

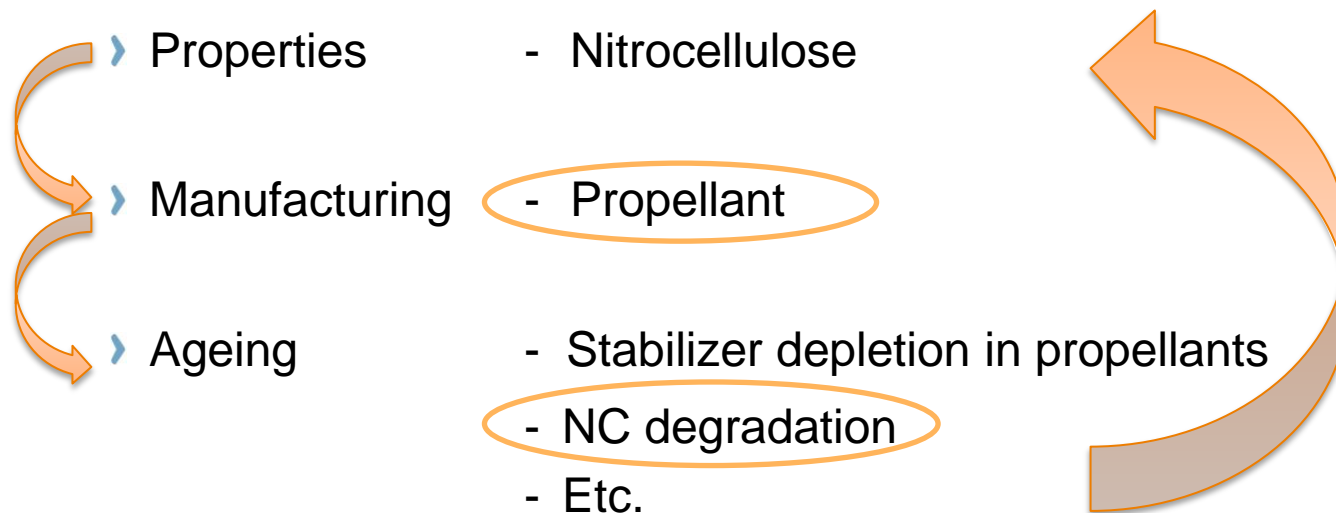
› DETERMINATION OF NITROGEN CONTENT OF NITROCELLULOSE BY CHROMATOGRAPHY

Monique van Hulst

TNO

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IMPORTANCE DETERMINATION OF %N



ANALYTICAL TECHNIQUES

- › Size-exclusion Chromatography (Hydrodynamic volume, “Mw”- “Chain length”)
- › Elemental Analysis (total C, H and N – with adjustment also O)
- › Titrations (nitrogen content)
- › Ultra High Pressure Liquid Chromatography (Patent US2013/0000382 A1)
- › X-Ray Diffraction (Crystallinity)
- › Near infrared (NO₂)
- › Etc.

CRYSTALLINITY

*Data presented at the 6th Nitrocellulose workshop (2014)

Sample	Holder	Crystallinity fitted (TOPAS) 1 crystalline / 3 crystalline signals	
Cellulose	Side-loader	54%	
Nitrocellulose-A	Side-loader	7%	14%
Nitrocellulose-B	Side-loader	8%	10%

is depending sample preparation, choice of fitting method and choice of crystalline/amorphous signals.

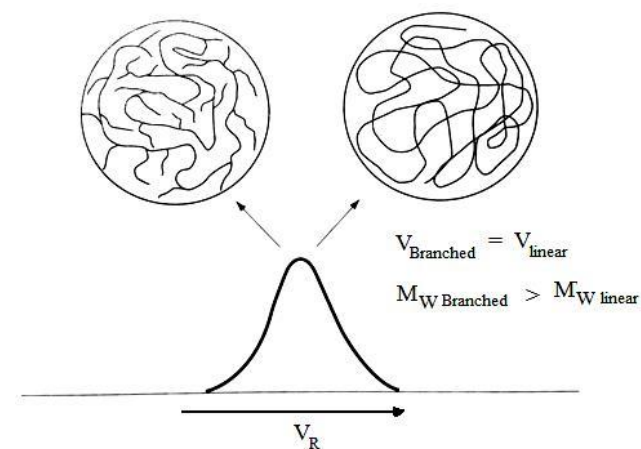
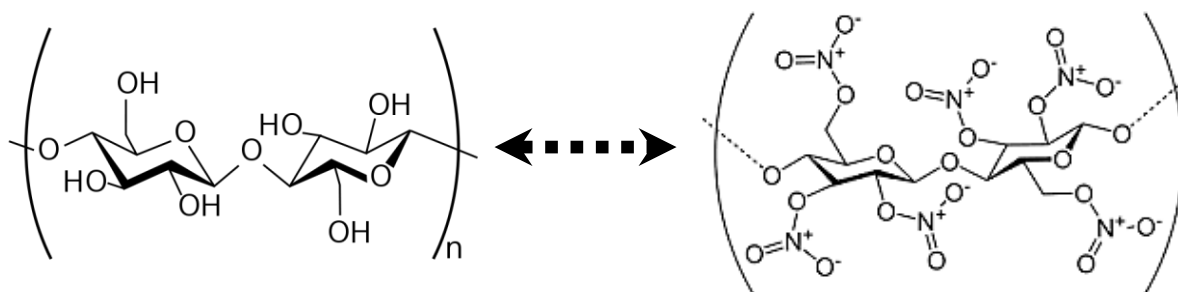
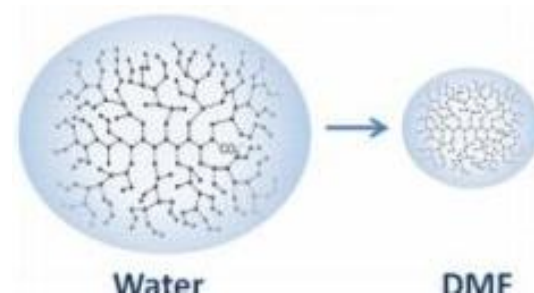
ELEMENTAL ANALYSES – NITROGEN CONTENT IN NITROCELLULOSE

