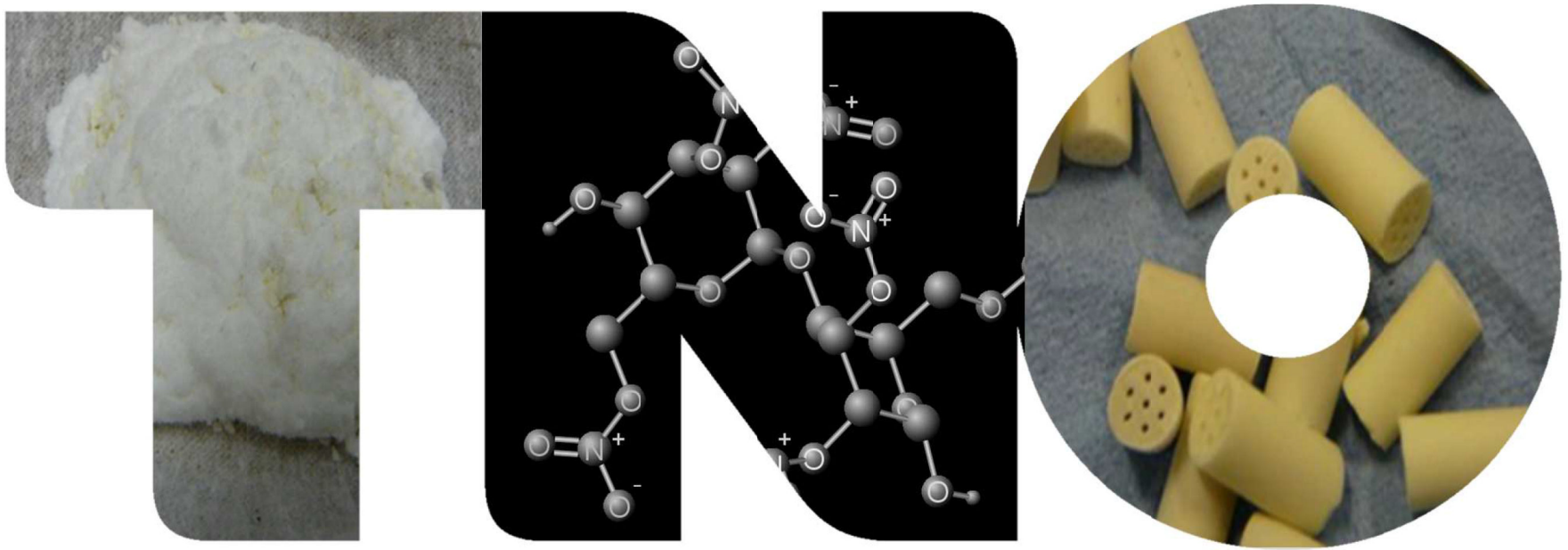
Cellulose and nitrocellulose

Analysing chemical properties

M. van Hulst and W. Duvalois



From Cellulose to Nitrocellulose/ Cellulose nitrate

- Sources of Cellulose:
  - Cotton, wood, synthetic micro organisms/man-made /man-controlled
  - Variation:
    - Chain length
    - Composition
    - Crystallinity
    - etc.

- *Process for the production of microbial cellulose, US 4929550 A*
- *Bacterial cellulose-containing molding material having high dynamic strength, US 4742164 A*

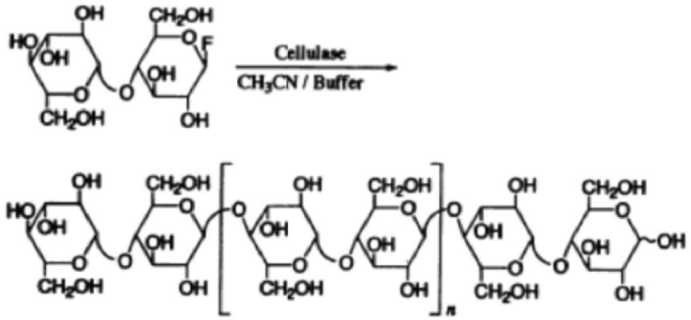


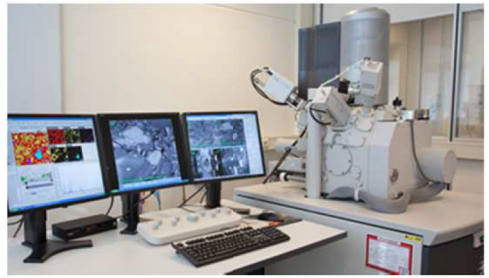
FIG. 1. Synthesis of cellulose by a condensation polymerization catalyzed by cellulase with use of β-CBF as a substrate monomer.

