# New Standards for Nitrocellulose Testing – STANAG 4178 Ed. 2 // MIL-DTL-244 B/ECP / C

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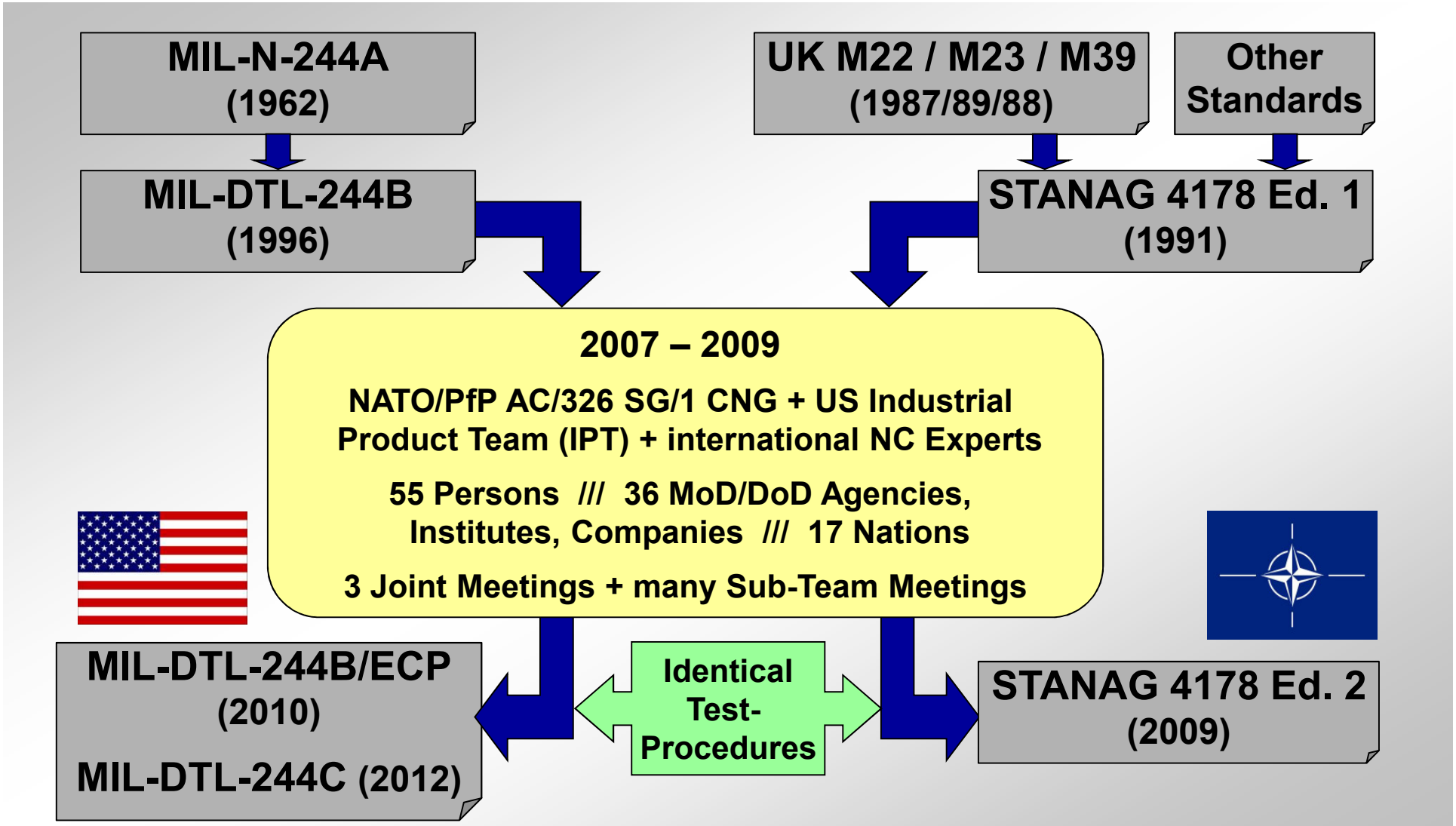
# Introduction – Recent History of Standards for NC Testing



# Differences between STANAG 4178 and MIL-DTL-244

| Standard | STANAG 4178 Ed. 2 | MIL-DTL-244 B/ECP / C |
|---|---|---|
| Classification of NCs | --- | ✓ (Grades A–F; Types I-III) |
| Specification for NCs | --- (only typical ranges) | ✓ |
| Testing Procedures NC | ✓ (all relevant tests) | ✓ (only required tests) |
| Testing Quality Requirements | ✓ | --- |
| Alterations for chalked NC | ✓ | --- |
| Requirements Raw Material | --- | ✓ |
| Requirements Prod. Process | --- | ✓ |

- STANAG 4178 is a compendium of nitrocellulose test procedures
- MIL-DTL-244 is a specification for nitrocellulose that also contains test procedures (but only the ones that are needed for this specification)

# Test Methods of STANAG 4178 Ed. 2 and MIL-DTL-244 B/ECP / C

## Basic Characterisation

- Nitrogen Content
  - Ferrous Ion Titration
  - Nitrogen Analyzer
  - Combustion Calorimetry
  - (Devarda's Alloy Method)
  - (Schulze-Tiemann)
  - (Nitrometer)
- Ether-Alcohol Solubles
  - Filtration Method
  - Evaporation Method
- Acetone Insolubles

## Stability

- 132°C Stability Test
  - Bergmann-Junk
  - Bergmann-Junk-Siebert
- 134.5°C Heat Test (MV)

## Purity

- Visual Purity Test
- Ash
- Grit
- Ionic Impurities
  - Ion Chromatography
  - Sulphate Content
- Residual Acidity
  - Alkalinity
  - Calcium by Spectroscopy
- Oil and Grease Content
- (Abel-Type Heat Tests)

## Fibre Quality

- Fineness
- Fibre Length Distribution
- Water Retention Value
- Drainability
- Agglomerates

## Polymeric Properties

- Viscosity
- Molecular Mass Distribut.