- › Based on the combustion of the material – resulting in %C, %H and %N (optional is %O)
- › Percentage based on sample mass
- › Mass is influenced by all impurities incl. water content
- › Influenced by other Nitrogen containing impurities
- › Suggestion: to eliminate the influence of weight by using ratio C/N of nitrocellulose. However not the influence of impurities containing carbon and/or nitrogen.

CHROMATOGRAPHY OF NITROCELLULOSE

SIZE EXCLUSION CHROMATOGRAPHY

- › Based on hydrodynamic volume:
 - › Depending on solvent
 - › Monomer type (and distribution)
- › Indirect measure, due to using PS standards for SEC- calibration and analysing “random” copolymers.



HPLC NITROCELLULOSE

United States

Patent Application Publication
Combs

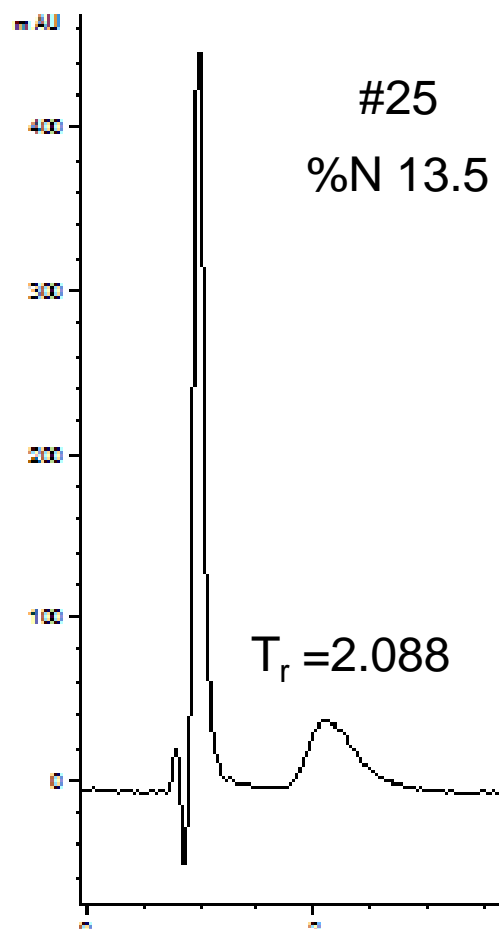
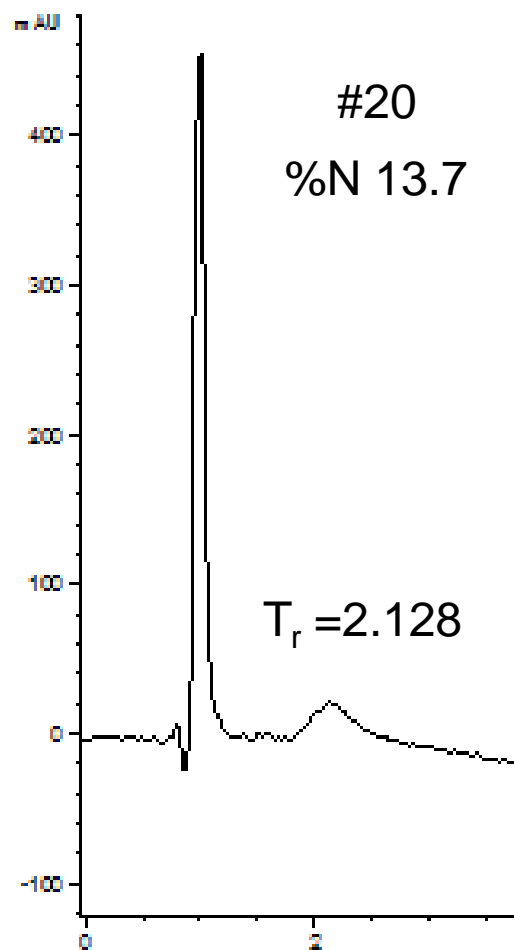
(10) Pub. No.: US 2013/0000382 A1

