Isotope Ratio Mass Spectrometry of Historical Nitrocellulose Samples

6th Nitrocellulose Workshop: Rijswijk, April 2014

Dr Paul Deacon

Explosive Materials & Initiation Science

paul.deacon@awe.co.uk

www.awe.co.uk

Nitrocellulose Origin

- Postulated that a source of NC supplied over many years could have originated from a single source
  - Not possible to consult manufacturer/distributor
  - Record samples appeared in good condition
- Isotope Ratio Mass Spectrometry (IRMS) has been used to test this hypothesis
  - Collaboration with Mass Spec Analytical in Filton, Bristol
  - 15 NC samples were assessed
    - 10 samples of NC - different batches spanning ~ 15 years
    - 3 samples of NC - same batch, chilled since the 1990s
    - 2 samples of NC - newly sourced in 2013
- NC samples stored wet with ~ 30% IPA in sealed containers (< 12% nitrogen)



IRMS

- More correctly referred to as Gas Chromatography Combustion Isotope Ratio Mass Spectrometry
- Highly specialised forensic analysis technique
- Complex materials are reduced to CO_2, H_2, N_2 and CO
  - Thermal combustion
  - Oxidation reactor
  - Reduction reactor
- Isotope detection is relatively straightforward
  - Typically EI and magnetic sector mass spectrometer
- “The difficult part is the sample preparation” Dr Tim Knowles (Mass Spec Analytical)

IRMS

- Stable isotope compositions are expressed in terms of delta values (δ)
- δ standard: quoted as parts per thousand (‰) differences from a standard material

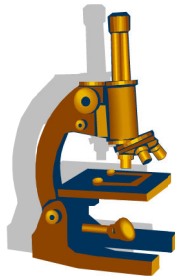
$$\delta X = [(R_{sample} / R_{standard}) - 1] \times 10^{3}\ *$$

- Proportions of stable isotopes in a material will vary according to its origin
- IRMS instruments are highly specialised for determination of light, stable isotope ratios
  - $^{2}H/^{1}H$, $^{13}C/^{12}C$, $^{15}N/^{14}N$, $^{18}O/^{16}O$ (and $^{34}S/^{32}S$)

* X represents the isotope of interest and R represents the ratio of the isotope of interest and its natural form (e.g. $^{13}C/^{12}C$)

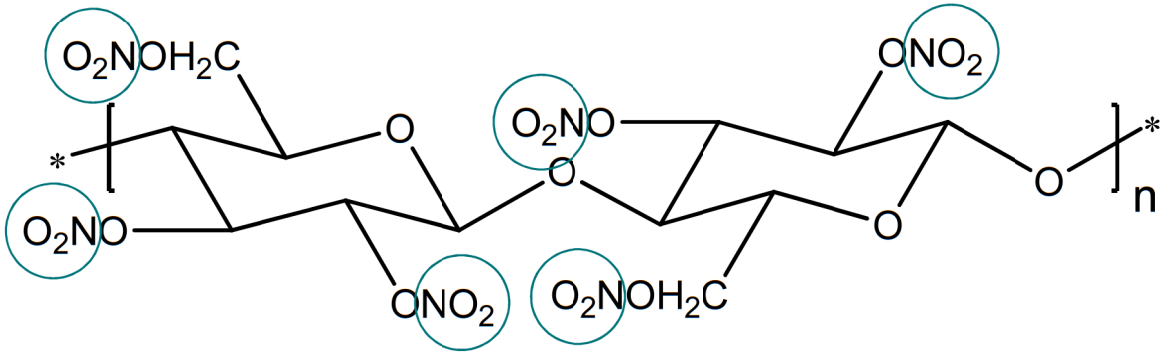
IRMS of Nitrocellulose

- Cellulose is derived from plants which use the C3 (Calvin Cycle) photosynthetic pathway
  - Stable carbon isotope ratio ($^{13}C/^{12}C$) is fixed
- Stable hydrogen isotope ratio ($^{2}H/^{1}H$) derived from rainwater
  - Varies seasonally
  - Varies according to geographical location
- NC contains many readily exchanged sites which must be stabilised prior to IRMS analysis
  - Repeated washing with IPA
  - Drying under mild conditions (< 50°C)
- Multiple samples to overcome inhomogeneity



IRMS of Nitrocellulose

- NC contains atoms from two sources
  - C, H and some of the O originate from the cellulose
  - N and the majority of the O originate from the nitric acid