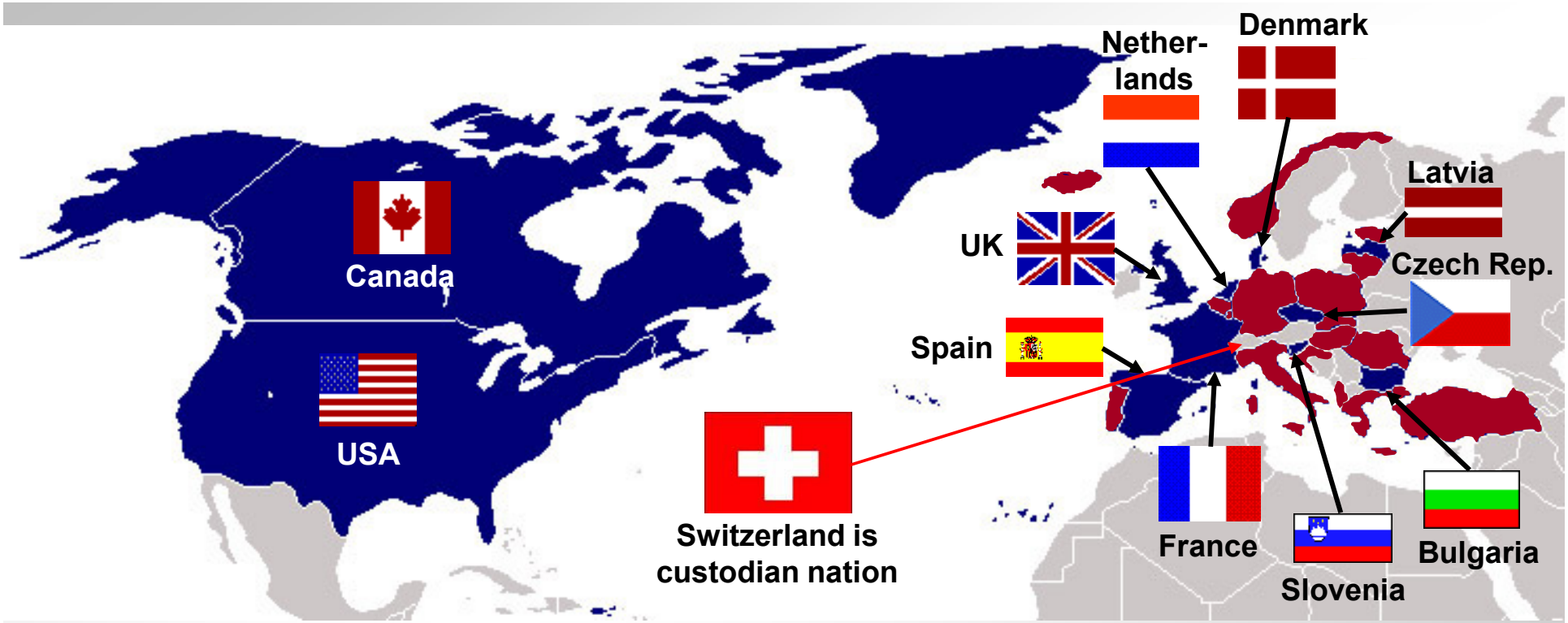
## Water / Alcohol Cont.

- Total Volatile Content
  - Oven Method
  - Moisture Analyzer
- Water Content
  - Karl-Fischer Titration
  - Karl-Fischer Oven
- Alcohol and / or Water
  - Gas Chromatography
  - NIR Spectroscopy

## Other Properties

- Temperature of Ignition
- Heat of Explosion

# STANAG 4178 Ed. 2 Ratification Status




- STANAG 4178 Ed. 2 is currently in NATO ratification
  - 11 nations including US, UK and France have already ratified
  - a total of 14 nations (50% of the 28 NATO nations) need to ratify
  - many nations have already implemented the new testing procedures

# MIL-DTL-244 B / C Status of Implementation

- MIL-DTL-244 B with ECP # R10C3001 (2010)
  - ECP = Engineering Change Proposal
  - Officially implemented
  - Currently used by the US ARMY, NAVY and Air Force
- MIL-DTL-244 C (2012)
  - Approved by the Nitrocellulose Configuration Manager (PM-CAS)
  - ARDEC standardization group is working on the document to ensure spec language complies with DoD requirements
  - Not yet implemented !

**Test procedures of MIL-DTL-244 B/ECP, MIL-DTL-244 C and STANAG 4178 Ed. 2 are identical**

# Round Robin Test (RRT) on Nitrocellulose Analysis

- **Mandate:** NATO/PfP AC/326 SG1 CNG
- **Organiser:** US ARDEC, GD-OTS Valleyfield, Nitrochemie Wimmis
- **Goals:**
  - Implementation of new methods (STANAG 4178 Ed.2 / MIL-DTL-244B/ECP)
  - To improve performance / get confidence in new testing methods
  - To obtain an idea about typical variations between labs
  - In the long term: To trigger communication within the NC community and to further improve testing methods
- **Samples:** 6 samples; each 2 samples Grade A, B, C
  - 3 samples with known results (to adjust procedures / gain confidence)
  - 3 samples with unknown results (for RRT).
- **Tests for RRT:** N-Content, EA-Solubility, Acetone Insolubles, 134.5°C Heat Test, 132°C Stability Test (Bergmann-Junk), Fineness, Viscosity

- If you are interested to participate, please inform the organisers

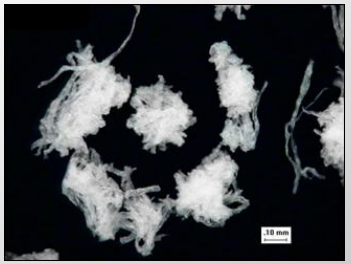
  

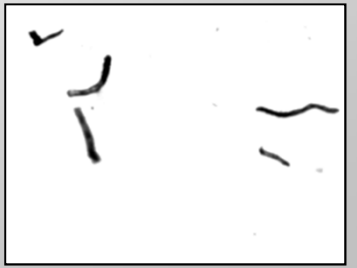
# Some Highlights of the new Standards

- **Ionic Impurities – Ion Chromatography Method:**
  - Modern method to assess numerous different ionic impurities simultaneously

- **Polymeric Properties – Gel Permeation Chromatography GPC:**
  - Modern method to assess the distribution of degree of polymerisation (conventional viscosity only results indirect measure for average degree of polymerisation)

- **Tests for Fibre Quality:**
  - Different test method to investigate the fibre properties
  - A new method to assess the fraction of the NC which is present as agglomerates
  - Several indirect methods to estimate the amount of cutting / grinding / refining the NC had undergone
  - A new direct method to determine the real fibre length distribution of the NC