(43) Pub. Date: Jan. 3, 2013

METHODOLOGY FOR DETERMINATION OF NITROGEN CONTENT IN NITROCELLULOSE

Inventor: **Michael T. Combs**, Shady Spring, WV
(US)

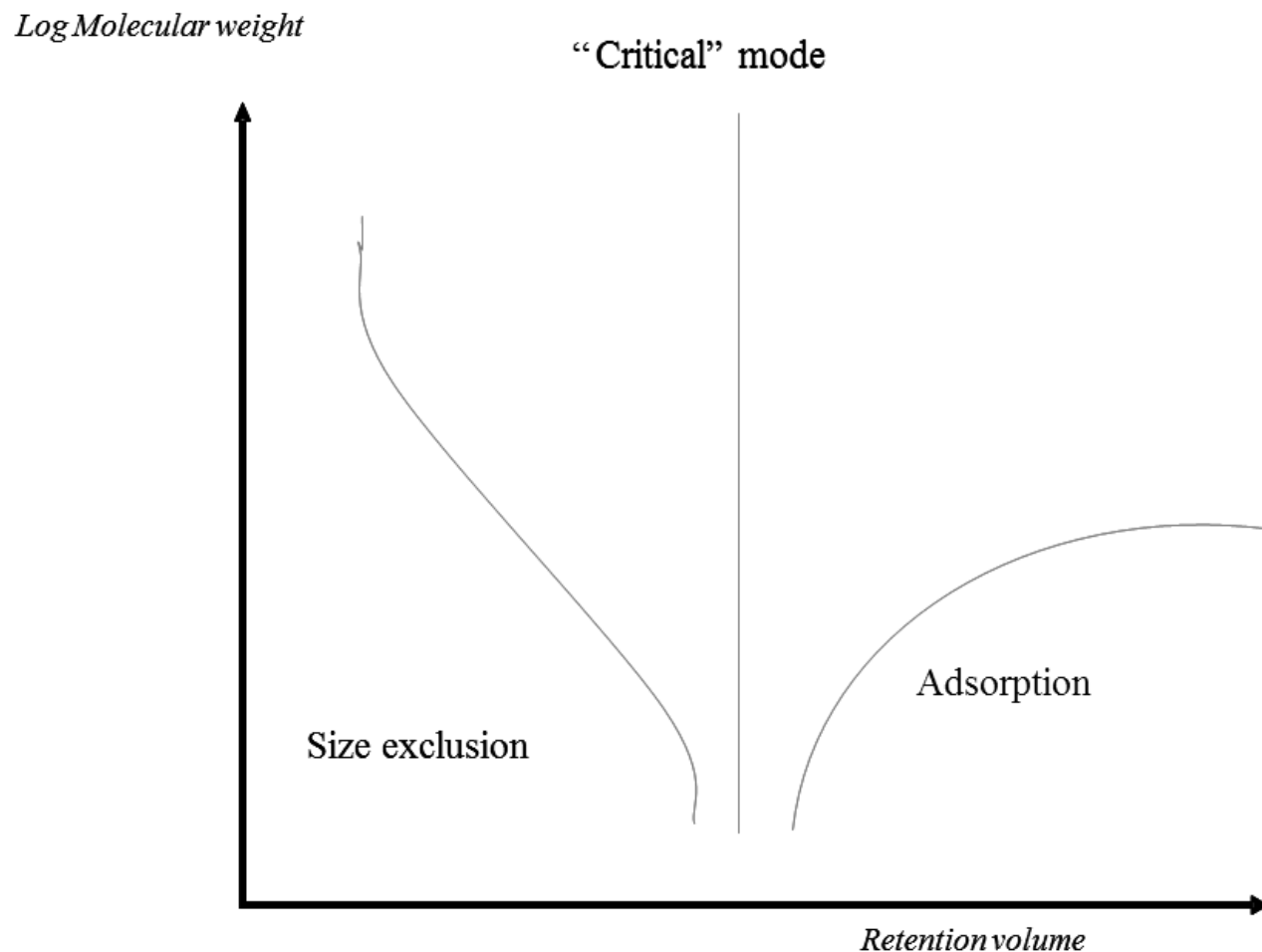
Assignee: **ALLIANT TECHSYSTEMS, INC.**,
Minneapolis, MN (US)