Lee, J.H., et.al., Proc. Natd. Acad. Sci. USA, Vol. 91, pp. 7425-7429, 1994,Biochemistry

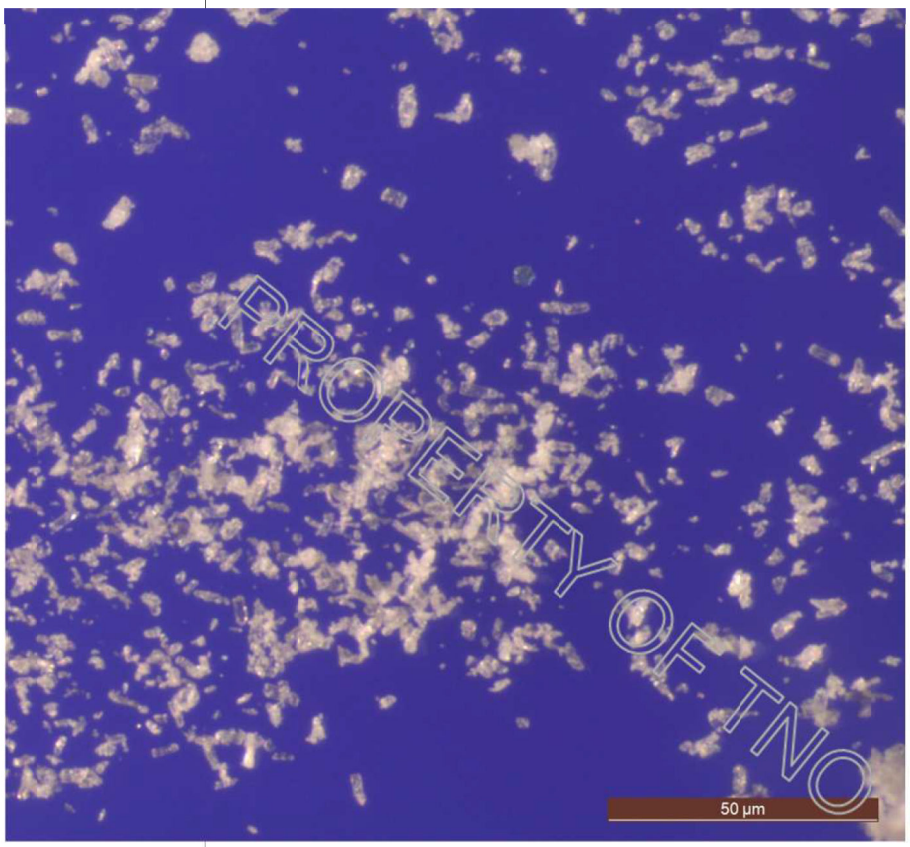
Cellulose vs. Nitrocellulose

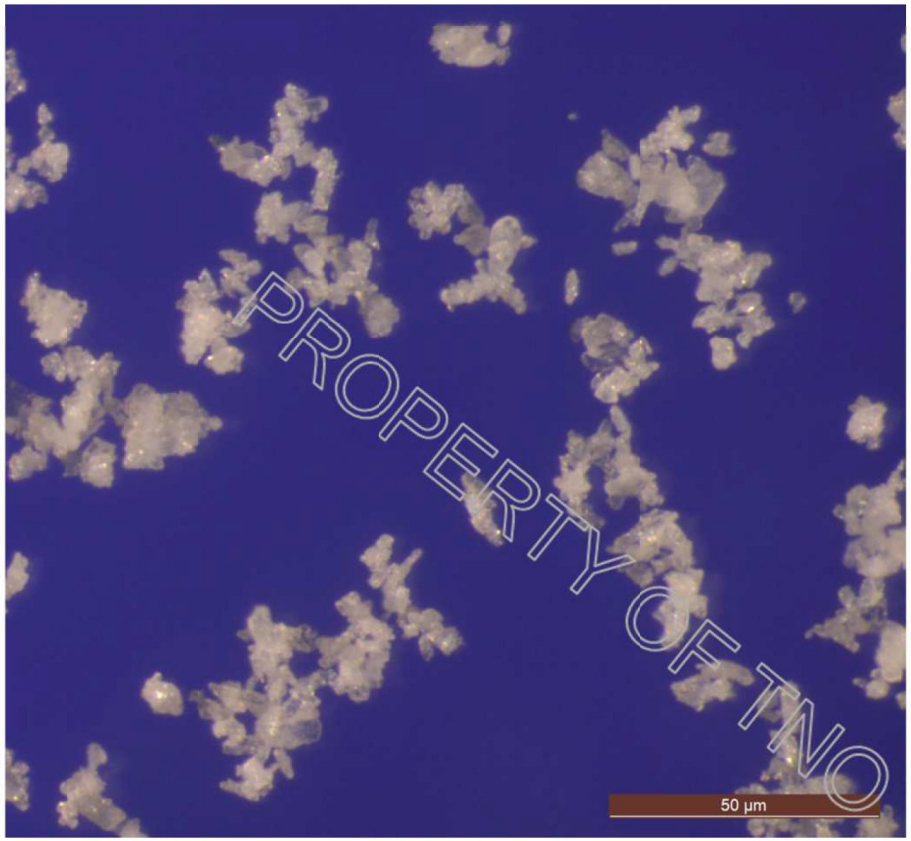
Analytical techniques

- Optical Microscopy
- Scanning Electron Microscopy
- Size-exclusion Chromatography
- Elemental Analysis
- Ultra High Pressure Liquid Chromatography
- X-Ray Diffraction