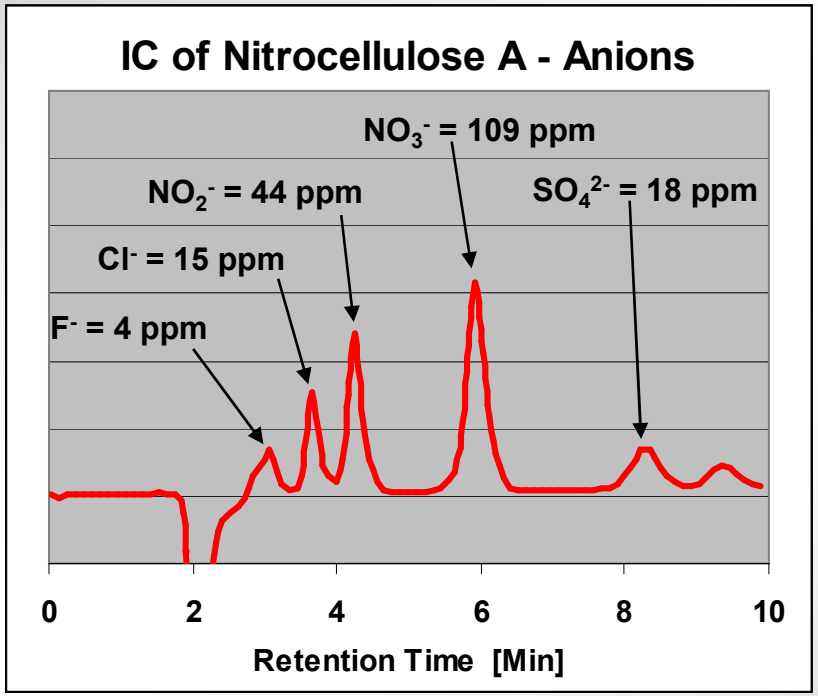


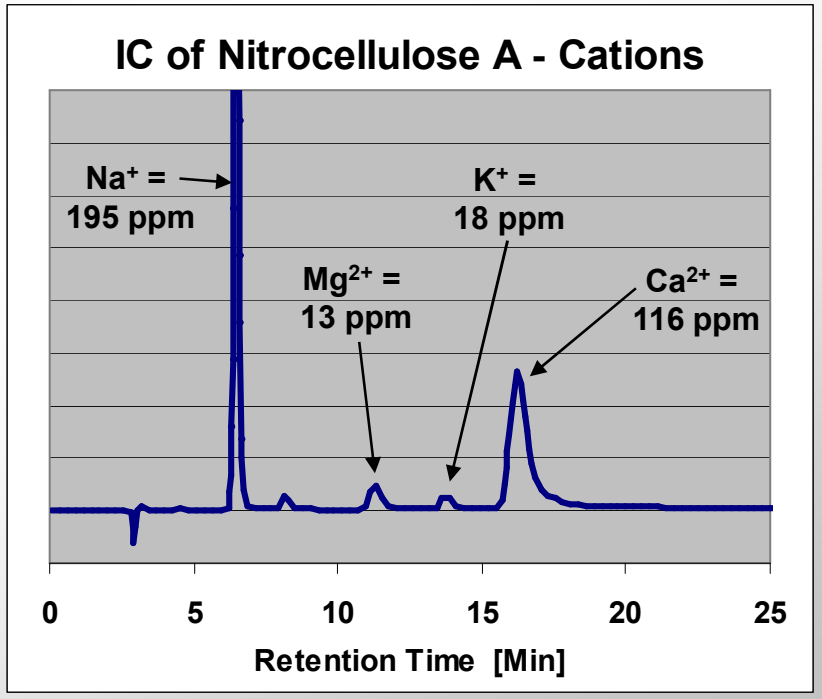
  

# Highlight 1: Ion Chromatography Method

- New method; procedure has been supplied by USA
- Can be used to assess numerous different ionic impurities
- Principle: Extraction of the ions from the NC with boiling water, followed by analysis with ion chromatography
- Recommended method in STANAG 4178 Ed. 2 !

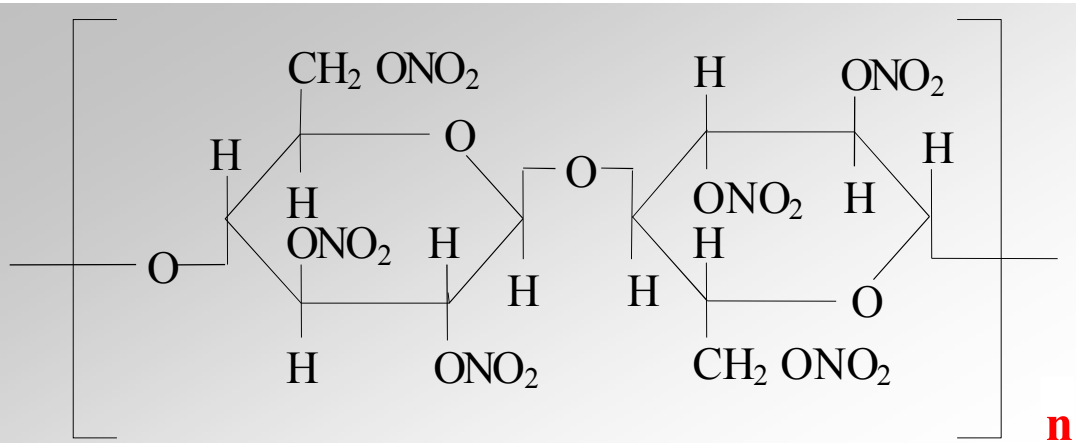
Chromatograms provided by SMP



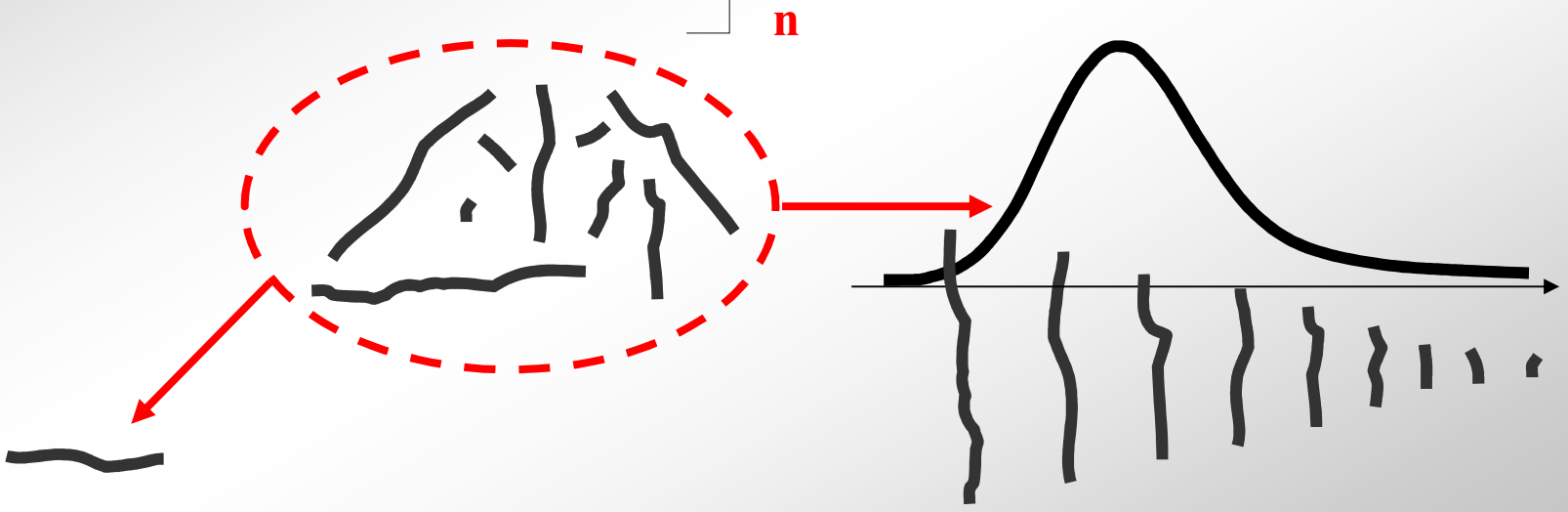
# Highlight 2: Gel Permeation Chromatography




**Degree of Polymerisation = Length of NC Polymer Chain**

**Typical Value: n = 500 – 1'400**

**(= Molecular Mass of 300'000 – 800'000 Daltons; may be lower or higher for specific NC qualities)**




- **Viscosity → Average Degree of Polymerisation**
- **GPC → Distribution of Degree of Polymerisation / Molecular Mass**