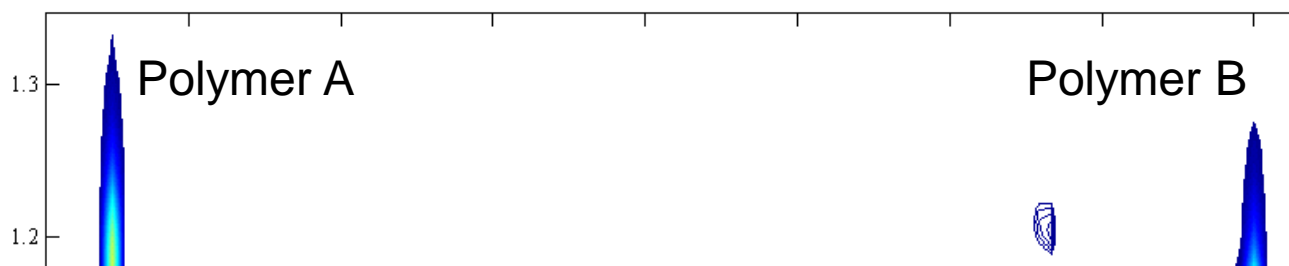
Cellulose "Mw" #20: $1.45 \cdot 10^6$ Da
#25: $1.36 \cdot 10^6$ Da

SEC shows similar PDI-values

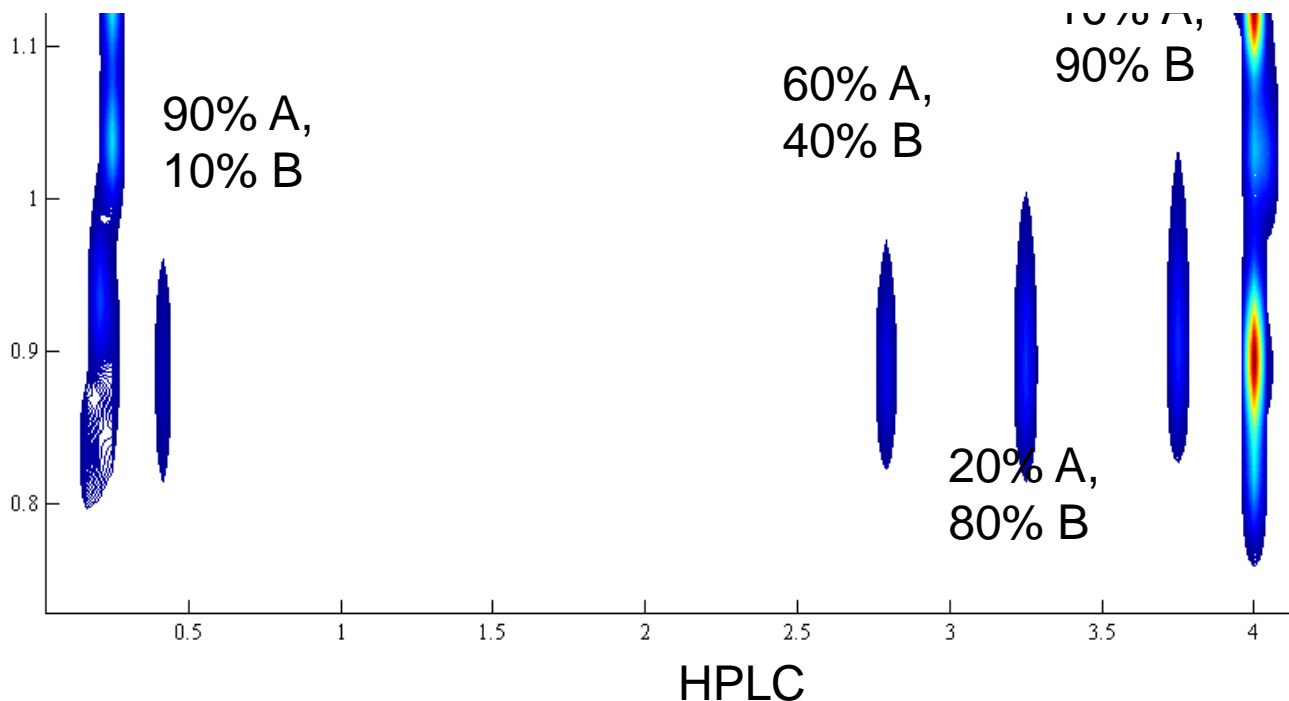
VARIOUS MODES OF LC FOR POLYMERS



COPOLYMER ANALYSIS (LC X SEC)

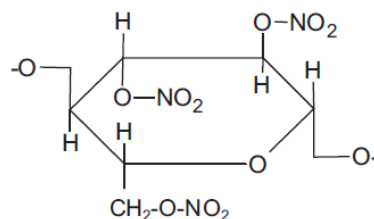


What about nitrocellulose, which contains monomer A, B, C and D?

