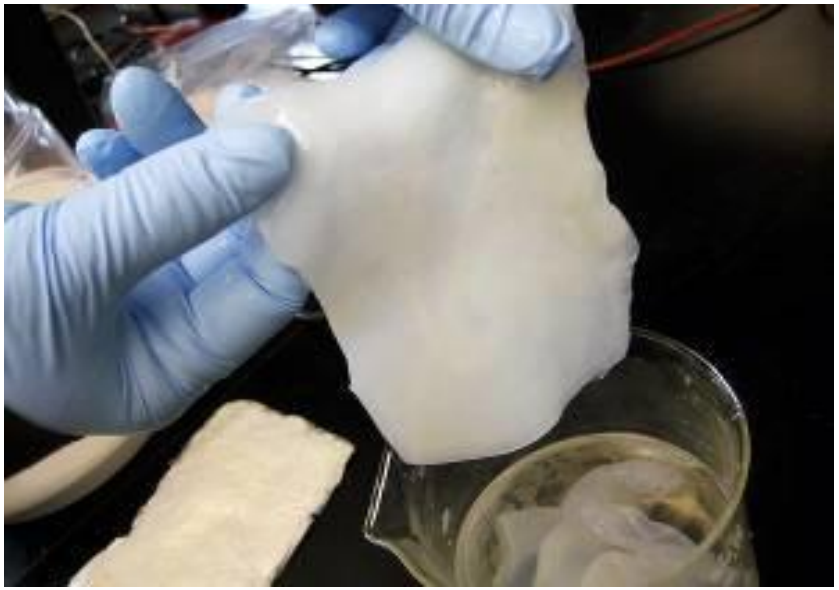
Bacterial Cellulose

- **Supplier AV1**
  - food additive
  - contained co-agents (ca. 40% Xanthan gum and Sodium carboxymethyl cellulose) to aid cellulose recovery from fermentation media
  - 1% in suspension in water activated with a high shear mixer
  - heated with hydrogen peroxide overnight at 50°C, “filtered”

- **Supplier AV2**
  - Wet cake (~15% cellulose stabilised with 0.1% sorbic acid), development material

- **Supplier BV1**
  - biomedical applications
  - freeze dried (water) cellulose sheet
  - need to be cut/macerated prior to nitration

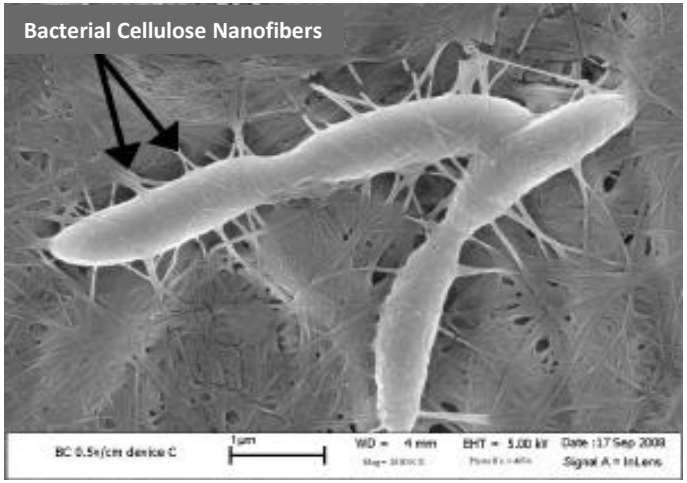
- **Supplier BV2**
  - “fibrous” form
  - freeze dried (ethanol) cellulose sheet



Bacterial Cellulose Analysis

- **FTIR**
  - without calibration, infrared spectroscopy could not distinguish between the cellulose and co-agent residue

- **NMR**
  - liquid state NMR
  - cellulose insoluble in most solvents due to high molecular weight, strong inter/intra-molecular hydrogen bonds, partially crystalline
  - identified a number of solvents/methods