# Highlight 3: New Methods for Fibre Length Determination

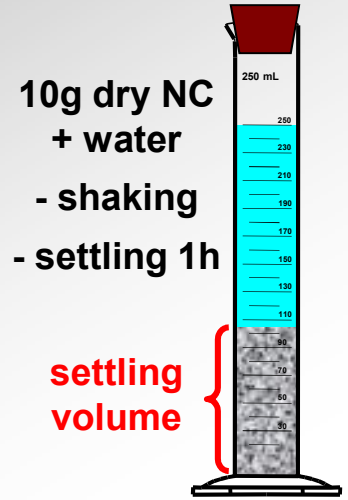
**The Fibre Length of NC is a process relevant property as it reveals the amount of cutting / grinding / refining the NC had undergone during manufacture**

## Indirect Methods

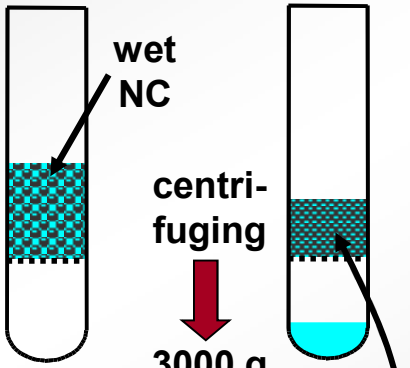
- Fineness
- Water Retention Value WRV
- Drainability

## Direct Method

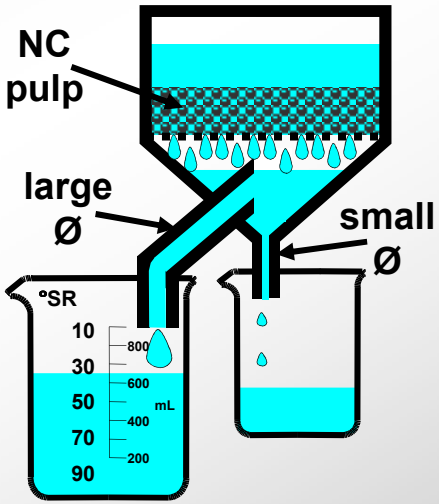
- Fibre Length / Shape Analyzer



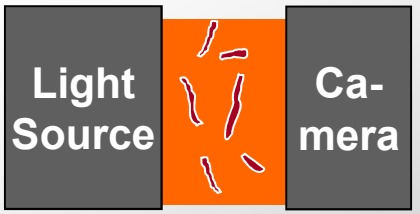

→ NC settling volume

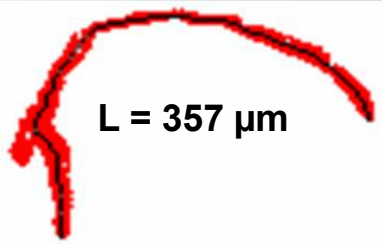



→ Water retention value = water content of centrifuged NC




→ Drainability = rate of dewatering of pulp

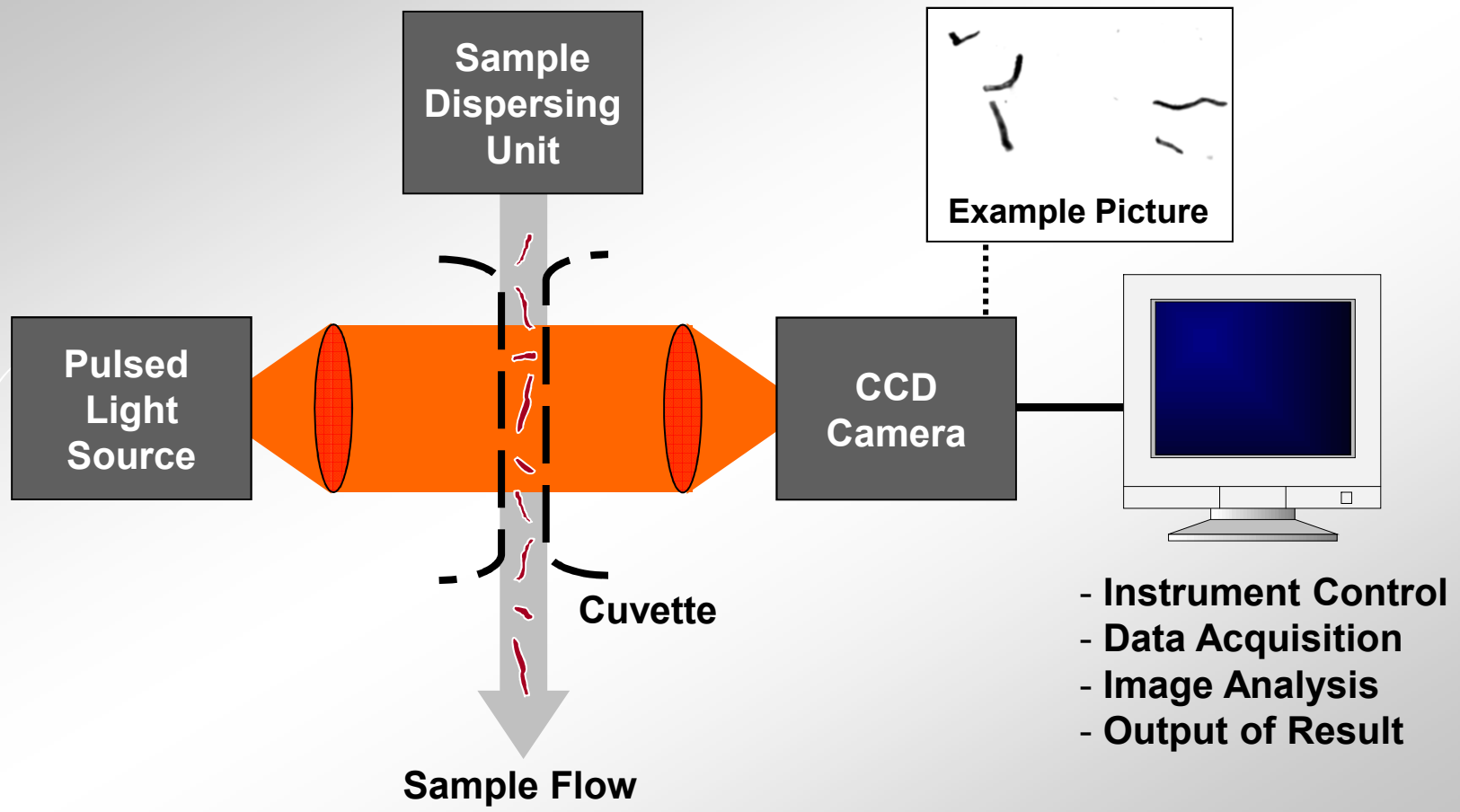



→ NC average fibre length and distribution

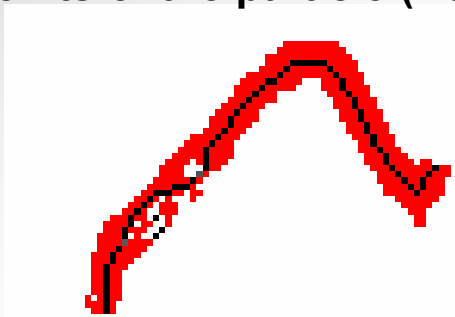
# Highlight 3: Fibre Quality Analyzer – Principle of Operation