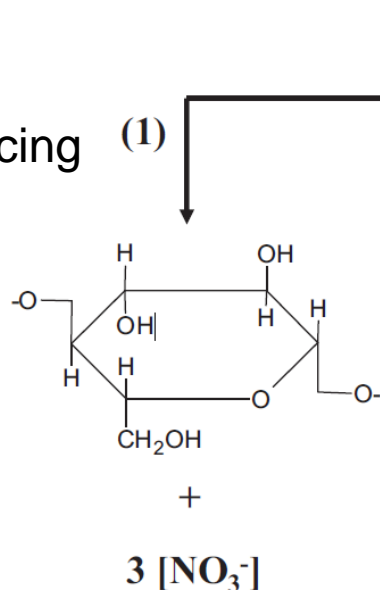


ION CHROMATOGRAPHY

%N IN NC IN PROPELLANT MATRIX BY ION CHROMATOGRAPHY

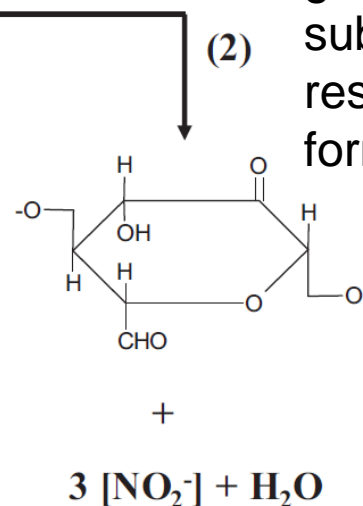


a simple ester
hydrolysis producing
nitrate

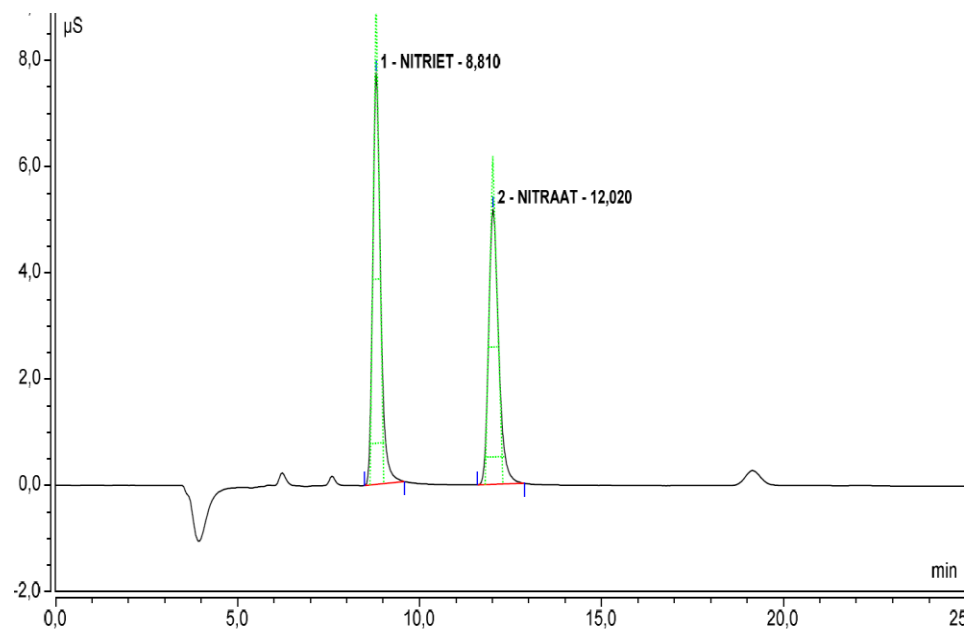
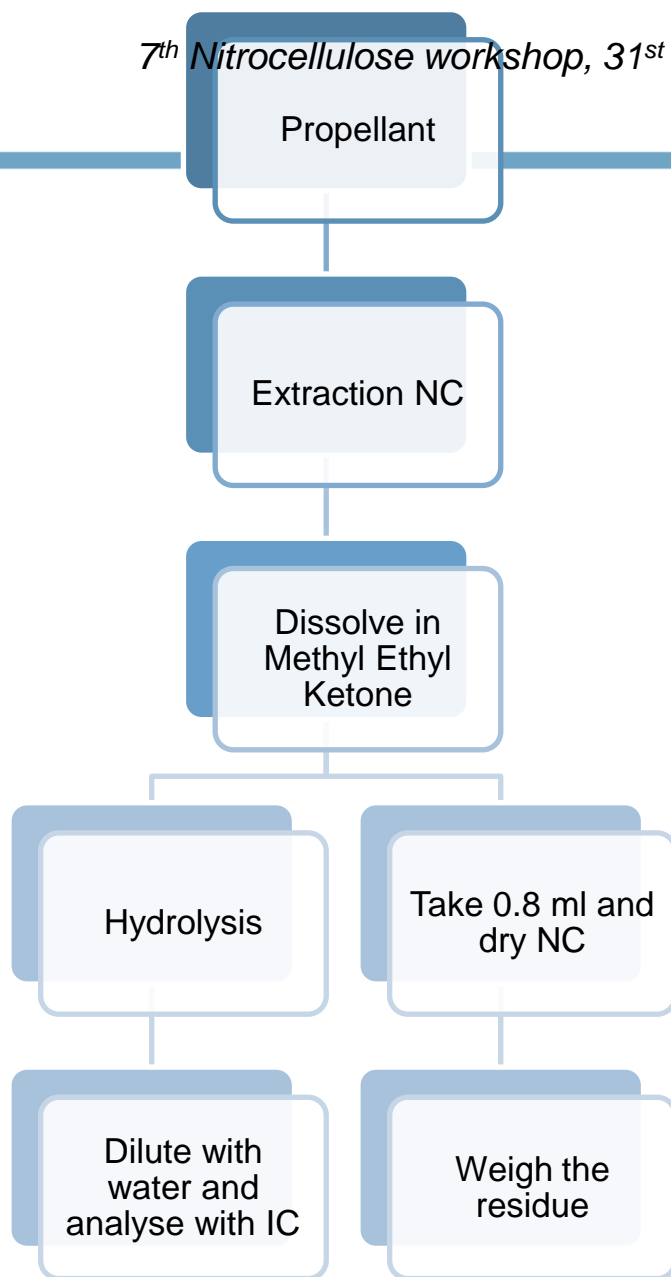