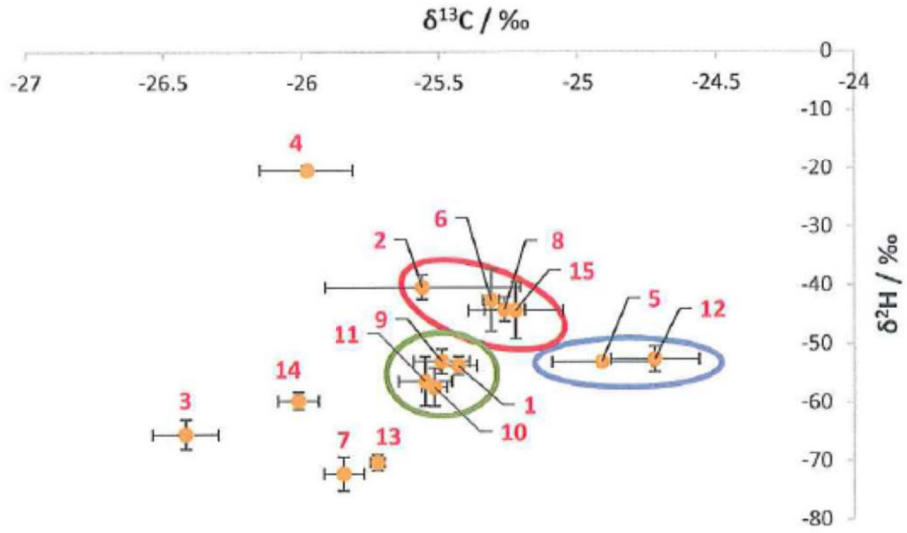


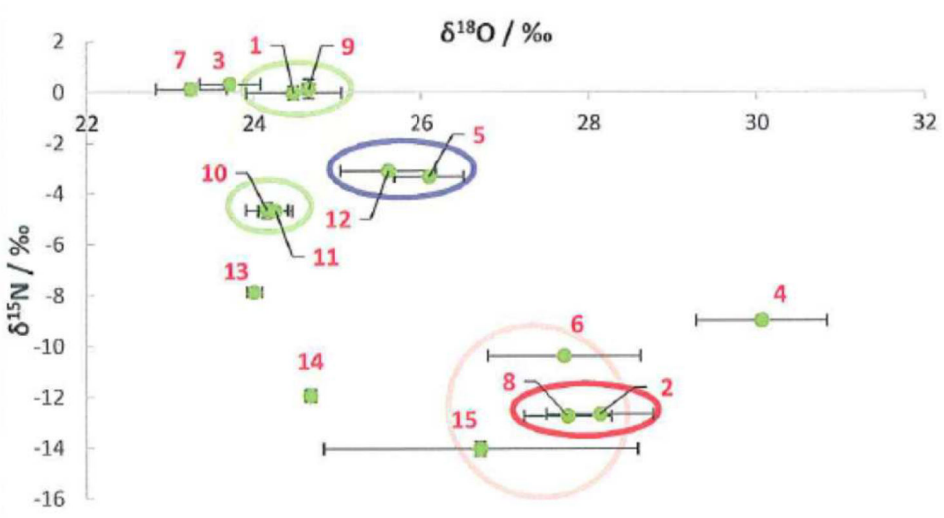
NC Samples

Sample No.	Year of Nitrocellulose Delivery	Nitrocellulose Identifier
1	2013	**B;** Replacement
2	1991	**A;** Drum 12
3	1994	**A;** Drum 15
4	1989	**A;** Drum 8
5	1996	**A;** Drum 16 (Cold Stored); Box 20
6	1990	**A;** Drum 10
7	1996	**A;** Drum 16 (Cold Stored); Box 6
8	1992	**A;** Drum 13
9	2013	**B;** Replacement
10	1998	**A;** Drum 18
11	1998	**A;** Drum 18
12	1996	**A;** Drum 16 (Cold Stored); Box 20
13	1989	**A;** Drum 9
14	1993	**A;** Drum 14
15	1990	**A;** Drum 11

IRMS Results - Examples

- $^{2}H/^{13}C$ ratios (cellulose)
- $^{15}N/^{18}O$ ratios (nitric acid)





Summary of Findings

- Samples 3, 4, 6, 7, 13, 14 and 15 were isotopically unique
  - Sample 7 is chilled NC A (Box 6)!
- The following groups of samples were indistinguishable
  - 5 and 12 (chilled NC A, Box 20)
  - 1 and 9 (NC B)
  - 10 and 11 (NC A, Drum 18)
  - 8 and 2 (NC A, Drums 12 & 13)
- The following groups of samples have cellulose sources that are indistinguishable
  - 1, 9, 10 and 11 (NC B, NC A Drum 18)
  - 2, 8, 6 and 15 (NC A, Drums 10 – 13)

Conclusion

- The hypothesis that all historical NC samples originated from the same batch is disproven
- The cold stored NC (i.e. Drum 16) appears to be made up of from multiple production ‘batches’
  - Box 6 & Box 20 are not the same material
  - Supported by the observation that NC molecular mass (by SEC) is unexpectedly different
- Further work required to characterise the chilled stock

Acknowledgements

- Mass Spec Analytical, Bristol
  - Dr Richard Sleeman
  - Dr Tim Knowles