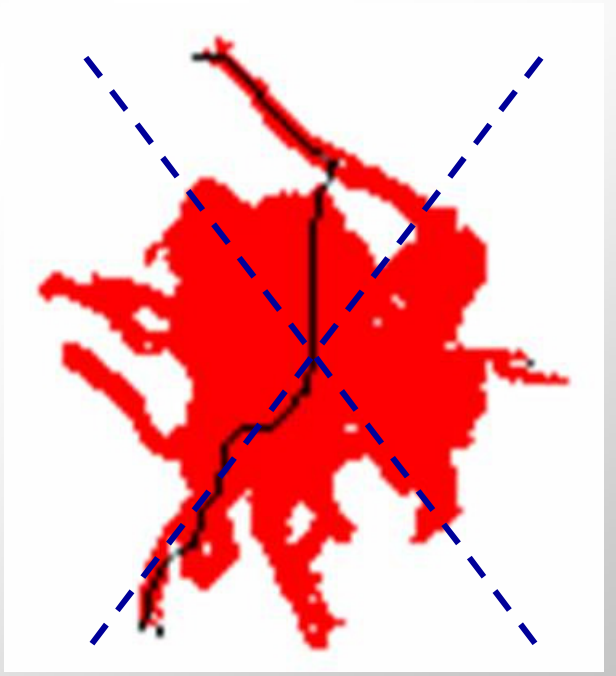


# Highlight 3: Fibre Quality Analyzer – Image Analysis

**Image analysis using the "Skeletonising Method": Fibre length is determined as longest direct way between two endpoints of the particle (fibre)**



