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

MIL-N-244A (1962)

MIL-DTL-244B (1996)

UK M22 / M23 / M39 (1987/89/88)

Other Standards

STANAG 4178 Ed. 1 (1991)

2007 – 2009

NATO/PfP AC/326 SG/1 CNG + US Industrial Product Team (IPT) + international NC Experts

55 Persons /// 36 MoD/DoD Agencies, Institutes, Companies /// 17 Nations

3 Joint Meetings + many Sub-Team Meetings

MIL-DTL-244B/ECP (2012)

MIL-DTL-244C (2014 ?)

(Mostly) identical Test-Procedures

STANAG 4178 Ed. 2 (2009)

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Differences between STANAG 4178 and MIL-DTL-244

Standard	STANAG 4178 Ed. 2	MIL-DTL-244 B/ECP
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 <u>compendium</u> of nitrocellulose <u>test procedures</u>
- MIL-DTL-244 is a <u>specification for nitrocellulose</u> that also contains test procedures (but only the ones that are needed for this specification)

*) This might change in the next edition (MIL-DTL-244 C): Cellulose requirements are in a separate specification that will be referenced; requirements on process will be dropped

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

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 Distribut. ***)
- Water Retention Value
- Drainability
- Agglomerates **)

Polymeric Properties

- Viscosity
- Mol. Mass Distribution ***)

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

Proposed changes in next edition of MIL-DTL-244

*) minor changes
**) to be replaced
***) to be removed

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STANAG 4178 Ed. 2 Ratification Status

- **STANAG 4178 Ed. 2 has been NATO approved and promulgated**
  - 16 nations including US, UK and France have ratified
  - promulgation requires ratification of 14 nations (50% of NATO nations)
  - most nations have implemented the new testing procedures

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MIL-DTL-244 B / C Status of Implementation

- **MIL-DTL-244 B with ECP # R10C3001 (2012)**
  - ECP = Engineering Change Proposal
  - Officially implemented (2012)
  - Currently used by the US ARMY, NAVY and Air Force
- **MIL-DTL-244 C (or D?) via ECP #Y13C2001 (2014)**
  - Document has been revised by ARDEC standardization group
  - Still under discussion; not yet implemented !

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

Several new test procedures will be added or existing procedures will be modified in MIL-DTL-244 C → these procedures then will differ from the ones in STANAG 4178 Ed. 2 !

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Proposed Major Changes in MIL-DTL-244 Revision

- **Requirements on Raw Material and Production Process**
  - Requirements for cellulose raw material will be transferred to other specification
  - Process requirements will be dropped (but: any significant change of NC production process necessitates a "product performance test" of the final product = charge / ammo)
- **Test Procedures and Specifications**
  - Will contain only test procedures with analytical requirements
    - that have been demonstrated and
    - for which a tolerance value can be specified and therefore
    - defect classification can be assigned (→ defect "Critical", "Major", "Minor")
  - The following tests will be removed since no specification can be established
    - Ionic Impurities: Both Ion Chromatography and Residual Acidity
    - Molecular Mass Distribution
    - Fiber Length Distribution

    } reference to STANAG; all 4 tests can be used if requested by customer
  - Agglomerates test (wet screening) will be replaced by Fiberization Quality (Elutriation method; Test 1 = Total Sinkers: Test 2 = Total Agglomerates)
  - Fineness method will be modified to be more specific
  - Nitrogen method by Ferrous Titration will be modified to account for weaknesses
  - A method for preparation and certification of Methyl Violet paper will be added

Some details are still under discussion → not yet finally decided !