OH⁻

formation of carbonyl
groups at the
substitution site,
resulting in the
formation of nitrite

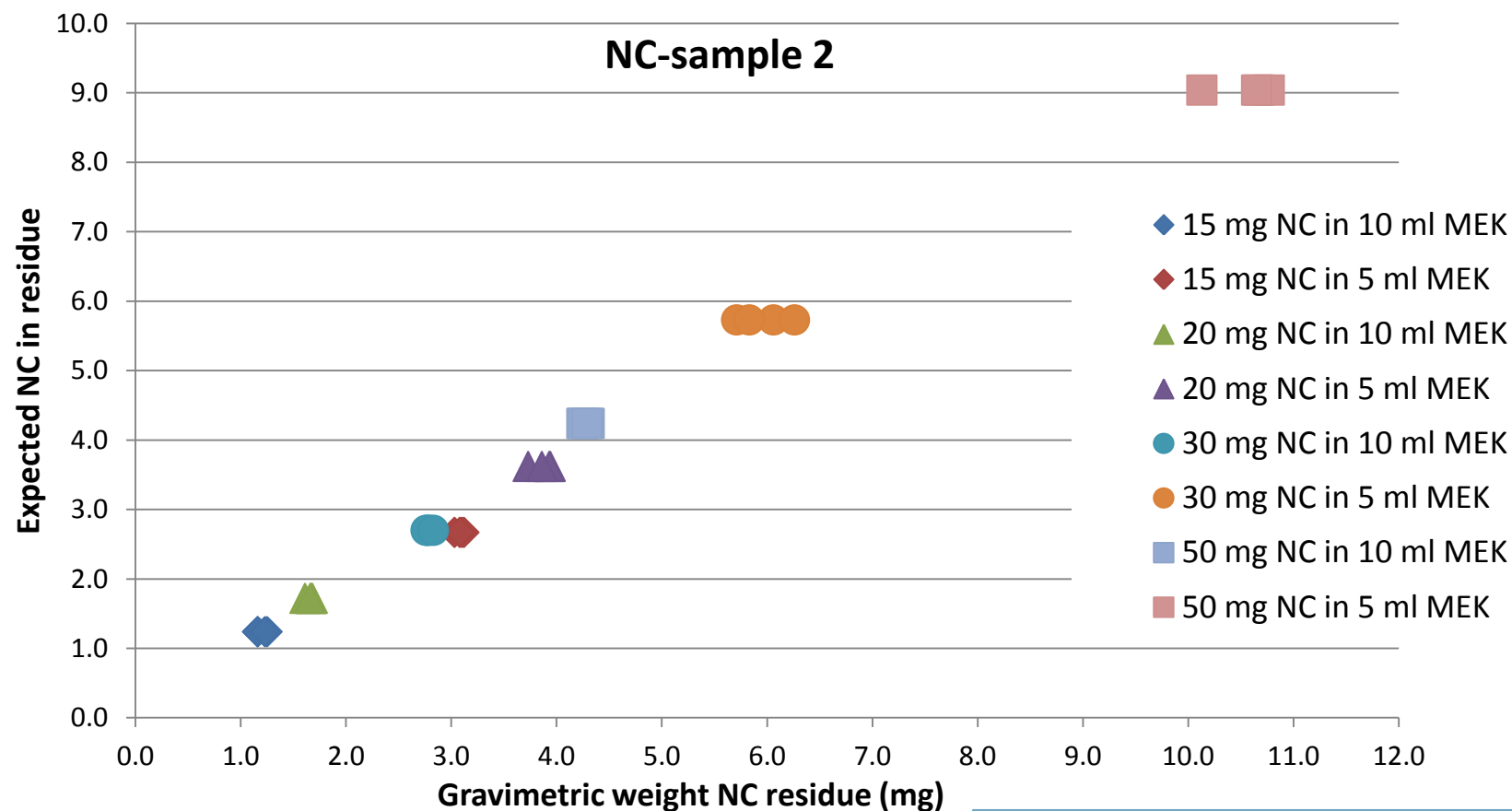


STEPS DETERMINATION OF %N IN NC IN PROPELLANT BY IC



M. López- López et al., *Analytica Chimica Acta* 685 (2011) 196-203

EXTRACTION OF PROPELLANT AND GRAVIMETRIC NC CONCENTRATION

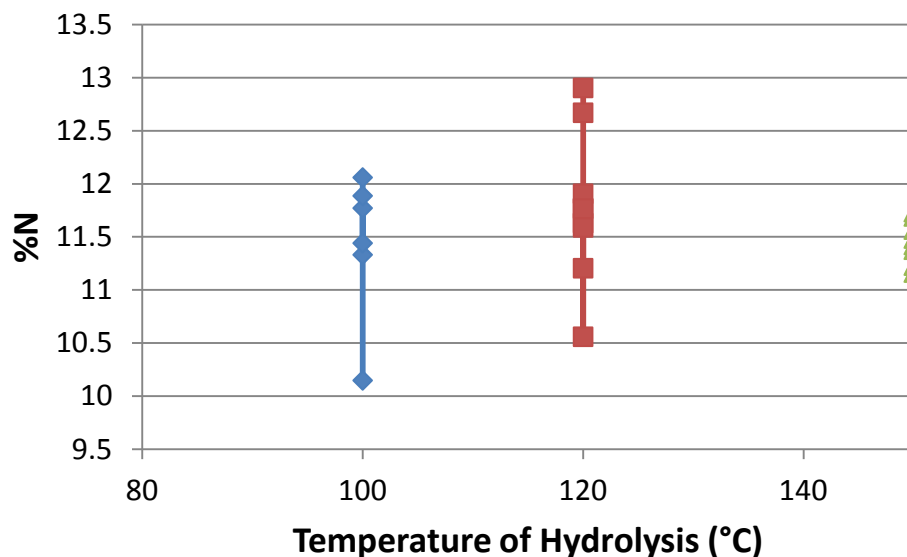


- › NC 1 - Recovery: 90.2% - 110.9%
- › NC 2 - Recovery: 93.5% - 119.1%