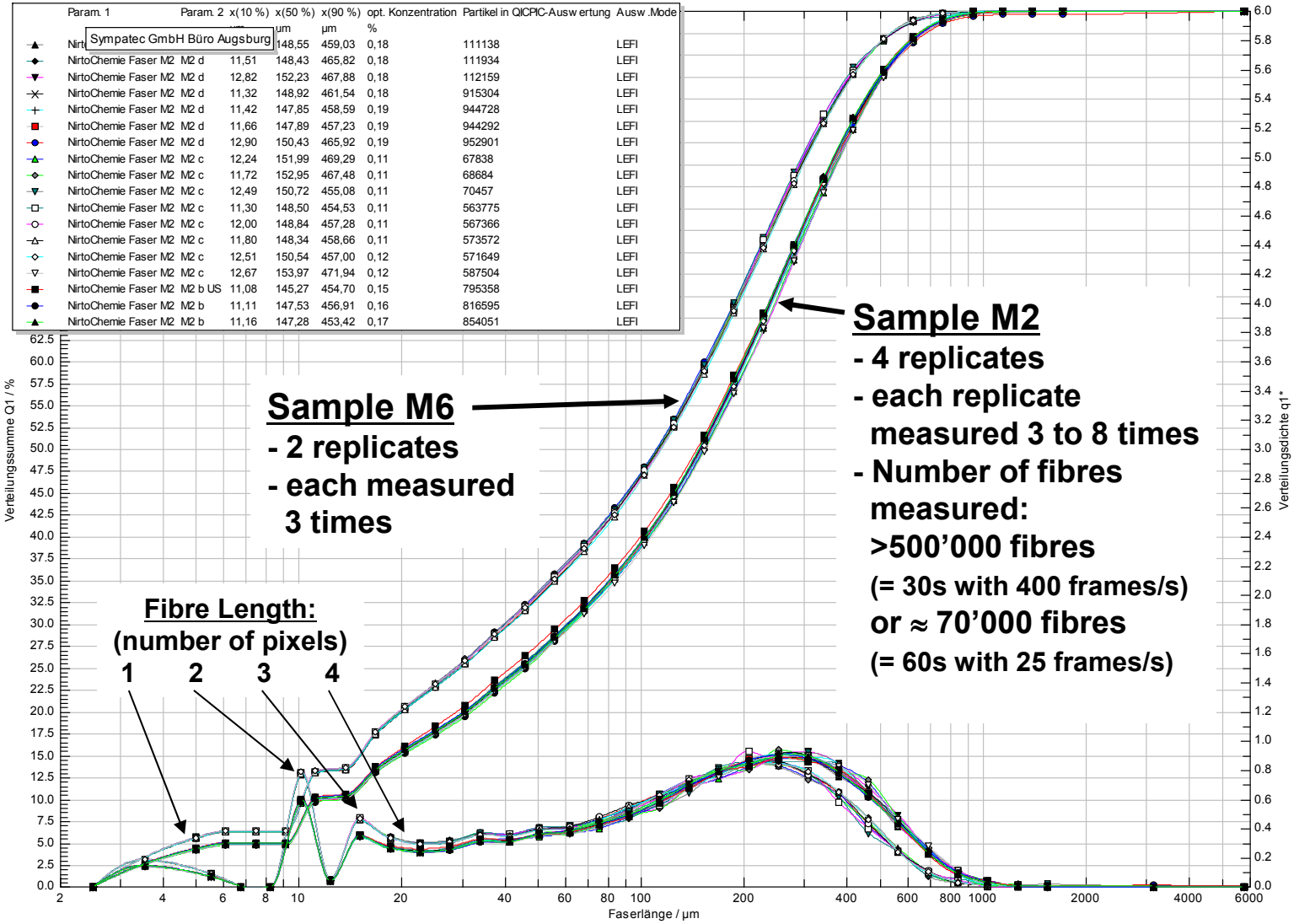


**Agglomerates can be eliminated from analysis**

# Highlight 3: Fibre Quality Analyzer – Repeatability

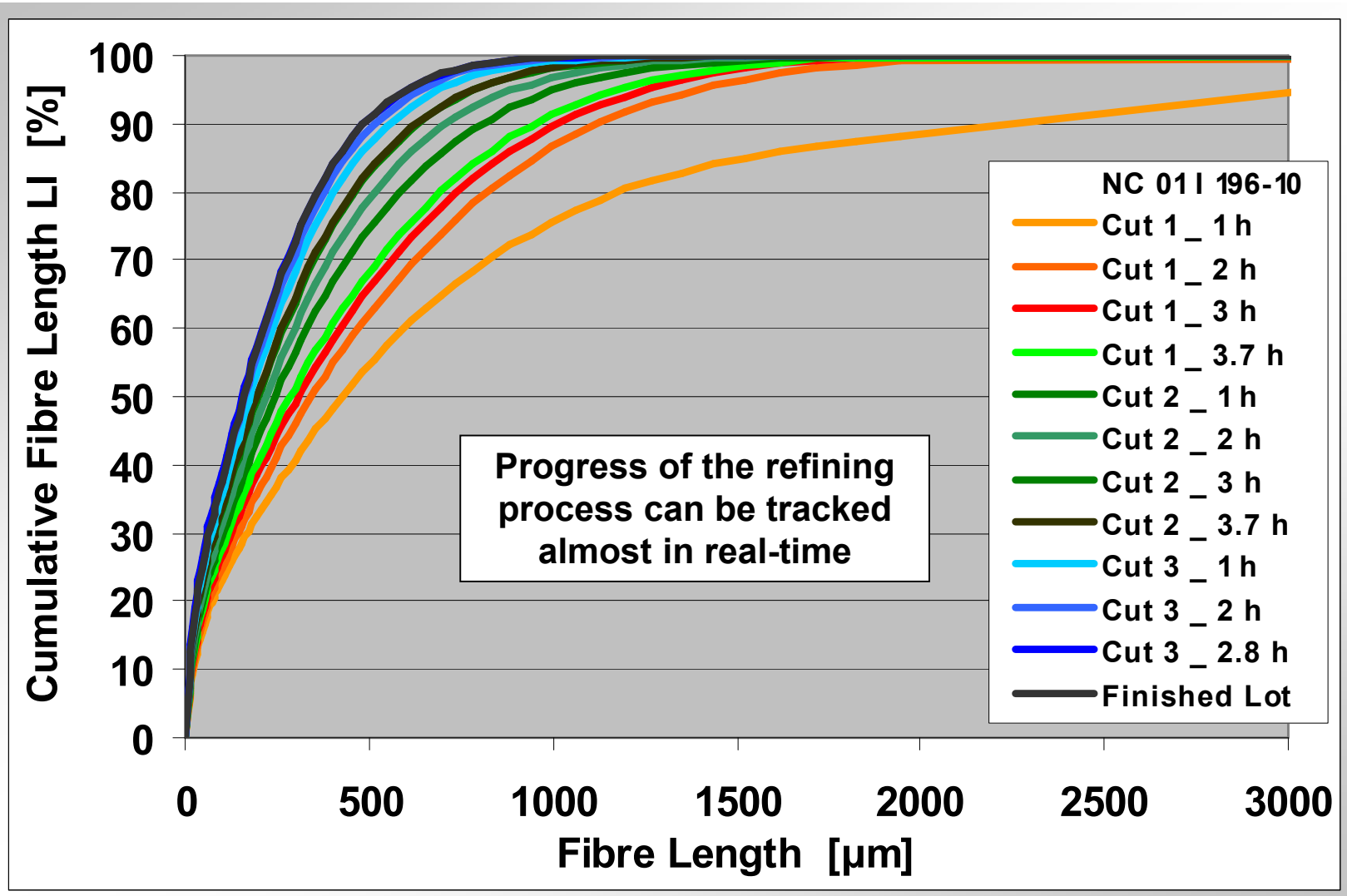
| Param. 1 | Param. 2 | x(10 %) | x(50 %) | x(90 %) | opt. Konzentration | Partikel in QICPIC-Auswertung | Ausw.Mode |
|---|---|---|---|---|---|---|---|
| | | µm | µm | µm | % | | |
| Nirt | Sympatec GmbH Büro Augsburg | | 148,55 | 459,03 | 0,18 | 111138 | LEFI |
| NirtoChemie Faser M2 | M2 d | 11,51 | 148,43 | 465,82 | 0,18 | 111934 | LEFI |
| NirtoChemie Faser M2 | M2 d | 12,82 | 152,23 | 467,88 | 0,18 | 112159 | LEFI |
| NirtoChemie Faser M2 | M2 d | 11,32 | 148,92 | 461,54 | 0,18 | 915304 | LEFI |
| NirtoChemie Faser M2 | M2 d | 11,42 | 147,85 | 458,59 | 0,19 | 944728 | LEFI |
| NirtoChemie Faser M2 | M2 d | 11,66 | 147,89 | 457,23 | 0,19 | 944292 | LEFI |
| NirtoChemie Faser M2 | M2 d | 12,90 | 150,43 | 465,92 | 0,19 | 952901 | LEFI |
| NirtoChemie Faser M2 | M2 c | 12,24 | 151,99 | 469,29 | 0,11 | 67838 | LEFI |
| NirtoChemie Faser M2 | M2 c | 11,72 | 152,95 | 467,48 | 0,11 | 68684 | LEFI |
| NirtoChemie Faser M2 | M2 c | 12,49 | 150,72 | 455,08 | 0,11 | 70457 | LEFI |
| NirtoChemie Faser M2 | M2 c | 11,30 | 148,50 | 454,53 | 0,11 | 563775 | LEFI |
| NirtoChemie Faser M2 | M2 c | 12,00 | 148,84 | 457,28 | 0,11 | 567366 | LEFI |
| NirtoChemie Faser M2 | M2 c | 11,80 | 148,34 | 458,66 | 0,11 | 573572 | LEFI |
| NirtoChemie Faser M2 | M2 c | 12,51 | 150,54 | 457,00 | 0,12 | 571649 | LEFI |
| NirtoChemie Faser M2 | M2 c | 12,67 | 153,97 | 471,94 | 0,12 | 587504 | LEFI |
| NirtoChemie Faser M2 | M2 b US | 11,08 | 145,27 | 454,70 | 0,15 | 795358 | LEFI |
| NirtoChemie Faser M2 | M2 b | 11,11 | 147,53 | 456,91 | 0,16 | 816595 | LEFI |
| NirtoChemie Faser M2 | M2 b | 11,16 | 147,28 | 453,42 | 0,17 | 854051 | LEFI |




- **Excellent Repeatability (replicate analysis)**
- **Significant difference between two different NC samples found (as expected)**