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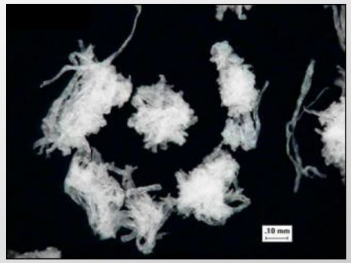
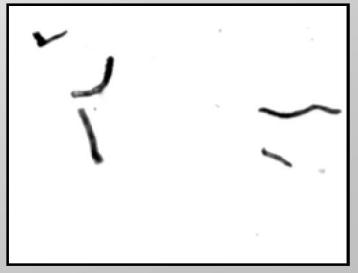
Supposed "Highlights" of the Actual Standards

- **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





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Errors / Problems in the Actual Standards – Overview (1)

- **Need to Update of STANAG 4178 Ed. 2:**
  - Date of last revision/edition: August 2009 (just before start of ratification)
  - Several errors / problems have been detected in the meantime
  - Improvements have been found (and already implemented in the labs !)
  - New / better test methods have been developed (and already introduced !)
  - **Several tests will differ from MIL tests after implementation of MIL-DTL-244 C !**
- **Length / Size / Type of Document:**
  - Document is too long for a STANAG (36 test procedures / 131 pages)
  - Changing of STANAGs is difficult (each change requires re-ratification)
  - Should be merged into a NATO document type than can be easily changed (e.g. AOP, AP)
- **Nitrogen Content of NC:**
  - Existing test methods are complex and error-prone
  - FAS/FS Titration is not robust → needs to be improved / corrected *)
  - NIR-Method developed; indirect but much faster / more robust → needs to be included in the standard

*) will be corrected in MIL-DTL-244 C

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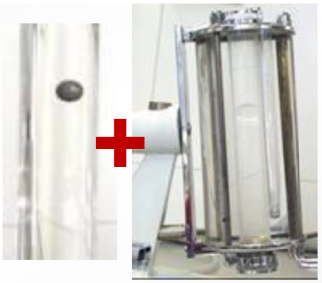
Errors / Problems in the Actual Standards – Overview (2)

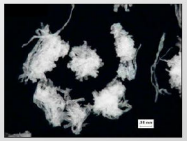
- **Polymeric Properties - Viscosity:**
  - Falling sphere viscosity method is not suitable for low-viscosity NC
  - Another viscosity test (e.g. Hoeppler) which is also suitable for low-viscosity NC required → needs to be added to the standard



- **Polymeric Properties – Molecular Mass Distribution:**
  - GPC method is not (yet) reproducible enough for routine testing (huge variation of results obtained by different labs)
  - Method thus only suitable for comparative testing → needs to be stated *)

- **Fibre Quality – Fineness:**
  - Error in actual test procedure causing wrong results → needs to be corrected *)

- **Fibre Quality – Agglomerate Content:**
  - Actual sieving method is not suitable for low agglomerate contents
  - New elutriation method is much more robust → needs to replace sieving method *)



- **Fibre Quality – Fibre Length / Shape Analyzer:**
  - Test result strongly depends on instrument type and chosen resolution
  - Method thus only suitable for comparative testing → needs to be stated *)

*) will be addressed in MIL-DTL-244 C

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Problem 1: Assessment of 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 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 !!!