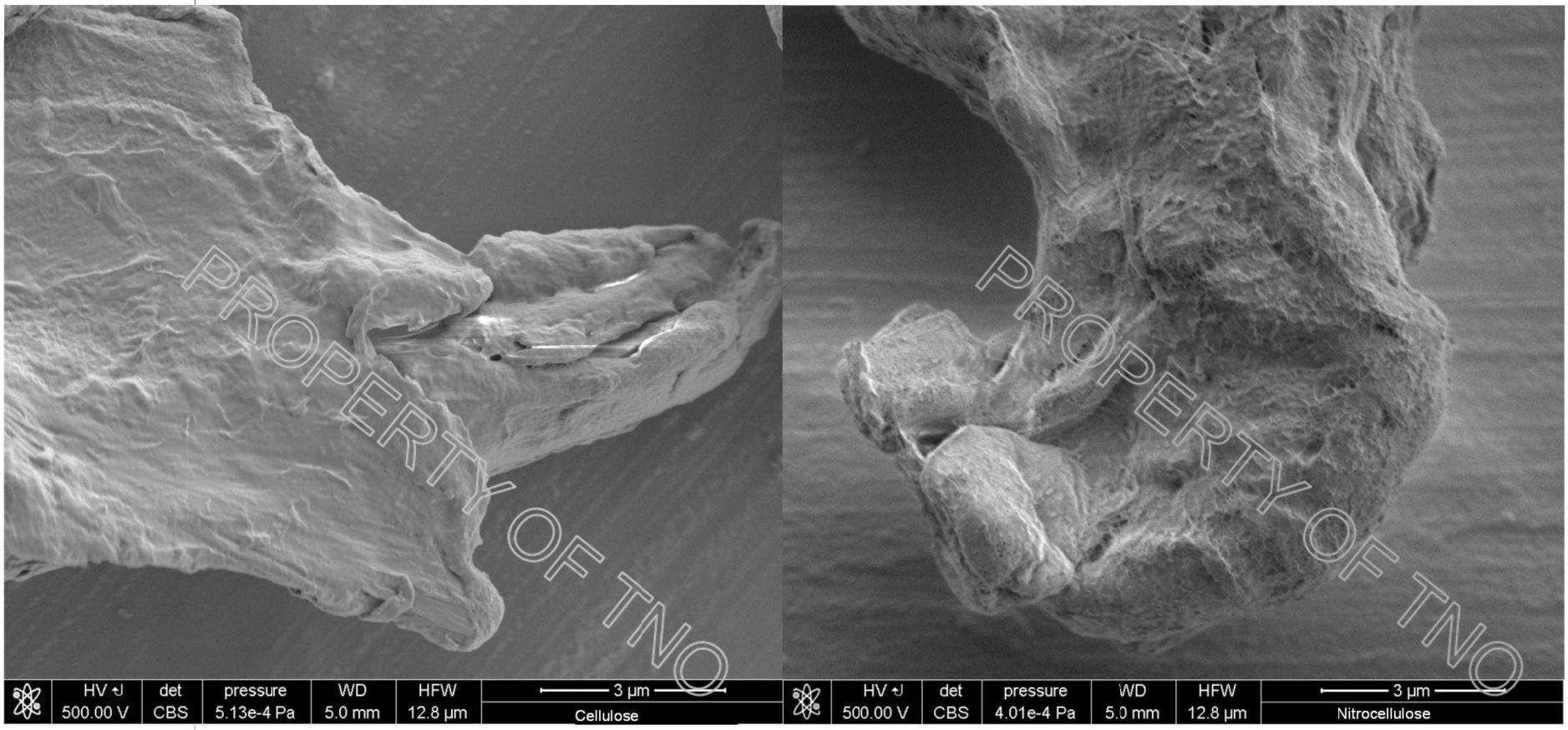
Optical Microscopy





- Cellulose vs. Nitrocellulose

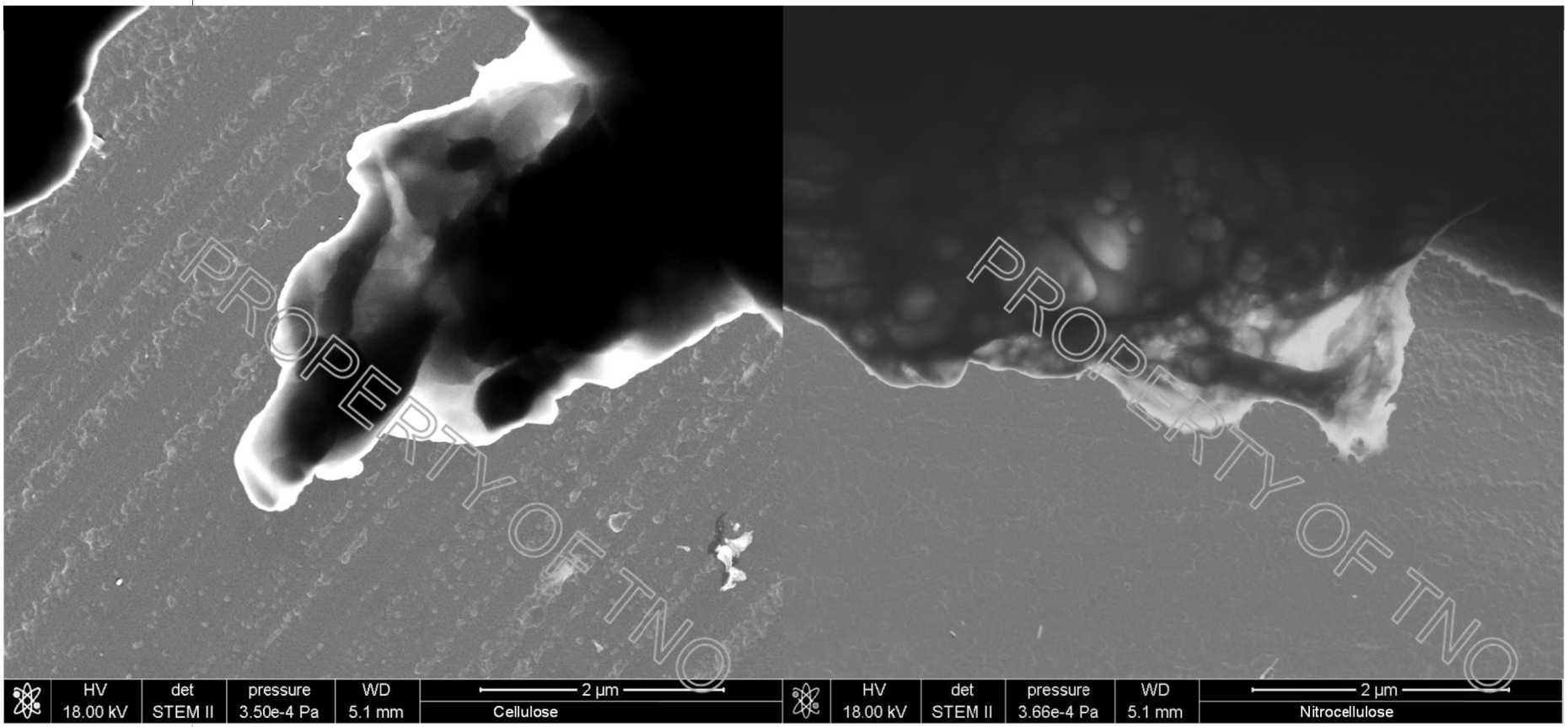
Scanning Electron Microscopy