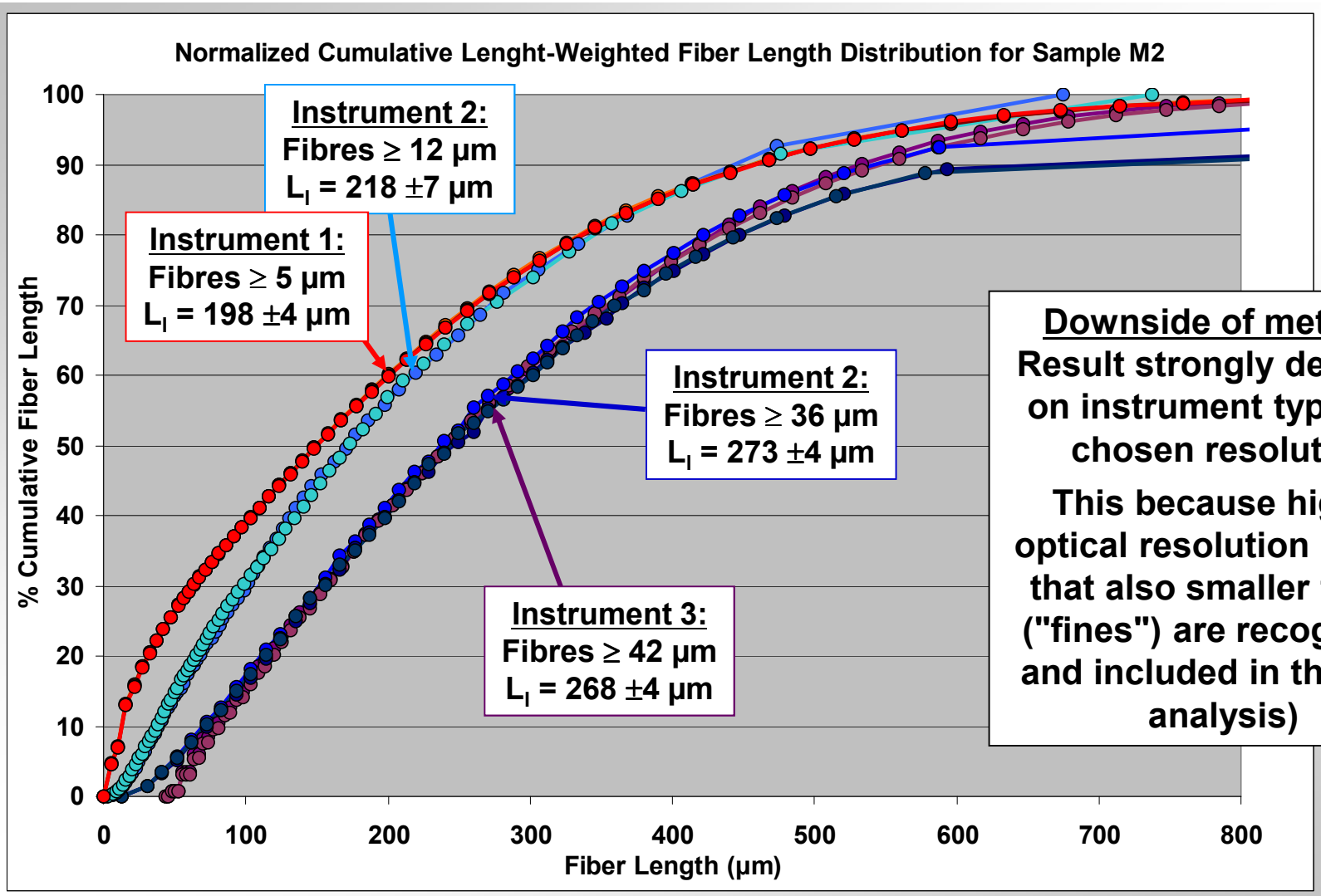

  

# Highlight 3: Fibre Quality Analyzer – Refining Process



# Highlight 3: Fibre Quality Analyzer – Different Instruments

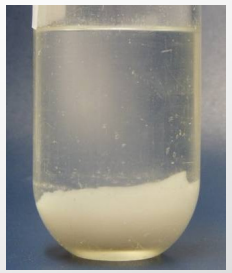


# Drawbacks / not yet solved Problems

- **General:**
  - Many NC tests are still "old-fashioned" wet-chemistry methods (time-consuming, difficult to automatise, yield little information)
  - No test for characterisation of NC processability available

- **Nitrogen Content of NC (Mean Value):**
  - Existing test methods are complex and error-prone



- **Distribution of Nitrogen Content of NC:**
  - No method for direct determination available
  - Is determined indirectly via solubility of NC in solvents

- **Polymeric Properties:**
  - GPC method is not (yet) reproducible enough for routine testing
  - Falling sphere viscosity method is not suitable for low-viscosity NC

- **Fibre Quality – Agglomerate Content:**
  - Actual method is not suitable for low agglomerate contents

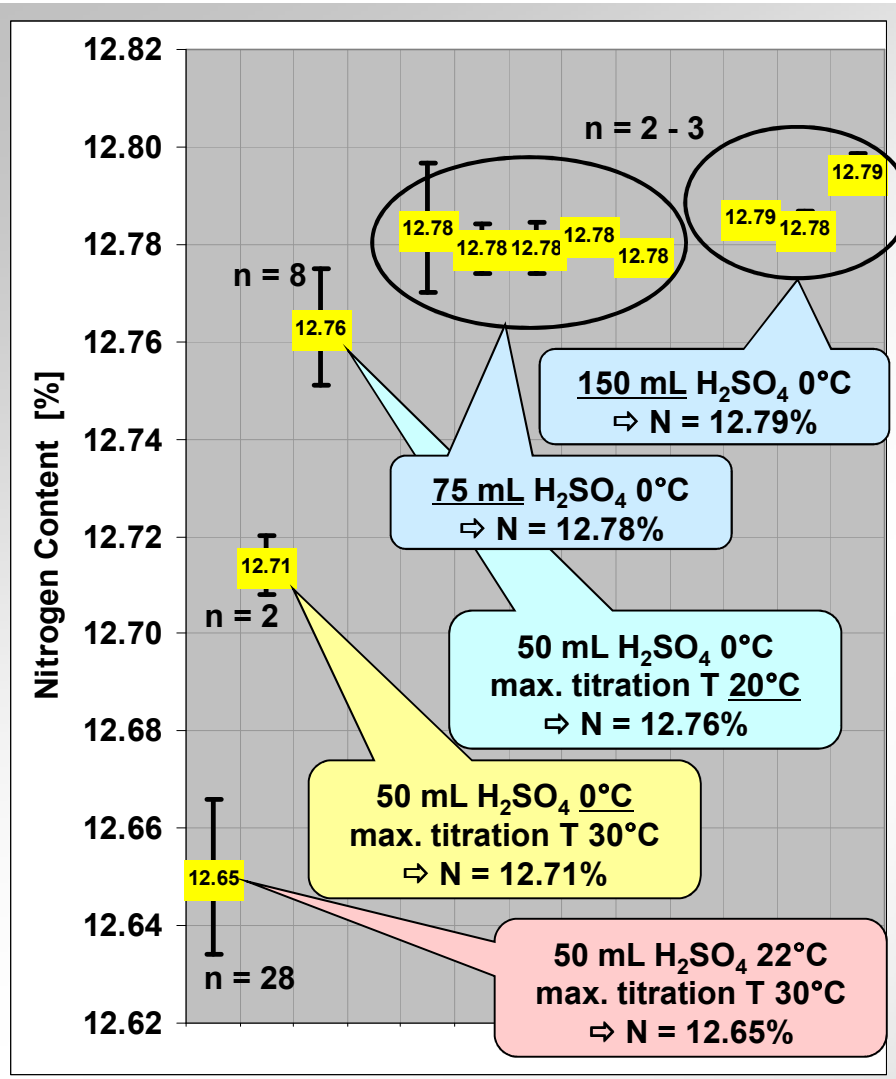
# Drawback 1: Assessment of Average Nitrogen Content of NC

- All existing test methods for average N-content are complex + error-prone
- Ferrous Ion Titration (FS/FAS) is reference method, but:
  - Many labs have reported problems with this method
  - Performance / results of FS/FAS depend strongly on several experimental parameters → method is not robust
  - Not tolerable (and difficult to recognise) systematic deviations may appear together with excellent precision
  - Exactly following the operating procedure as described in the standards (MIL/ STANAG) does not guarantee correct results !