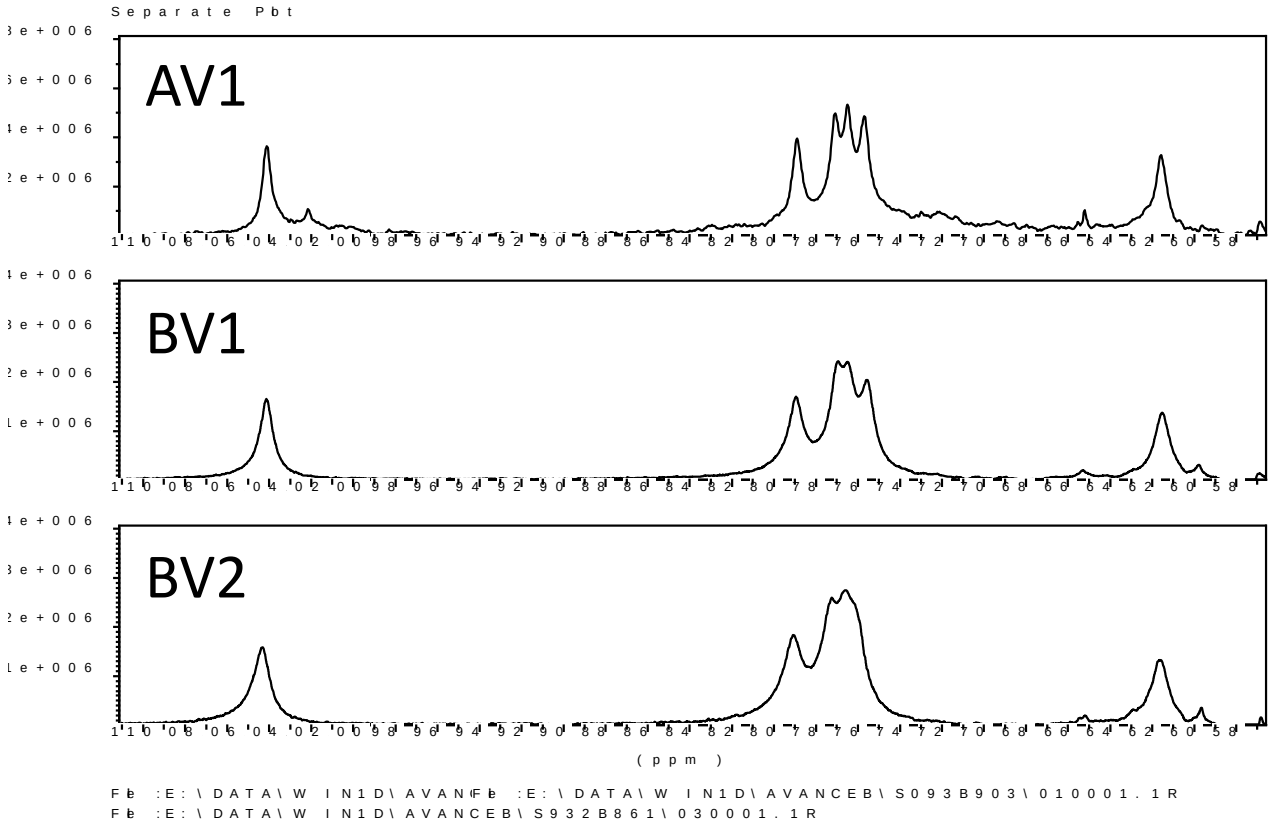


Dissolution

Solvent	AV1 Dissolution Observations
LiCl/Dimethylacetamide	Little or no dissolution
LiCl/N-Methyl-2-Pyrrolidinone + steaming	Little or no dissolution
1-Ethyl-3-methylimidazolium acetate ionic liquid	Soluble (up to 5%) ^{13}C peaks broad at 35°C Partial degradation of cellulose at 75°C. Impurity signal hidden under solvent peak.
Cadoxen (deuterated water, ethylenediamine and cadmium oxide, NaOD)	Soluble (up to 4%) ^{1}H NMR too broad ^{13}C typically 24 to 60 hours Observed co-agent signals at 165-185ppm