backscattered electron imaging



› Cellulose vs. Nitrocellulose

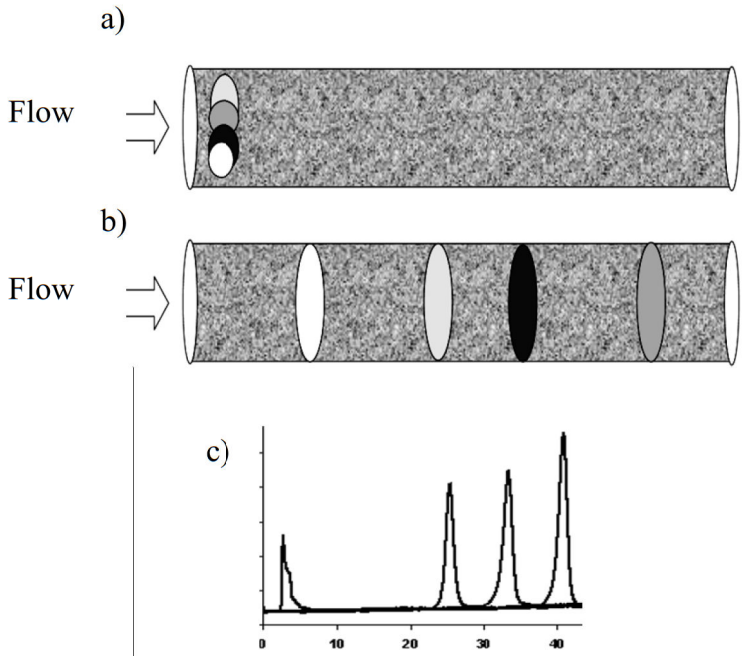
Scanning Transmission Electron Microscopy