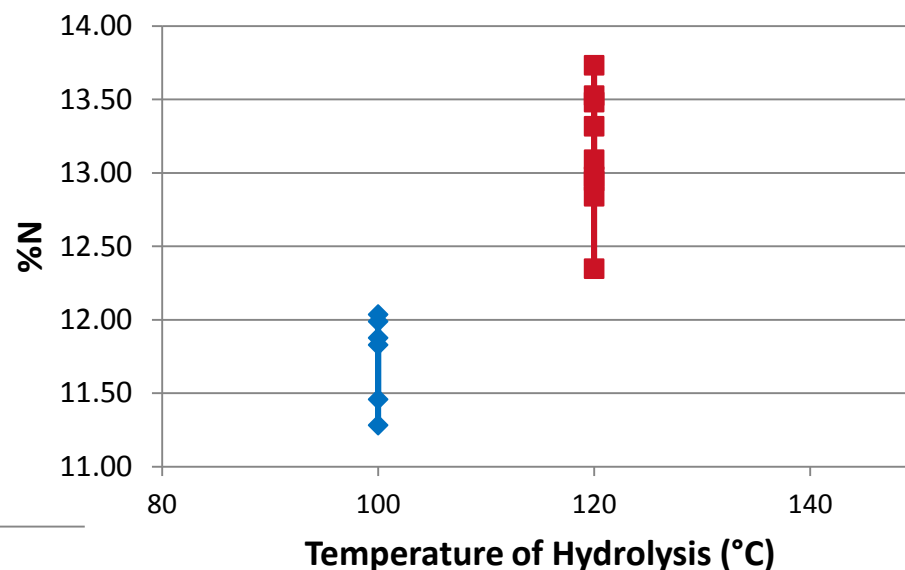
HYDROLYSIS

- ◆ 100° C for 2 hours
- 120 °C for 2 hours
- ▲ 150 °C for 1/2 hour

NC 1



NC 2




EA NC 1:

11.69 (2008)
11.85 (2009)
11.71 (2015)

EA NC 2:

13.55 (2008)
13.56 (2009)
13.45 (2015)

%Nitrogen = based
concentration from $\text{NO}_2 + \text{NO}_3$

Use button 'Pictures'  to change background
Text-only start sheets can be added using
'New slide/Nieuwe dia'