Slightly improved method in MIL-DTL-244 C

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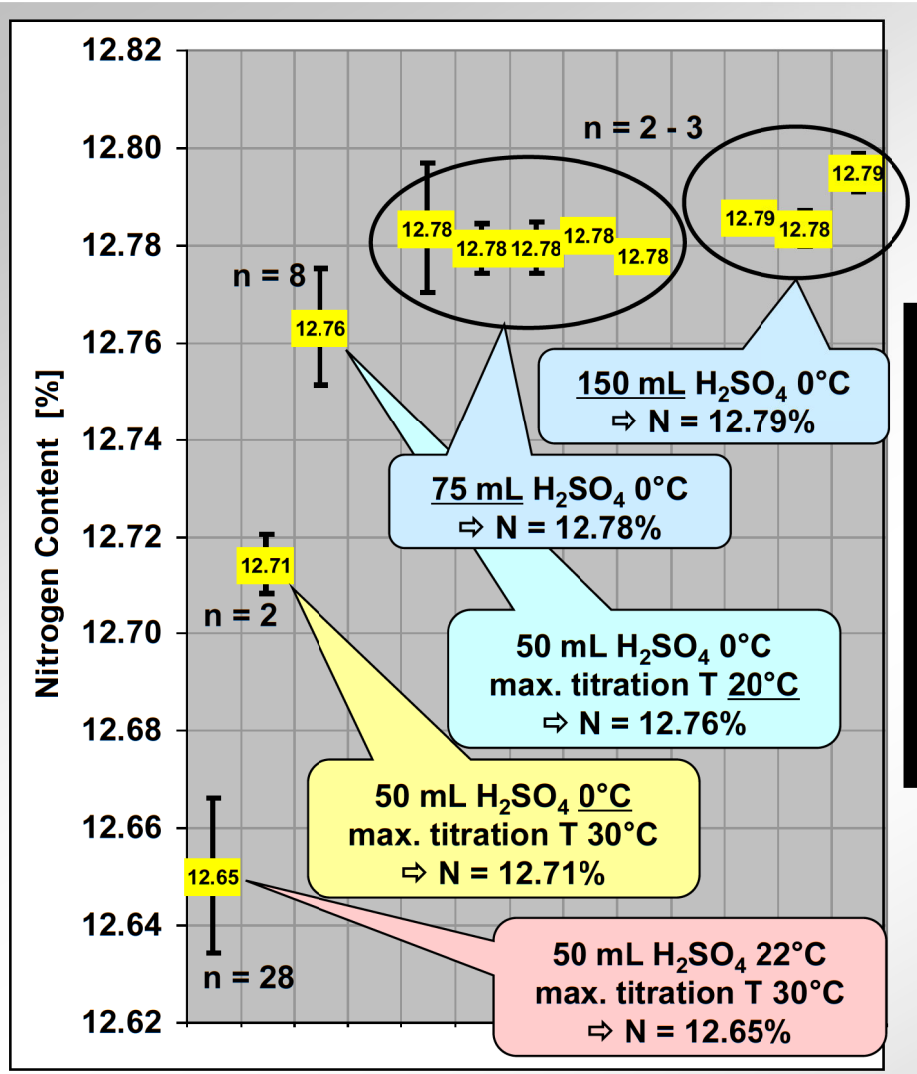
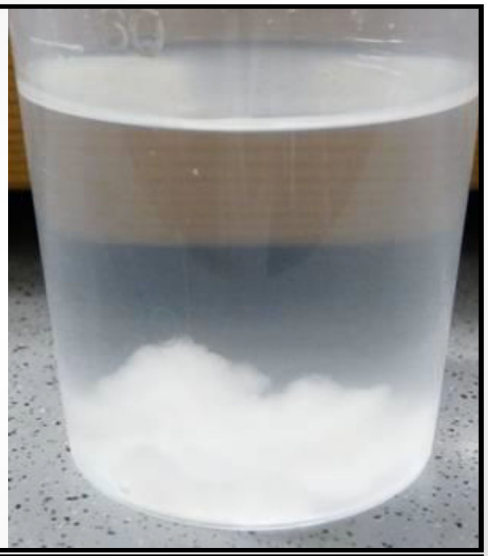
Problem 1: Nitrogen Content of NC – FAS Method



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"