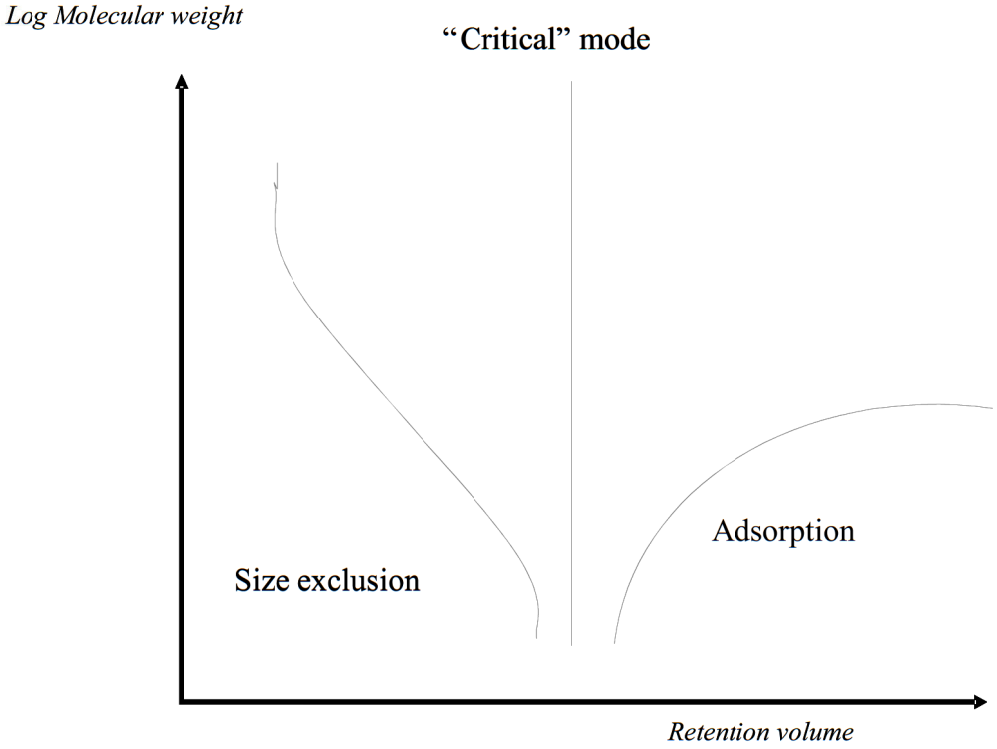
Dark-field



› Cellulose vs. Nitrocellulose

Liquid Chromatography of polymers





Size- exclusion Chromatography
"*Degree of polymerisation*"

- "The average configuration of polymer molecules in solution is markedly influenced by the obvious requirement, ordinarily disregarded in problems relating to molecular configuration, that two elements of the molecule are forbidden from occupying the same location in space".*

- How can SEC tell us as stand-alone technique anything about degree of polymerization of the nitrocellulose polymers?

**The Configuration of Real Polymer Chains, J. Chem. Phys. 17, 303 (1949), by Paul J. Flory, Cornell University, Ithaca, New York*

Relative Mw and PDI depending on column resolution, peak broadening, detector sensitivity etc.

- NC-A:

  "Mn"=2,5831*e5

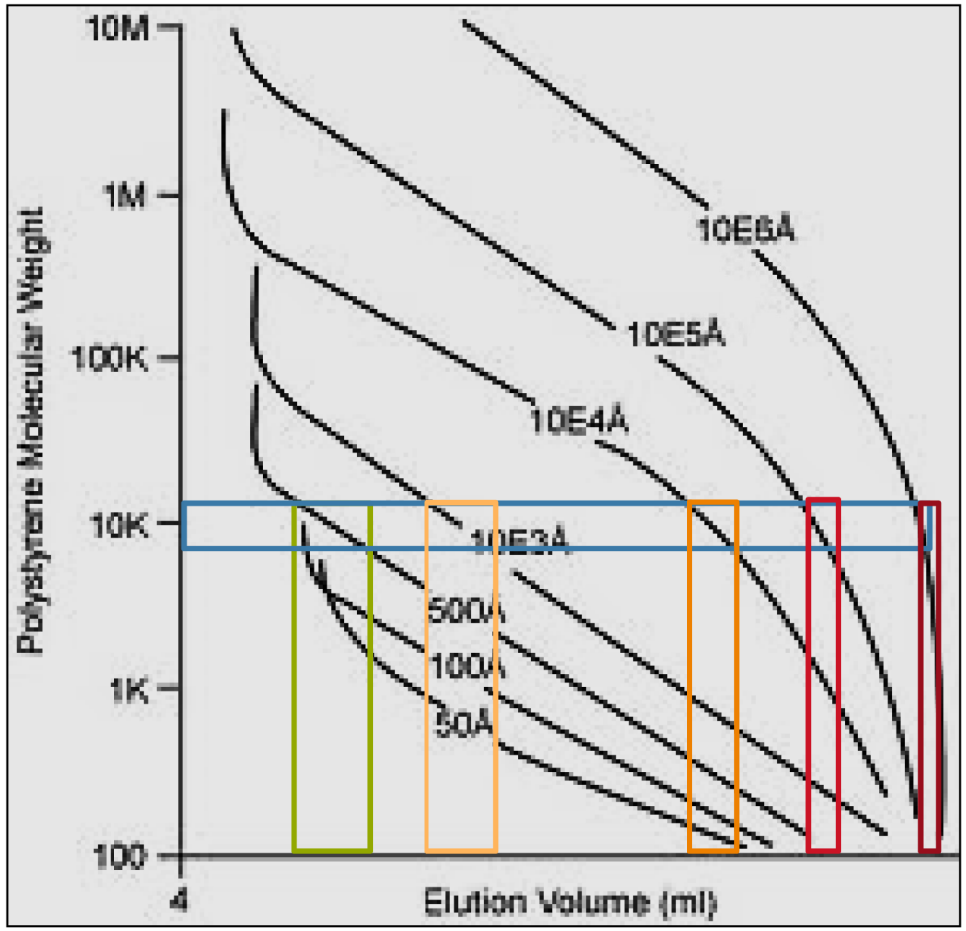
  "Mw"=3,9626*e5

- NC-B:

  "Mn"=2,6286*e4

  "Mw"=1,3966*e5

(Relative to Polystyrene)



"Degree of substitution"

LC and CHNO-element Analyser

NC-A	M (mg)	%N	%C	%H
1	20.027	12.71	23.7	2.63
2	20.528	13.03	23.82	2.66
3	20.242	12.78	23.71	2.62
4	20.396	12.88	23.76	2.60
5	20.203	13.06	23.73	2.59
	Average	12.89	23.74	2.62
	st dev	0.15	0.05	0.03

Sample	%N	Average degree of Substitution
NC-A	12.89	2.73
NC-B	12.56	2.66

**4th NC-workshop 2010, presentation Mario Paquet: "Accessibility amorphous fraction and outer layer of crystalline fraction to nitration acid."*

METHODOLOGY FOR DETERMINATION OF NITROGEN CONTENT IN NITROCELLULOSE

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

United States
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Combs
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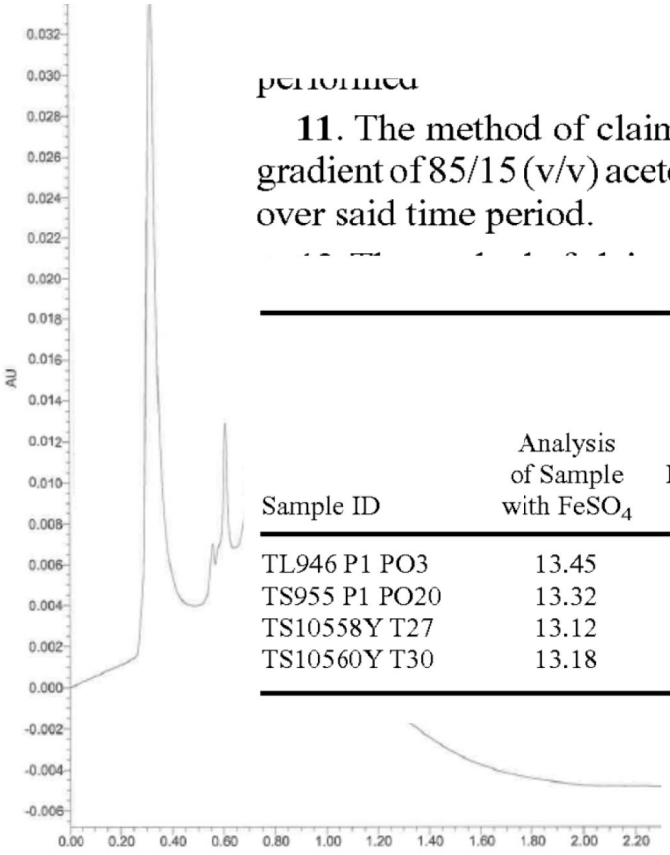
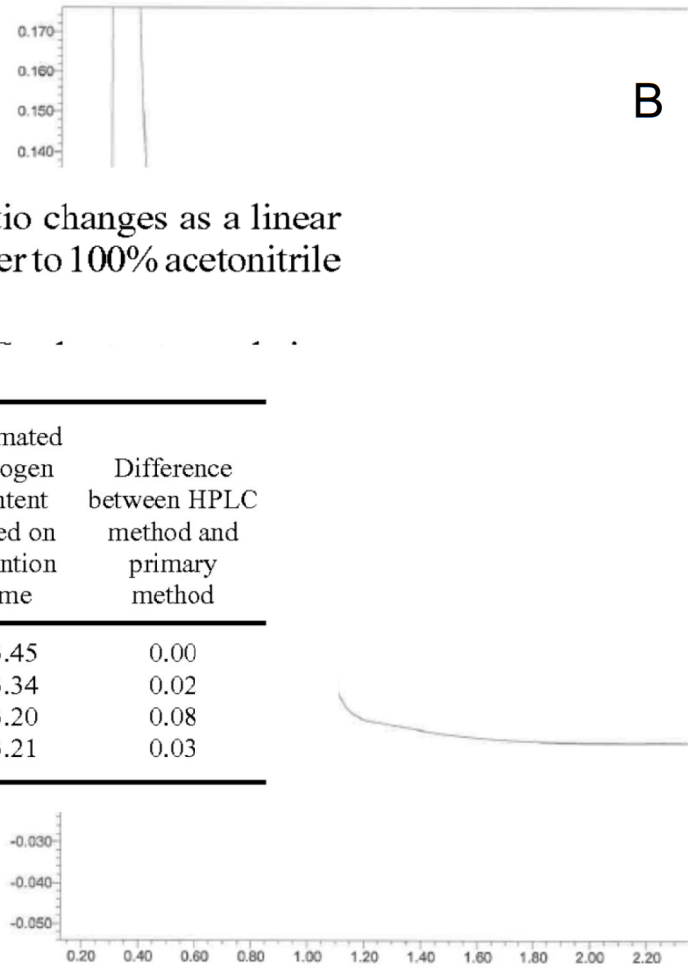
(43) **Pub. Date: Jan. 3, 2013**