Bacterial Cellulose NMR

- **Cellulose AV1 soluble, BV1, BV2 swelled**
  - Added NaOH:water (0.035:1): aided dissolution BV1
  - BV2 gel like
- **^{13}C NMR indicated xanthan gum and sodium carboxymethyl cellulose absent**
- **BV2 cellulose signal broader than the AV1 indicating lower molecular motion**



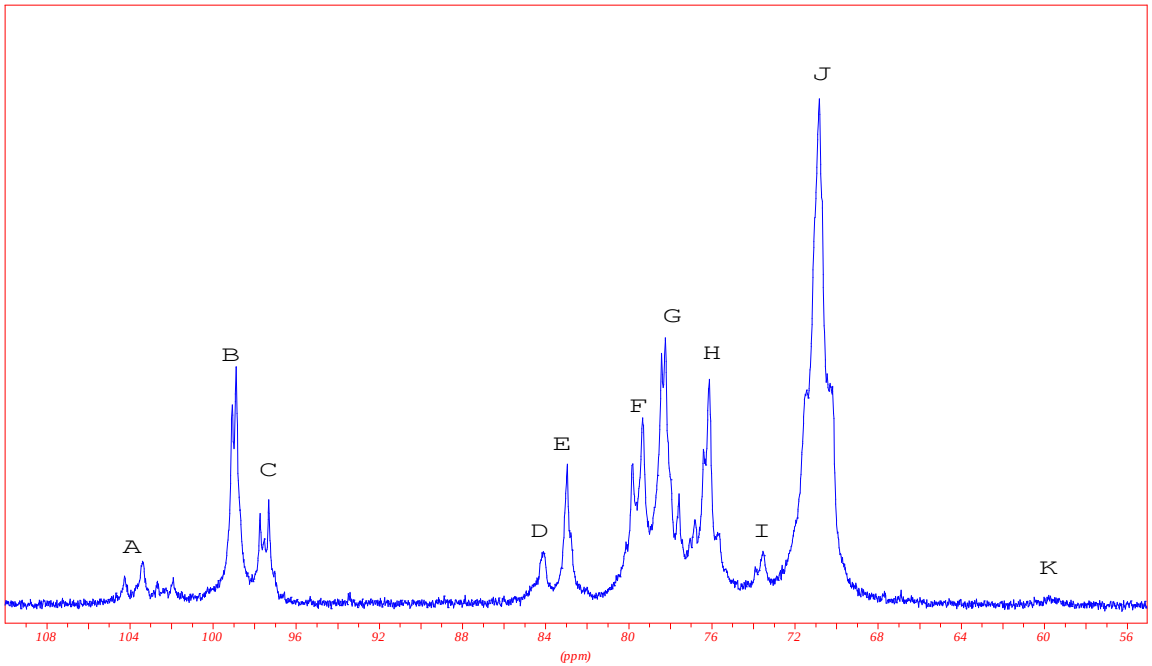
NC Analysis - NMR

- **Degree of nitration (S) and %N of nitrocellulose calculated from the areas ^{13}C NMR peaks as per below equations**
  - dissolved in DMSO at 60°C
  - nitrogen content can only be calculated if the nitrocellulose's NMR peaks are resolvable (integration or deconvolution)
  - only quantitative for species with small T1 relaxation time constants