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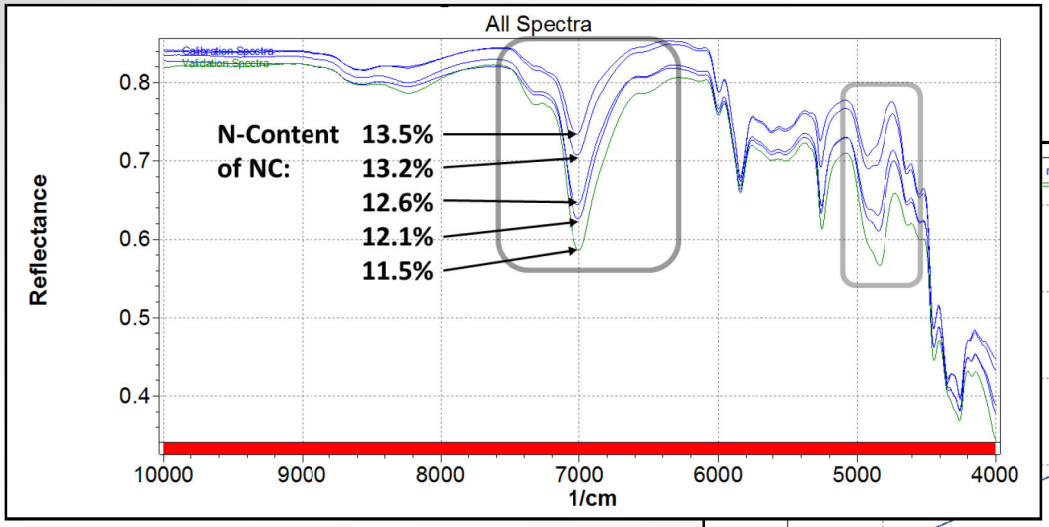
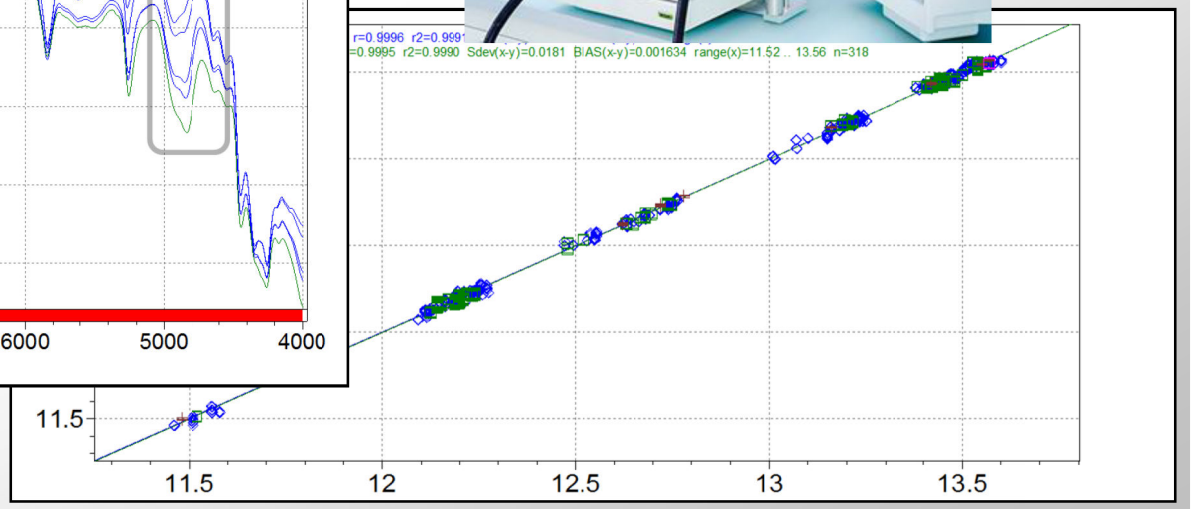
Problem 1: Alternative NIR-Method not yet in Standard

- **Near Infrared (NIR) Spectroscopy is excellent alternative method !**
  - **Disadvantages: Indirect method; cost of equipment; calibration time-consuming**
  - **Advantages: Very fast (5' per NC) and thus cheap method; good reproducibility; very robust method (large amount of sample; variation in NC water content has negligible influence if included in calibration; no systematic errors caused by agglomerates / insoluble fibres / etc.)**
  - **NIR method needs to be added to the standards**