A



B

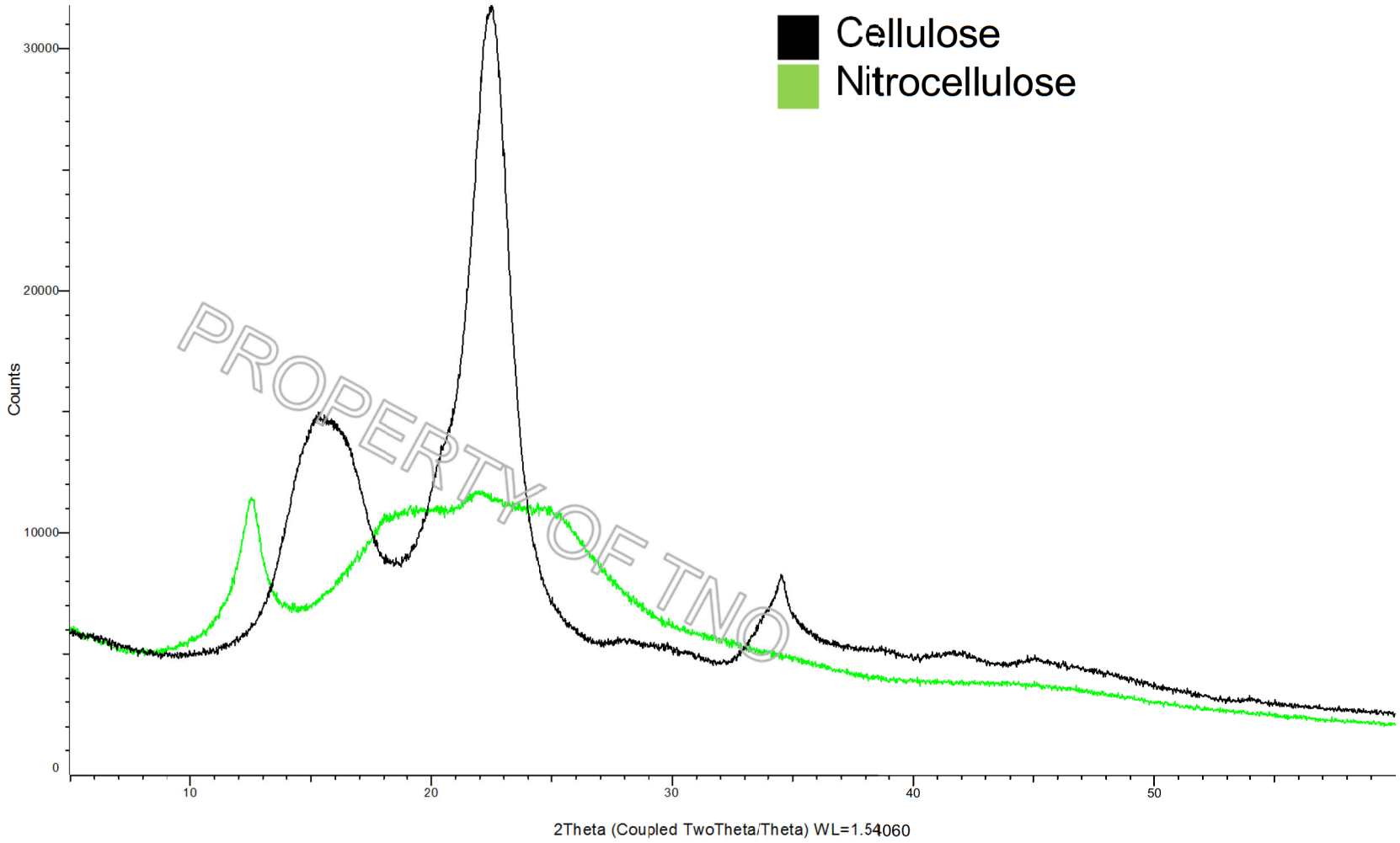


performed

11. The method of claim **10**, the ratio changes as a linear gradient of 85/15 (v/v) acetonitrile/water to 100% acetonitrile over said time period.