$$S = 3A_B + 2A_C + 2A_D + A_{A2}$$

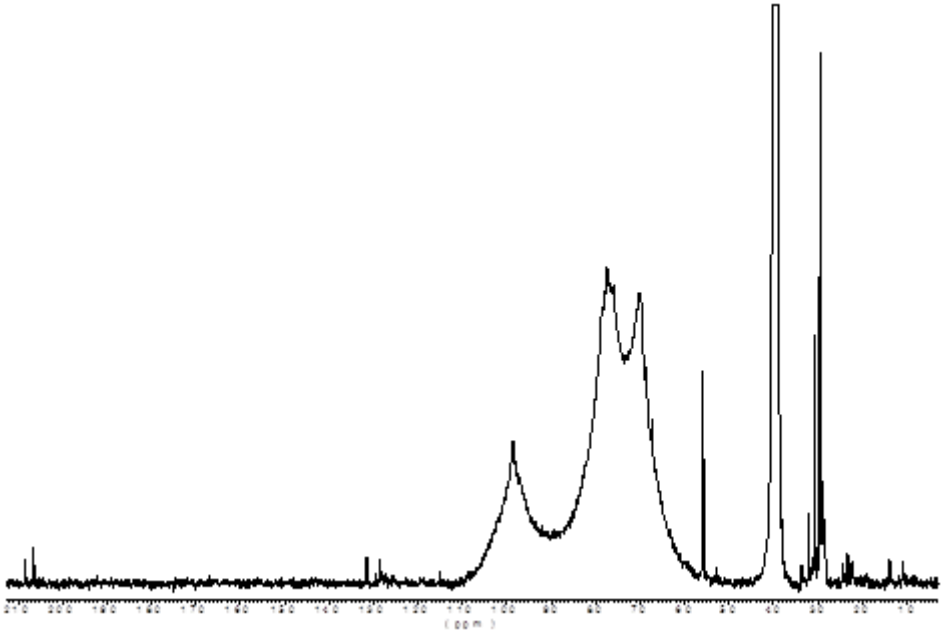
$$A_{A2} = A_A - A_D - A_K$$

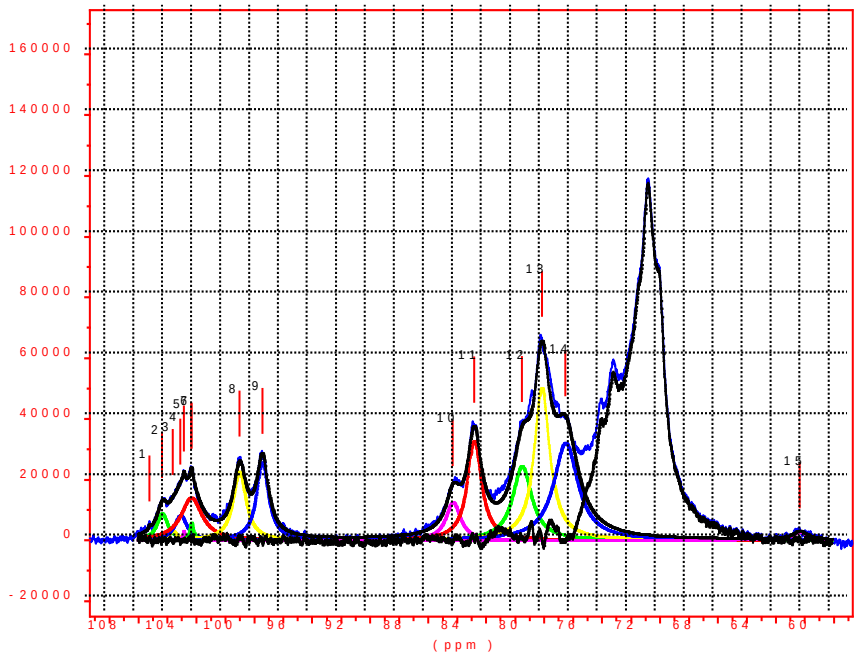
$$\%N = \frac{14S}{162.1 + 45S} \cdot 100$$