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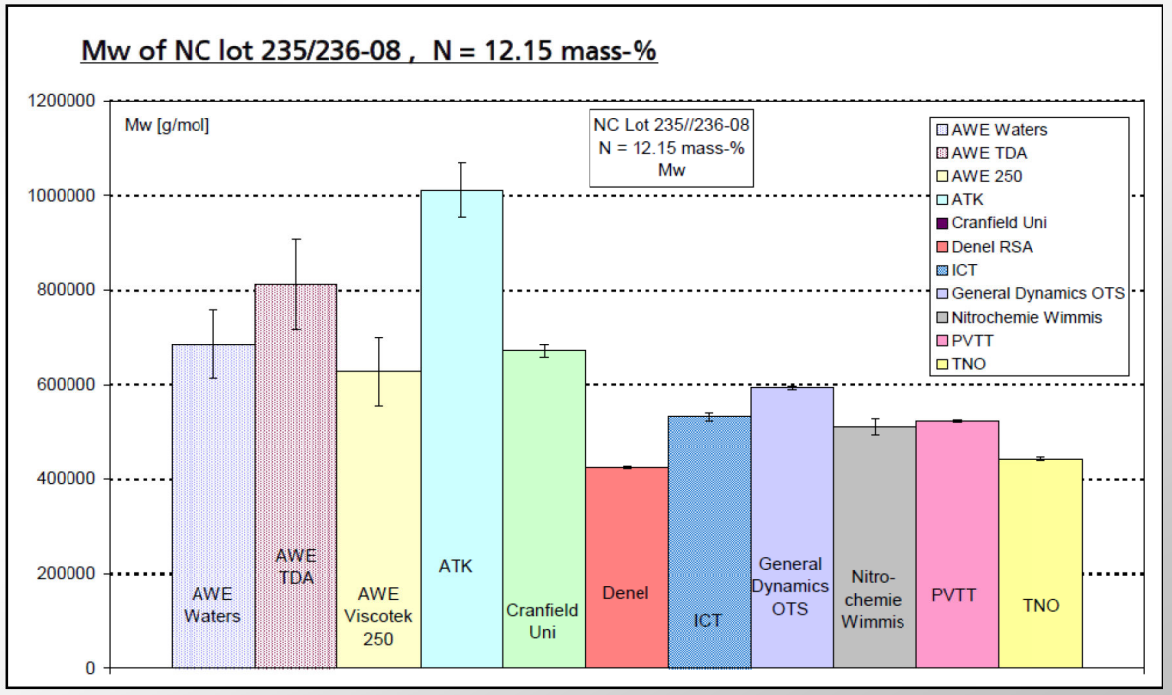
Problem 2: Molecular Mass Distribution – GPC Method

- Excellent method for comparative testing (comparing molecular mass of different NC samples; all measured in same campaign by same operator on same instrument)
- But: Huge differences (results differing by factor of 2 and more) between M_w-values of the same NC obtained from different labs; even under controlled RRT-conditions (all labs use same procedures, same GPC columns, same calibration standards, …)
  - Problem is inherent to NC as shown by the fact that little variability between labs is obtained for M_w of polystyrene reference sample!
  - GPC method is thus not suitable to be used for NC specification

Method not included in MIL-DTL-244 C



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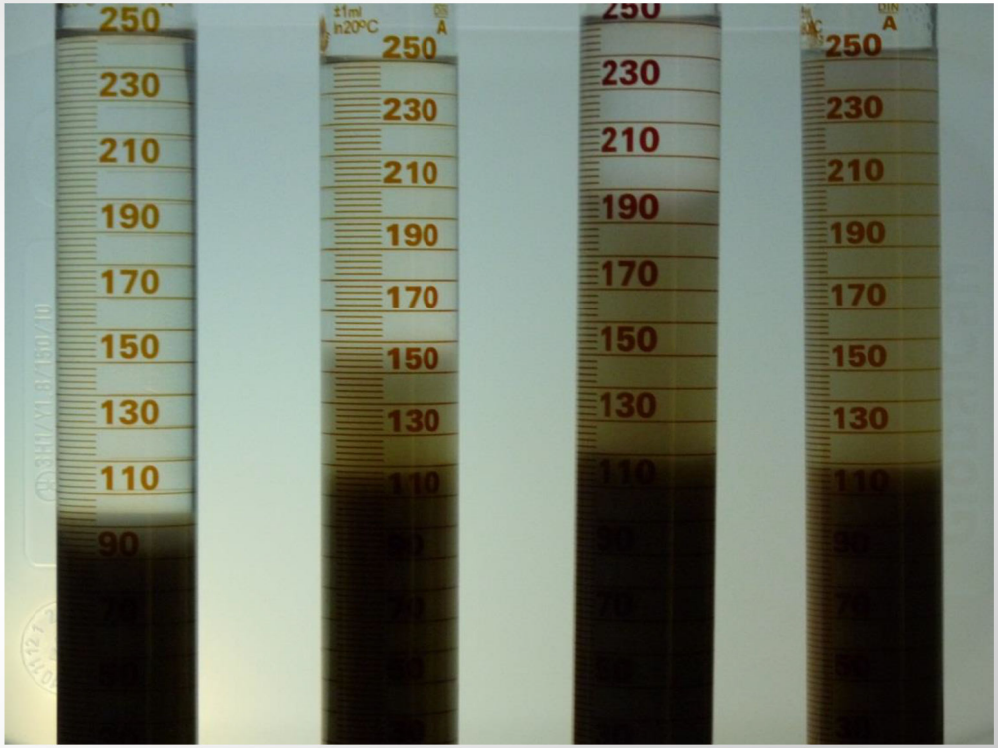
Problem 3: Error in Standards regarding Fineness-Test