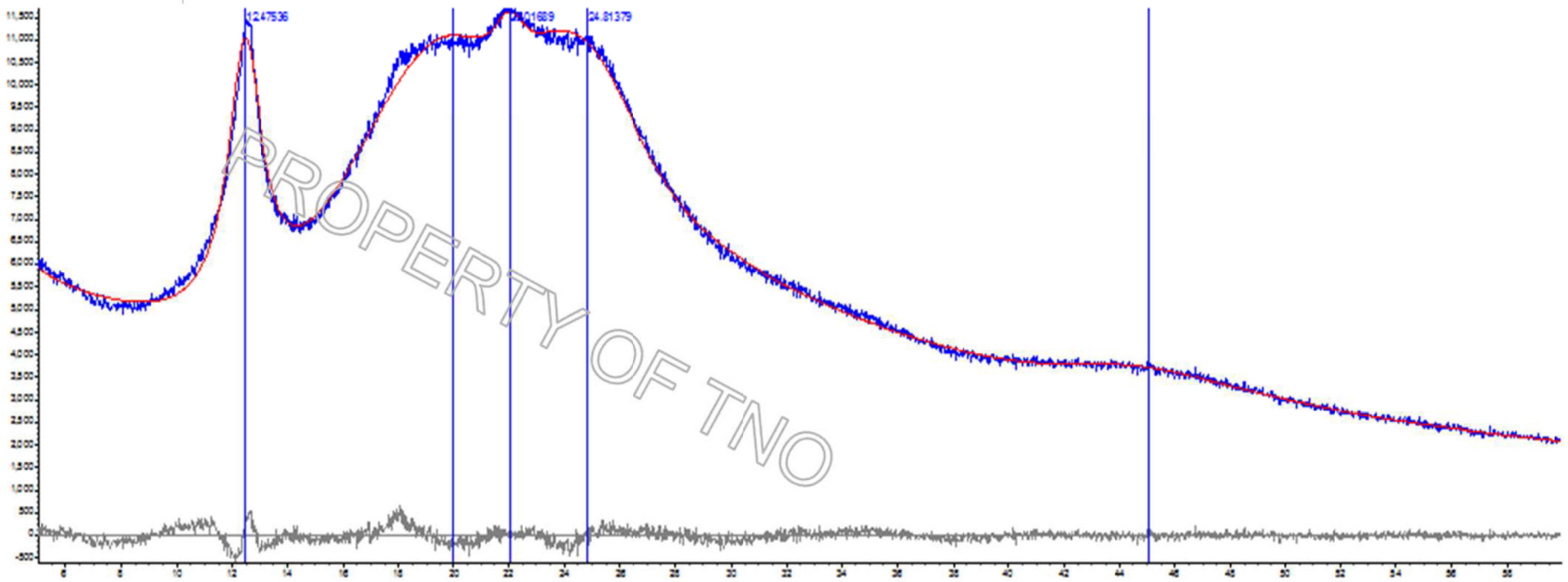
Sample ID	Analysis of Sample with $FeSO_4$	HPLC Retention Time	Estimated nitrogen content based on retention time	Difference between HPLC method and primary method
TL946 P1 PO3	13.45	4.323	13.45	0.00
TS955 P1 PO20	13.32	4.202	13.34	0.02
TS10558Y T27	13.12	4.051	13.20	0.08
TS10560Y T30	13.18	4.070	13.21	0.03

X-Ray Diffraction



Determination of Crystallinity

Fitting Crystalline and Amorphous fraction



Crystallinity

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%

- 54% Crystallinity to >14% due to nitration
- Average N% from 0% (cellulose) to 12.89%

Approx. 91% of the cellulose is nitrated from which 86% is amorphous

**4th NC-workshop 2010, presentation Mario Paquet: "Accessibility amorphous fraction and outer layer of crystalline fraction."*

Conclusions

- By looking at the materials with the electron microscope it shows a some structural change after nitration.
  - A more porous structure (STEM)
  - A rough surface (Backscatter SEM)

- Degree of nitration on average CHN-analyses:
  - NC-A: 2.73 (12.89 %N) and NC-B: 2.66 (12.56 %N) LC seems to show some chain length (Mw) effect

- Crystallinity of the materials is depending sample preparation, choice of fitting method and choice of crystalline/amorphous signals.

- The combination of the various techniques is essential if we want to understand Nitrocellulose its chemical and physical properties and the relationship with respect to each other.

Acknowledgement

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