BNC Analysis - NMR

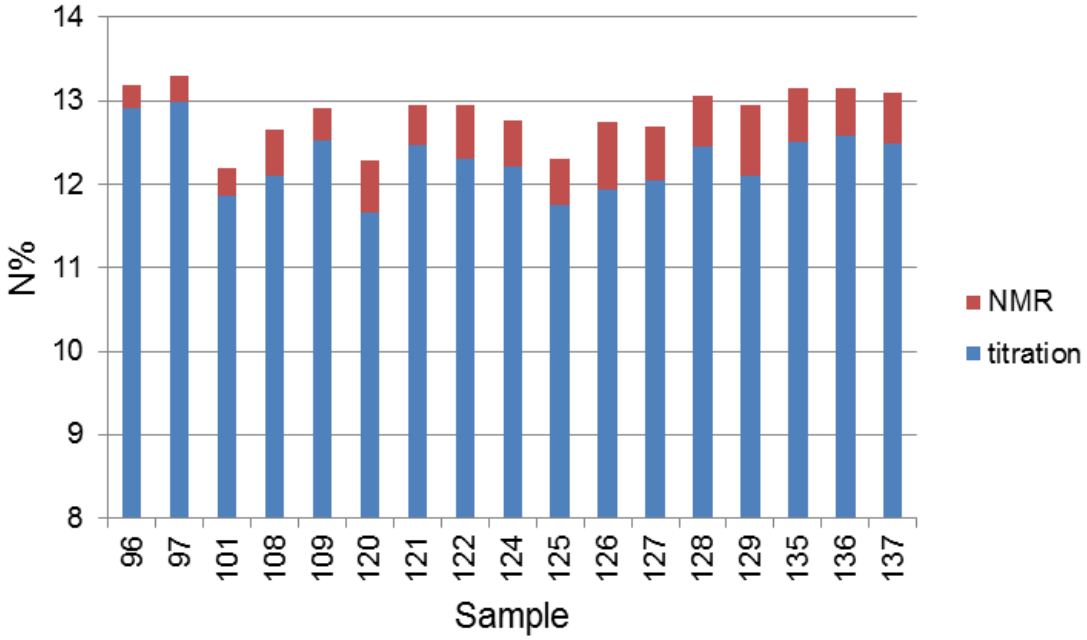
- **Insoluble behaviour of cellulose BV1 and BV2 carried through to nitrated material**
  - very broad peaks – not amenable to ^{13}C NMR %N measurement
  - deconvolution required for some nitrated materials
  - investigated other solvents/additives: caused NC degradation





BNC Analysis – Ferrous Ion Titration (FIT)

- **Redox electrode in an auto-titrator, conc. sulphuric digestion**
  - digestion and titration temperature tightly controlled to 5°C and always below 10°C
  - higher temperatures under-measured nitrogen content
  - cotton NC dissolved within 15mins at 5°C
    - measured N% 12.18±0.08 (NMR 12.2%)



- **BNC took considerably longer to dissolve**
  - up to 2.5 hours at 6.6°C (~ 4 to 6 x longer than normal NC)
  - FIT values lower than NMR results

BNC Nitration

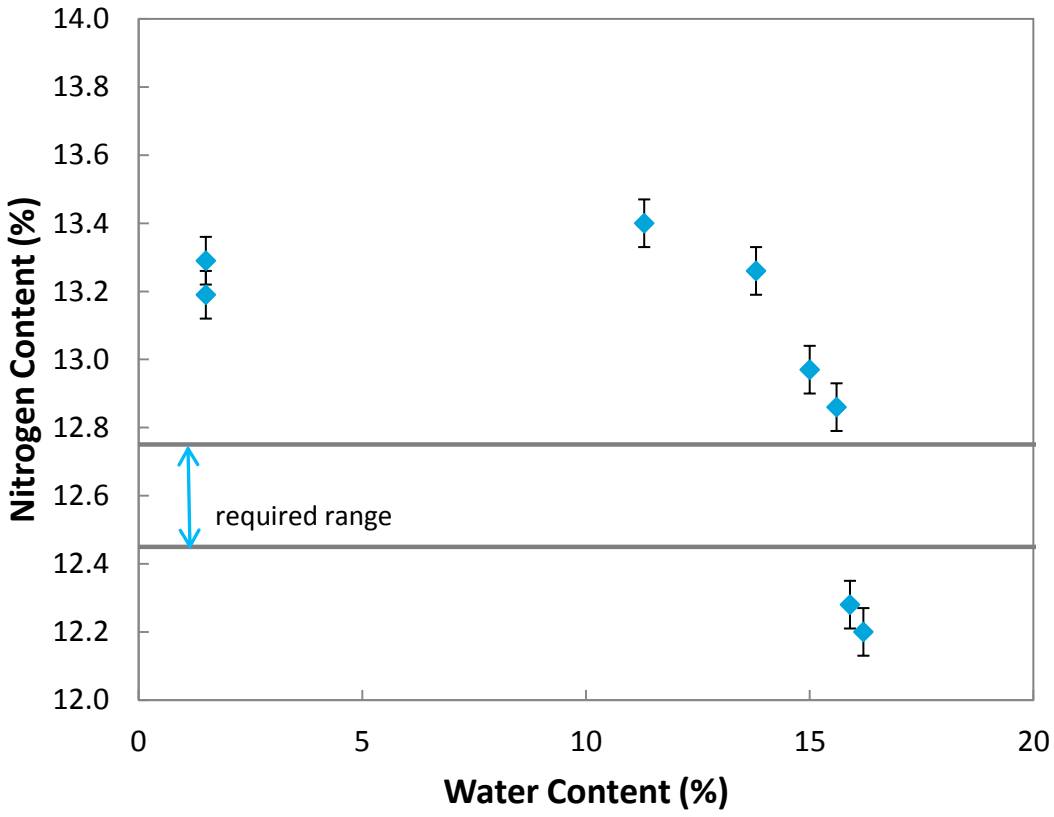
- **Parametric nitration studies performed on cellulose AV2 (varying, pre-processing method, time, temperature, nitrating mixture and water content)**