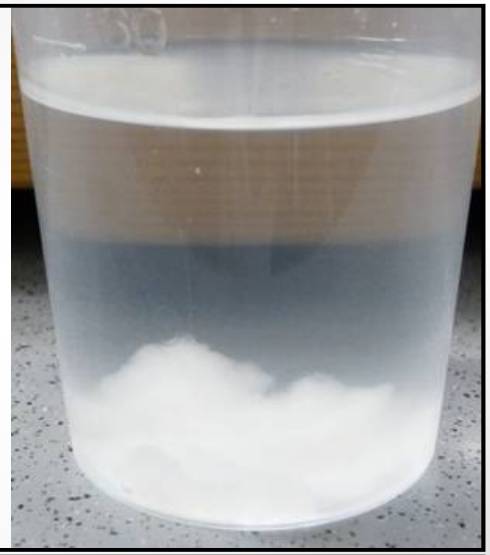
- For example, STANAG 4178 Ed.2 / MIL-DTL-244B/ECP:
  - Allows to use from 50 mL to 125 mL of sulphuric acid
  - Does not specify the temperature of the acid (as long as below 25°C)
  - Specifies titrant temperature to not exceed 25°C for >30 s and to not exceed 35°C for >10 s and to not exceed 40°C at all
  - However, changes within this range already markedly alter the result !!!

# Drawback 1: Average Nitrogen Content of NC – FAS Method




Adding cold sulphuric acid to NC
→ no bubbles
→ no "loss of nitrogen"

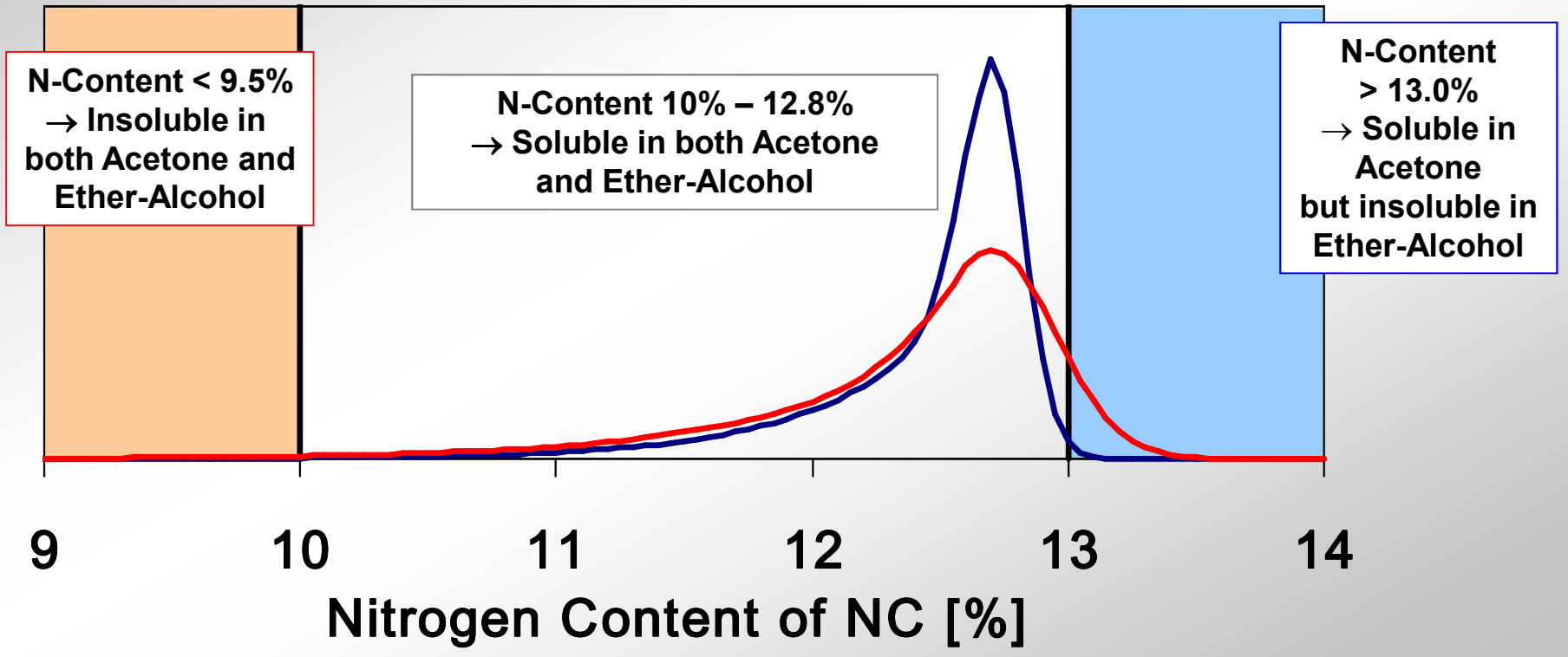


These effects seen for NC (bubbles → strong sensitivity on $H_2SO_4$ volume and T as well as on titration T) are almost negligible for $KNO_3$ calibration standard !!!

Adding 22°C warm sulphuric acid to NC
→ micro-bubbles of NO → "loss of nitrogen"

# Drawback 2: No Method for Distribution of Nitrogen Content

- No standardised method for direct determination of the distribution of nitrogen content of NC (→ quality of nitration) is available
- Solubility of the NC in Ether-Alcohol and Acetone gives only crude indication regarding N-content distribution but is the only available method



# Summary

- The new standards STANAG 4178 Ed. 2 and MIL-DTL-244B/ECP / MIL-DTL- 244C provide for the first time in history an internationally accepted set of NC testing methods
- STANAG 4178 Ed. 2 is currently in NATO ratification (11 nations including US, UK and France have already ratified; a total of 14 is needed)
- MIL-DTL-244B/ECP is currently used in US ARMY, NAVY and Air Force; MIL-DTL-244C will be implemented by US when ARDEC Standardization Group complete the review
- The new test methods are already implemented in many nations
- An international Round Robin Test will be organised to support further implementation of the new methods
- Test methods in these standards are neither perfect nor complete; further work is necessary to improve the actual methods as well as to develop new / better tests

# Outlook

- Ratification / approval / implementation of STANAG 4178 Ed. 2 / MIL-DTL-244C needs to be completed
- Tests which are new in these standards or known to produce problems should be carefully examined and, if necessary, further improved (e.g. Nitrogen Content, Ion Chromatography, Gel Permeation Chromatography* and Fibre Length Distribution)
- New / improved test methods should be developed and included:
  - Test methods that better characterise the Processability of NC
  - Better test methods for Nitrogen Content Distribution* to replace Ether-Alcohol / Acetone Solubility (e.g. chromatographic method)
  - New method suitable for low Agglomerate* contents
  - Modern spectroscopic methods such as IR / Near IR* / Raman Spectroscopy with multivariate analysis to predict important properties such as moisture content, nitrogen content, solubility, viscosity, etc.

*** Presentations on these issues will be given in the 5th NC Symposium**

# Thanks very much for your attention !

RHEINMETALL NITROCHEMIE

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