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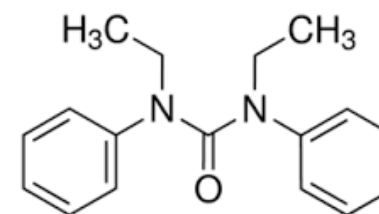
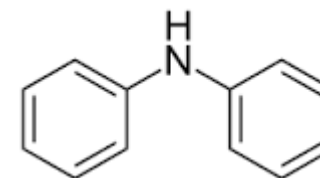
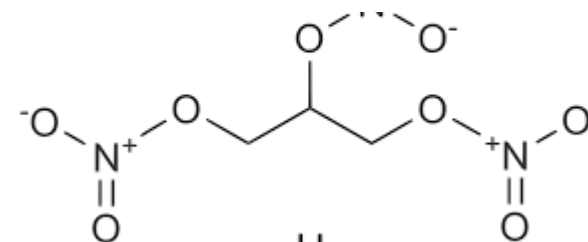
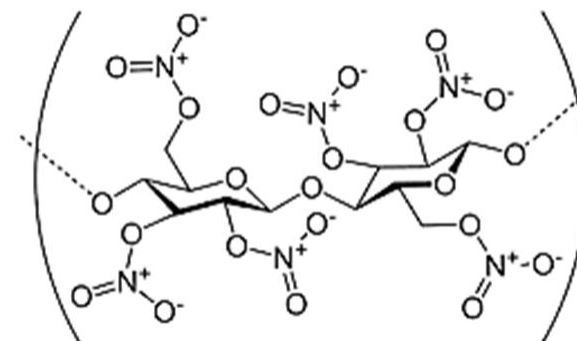
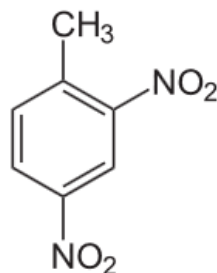
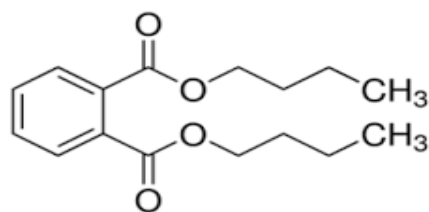
PROPELLANTS

PROPELLANTS

› By elemental analyse N, H and C

- › Nitrocellulose
- › Nitroglycerin
- › Stabilizer
- › Plasticizer

Etc. (more C, H and N)



Possible by fitting:

With increasing # of components and/or similar ratio CHN; decreasing accuracy

IC ANALYSIS OF PROPELLANTS

Samples

› Propellant without stabilizer:

- 97 wt% NC 13.2 N%
- 3% plasticizer

› Propellant with stabilizer:

- 94 wt% NC 13.2 N%
- 3% stabilizer
- 3% plasticizer

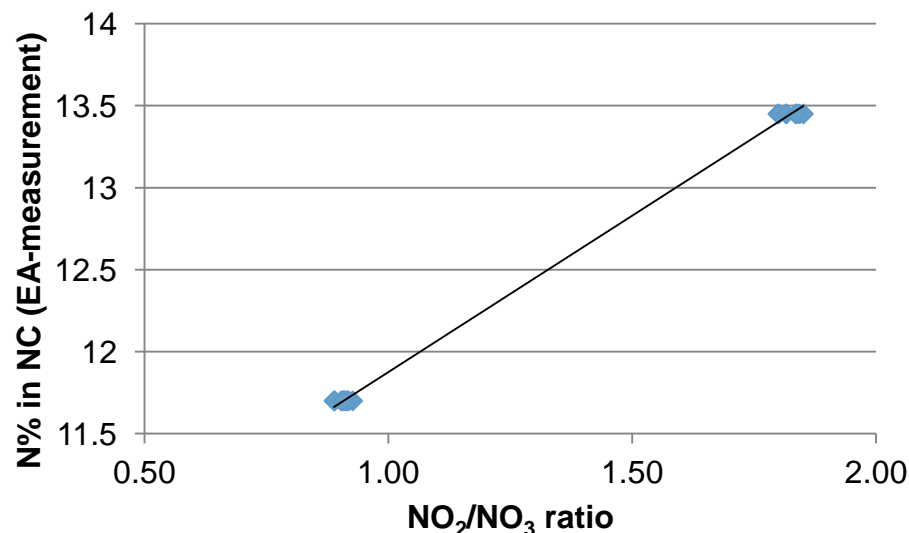
Triple base- N% of NC:

- | | |
|---------------------------------------|-----------|
| - EA | - 19.3 %N |
| - EA-C/N | - 16.0 %N |
| - IC (SUM) | - 6.8 %N |
| - IC-NO ₂ /NO ₃ | - 12.4 %N |
| - <i>Info NC used</i> | - 12.5 %N |

Result:

Average 13.20 %N; STDV. 0.05

Average 13.17 %N; STDV. 0.11



CONCLUSIONS

- › Working with ratio NO_2/NO_3 shows less variations than total %N
 - › No influence on the sample mass variation
- › Separation NC from other components in propellant is needed
- › The analyses of propellant looks promising especially dealing with triple base with stabilizer and plasticizer content. Calibration ratio NO_2/NO_3 with NC-samples seems possible (%N by Elemental analysis). IC calibration with NO_2^- and NO_3^- ion standards
- › Further research needed to understand nitrocellulose and the dependence of the ratio of the nitrite / nitrate formation

CONTACT INFORMATION

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› **THANK YOU FOR YOUR ATTENTION**

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