- **Pre-processing methods:**
  - A. 89g, freeze-dried, stirred in ethanol to remove the sorbic acid, filtered, dried under vacuum and ground using a lab mill
  - B. 89g, freeze dried, ground using a lab mill, stirred in ethanol, filtered, dried under vacuum
  - C. Material from A and B combined
  - D. 153g freeze dried, stirred in ethanol, dried under vacuum and ground using a lab mill
  - E. As per D, using 173g of wet cellulose

BNC Nitration

Expt.No./ method	Nitrating Mixture / %			Mass NC (g)	Nitrogen Content (%N)	Yield (%)
	H_2SO_4	HNO_3	H_2O			
096 (A)	73.2	25.3	1.5	3.13	13.19	89.7
097 (B)	73.2	25.3	1.5	3.05	13.29	87.3
100 (A)	65.9	22.8	11.3	3.11	13.40	87.6
103 (C)	64.0	22.2	13.8	3.00	13.26	85.6
105 (D)	63.1	21.9	15.0	2.94	12.97	85.8
107 (D)	62.7	21.7	15.6	2.98	12.86	86.5
120 (D)	62.5	21.6	15.9	2.77	12.28	83.8
101 (B)	62.2	21.6	16.2	2.77	12.20	83.4

BNC Nitration

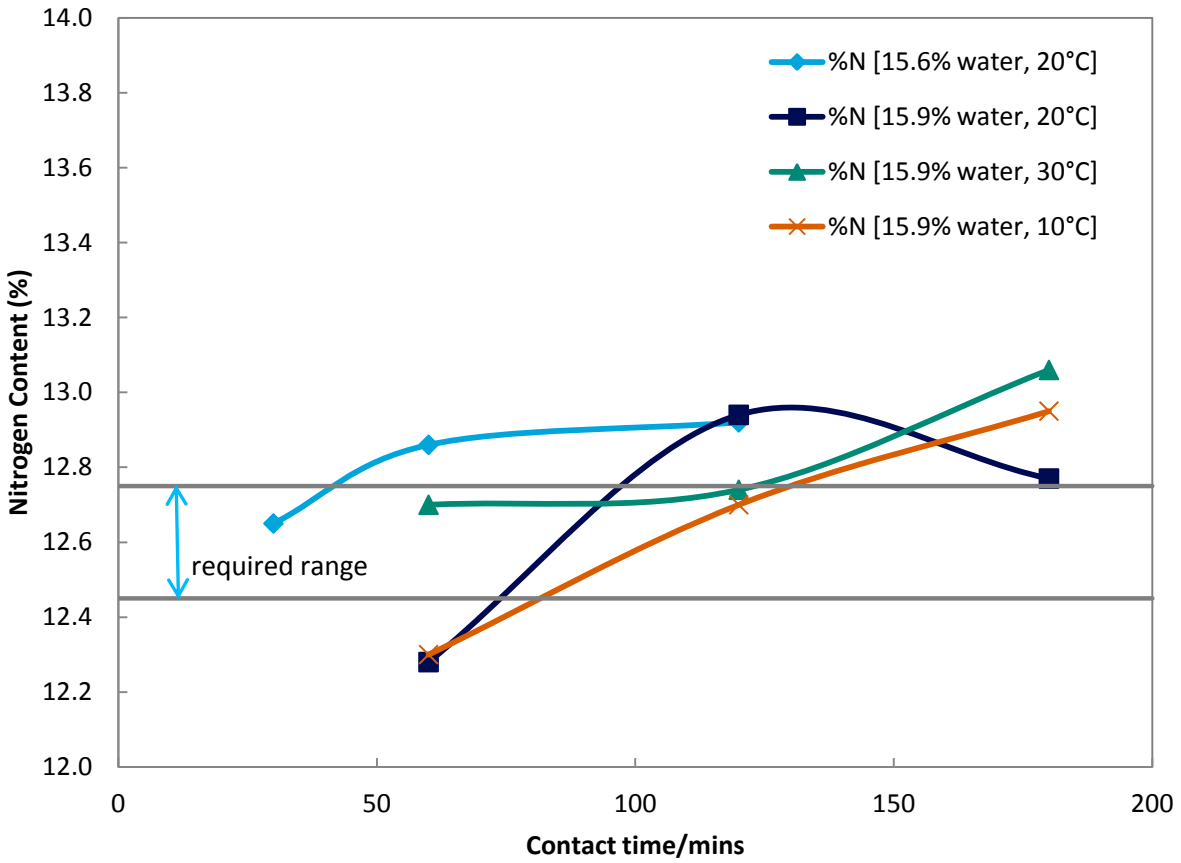


Results of the nitration of bacterial cellulose AV2 with varying water content (20°C, 1Hr)

BNC Nitration

Expt. No.	Nitrating Mixture	Time (min)	Temperature (°C)	Mass NC (g)	Nitrogen Content (%N)	Yield (%)
108 (D)	15.6% water	30	20	2.88	12.65	85.4
107 (D)	15.6% water	60	20	2.98	12.86	86.5
109 (D)	15.6% water	120	20	2.74	12.92	79.7
120 (D)	15.9% water	60	20	2.77	12.28	83.8
121 (D)	15.9% water	120	20	2.97	12.94	86.4
122 (D)	15.9% water	180	20	2.80	12.77	82.5
124 (D)	15.9% water	60	30	2.77	12.70	81.9
126 (D)	15.9% water	120	30	2.86	12.74	84.4
128 (D)	15.9% water	180	30	2.95	13.06	85.5
125 (D)	15.9% water	60	10	2.61	12.30	78.8
127 (D)	15.9% water	120	10	2.76	12.70	81.6
129 (E)	15.9% water	180	10	2.88	12.95	84.0

BNC Nitration



Results of the nitration of bacterial cellulose AV2 with varying time and temperature

BNC Nitration

- **Three nitrations were carried out on 10g scale using optimised conditions (20°C, 2 Hrs)**
  - recovered mass and nitrogen content were consistent across the three samples
  - the nitrogen content above the desired range (12.4% - 12.8%)
  - slightly higher than that for material produced under similar conditions on a smaller scale (2g cellulose, 15.9% water, 12.9% N)

Reference	Mass recovered /g	Nitrogen content /%
135	15.1	13.2
136	14.8	13.2
137	14.8	13.1

Conclusions

- **Nitration of BNC: %N is sensitive to**
  - time, temperature
  - but most sensitive to water content in the nitrating mixture
- **Nitrogen contents measured by titration were lower than NMR measurements of bacterial NC**
- **NC from the latest batch of "wet cake" from Supplier A (AV2) gave the NC with the most potential**
- **The nitration process was scaled up – the %N for 10g scale reactions was different to that measured for the 2g scale reactions**
- **Material made on 10g scale has %N that can be potentially exploited in gun propellants**
- **Next steps would be to engage a large scale commercial supplier of bacterial cellulose**

Acknowledgments

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