- **Settling Volume:**
  - **MIL-DTL-244B: NC slurry preparation in beaker, transfer to measuring cylinder + filling up to 200 mL before shaking / topping off to 250 mL → always correct results**
  - **MIL-DTL-244C / STANAG Ed. 2: NC slurry preparation directly in measuring cylinder; result depends on amount of water added before shaking → wrong result if amount << 200 mL**



Example: NC with Fineness = 120 mL if measured according to MIL-DTL-244B

Amount of Water added before shaking:	100 mL	150 mL	200 mL	250 mL
Amount of Water added after shaking:	150 mL	100 mL	50 mL	----
Obtained NC Settling Volume / Fineness:	102 mL !!!	118 mL	120 mL ✓	120 mL ✓

Corrected in MIL-DTL-244 C

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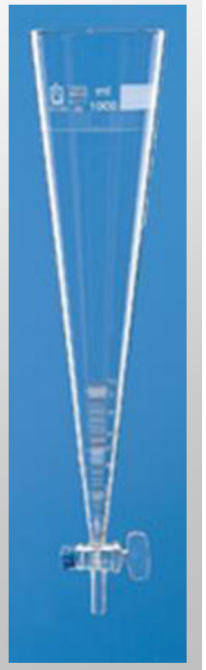
Problem 4: Agglomerate Content – Sieving Method

- Actual method based on sieving under a stream of water works well for most NG types but may yield erroneous results for certain NC grades
  - Not suitable for NC with low agglomerate contents (agglomerate content is below limit of detection of method)
  - Not suitable in cases when NC forms "slimy" pouches which incorporate the fibres → unless washing time is increased from approx. 7 min to well above 1 hour, agglomerate contents which are too high (by up to factor 20) may be obtained

- A new agglomerates test based on elutriation in a water flow through a cone has been developed
  - New method is much more robust
  - New method is also suitable to assess low agglomerate contents
  - New method should be added or better replace the sieving method in standards



New method implemented in MIL-DTL-244 C

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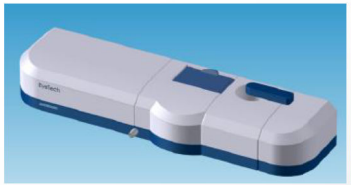
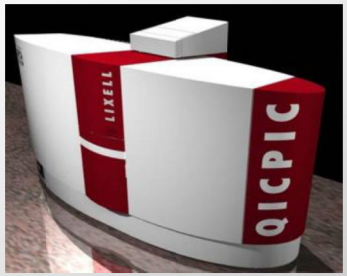
Problem 5: Fibre Quality Analyzer

- Since the Fibre Quality Analyzer section in STANAG 4178 Ed. 2 was written, knowledge regarding the application of this method has strongly increased
- From todays point of view, the following corrections should be made
  - The list of recommended instruments to perform this test is obsolete
  - The numerical result of this test (fibre length distribution / average fibre length) strongly depends on instrument type and parameter setting – therefore this method is only suitable for comparative testing – this needs to be noted
  - The entire test procedure should be rewritten as the current method is based on a poorly automated instrument which is no longer on the market; in particular the described manual data analysis is no longer necessary since all instruments currently on the market are capable of automated data analysis

Method not included in MIL-DTL-244 C





Instrument no longer available

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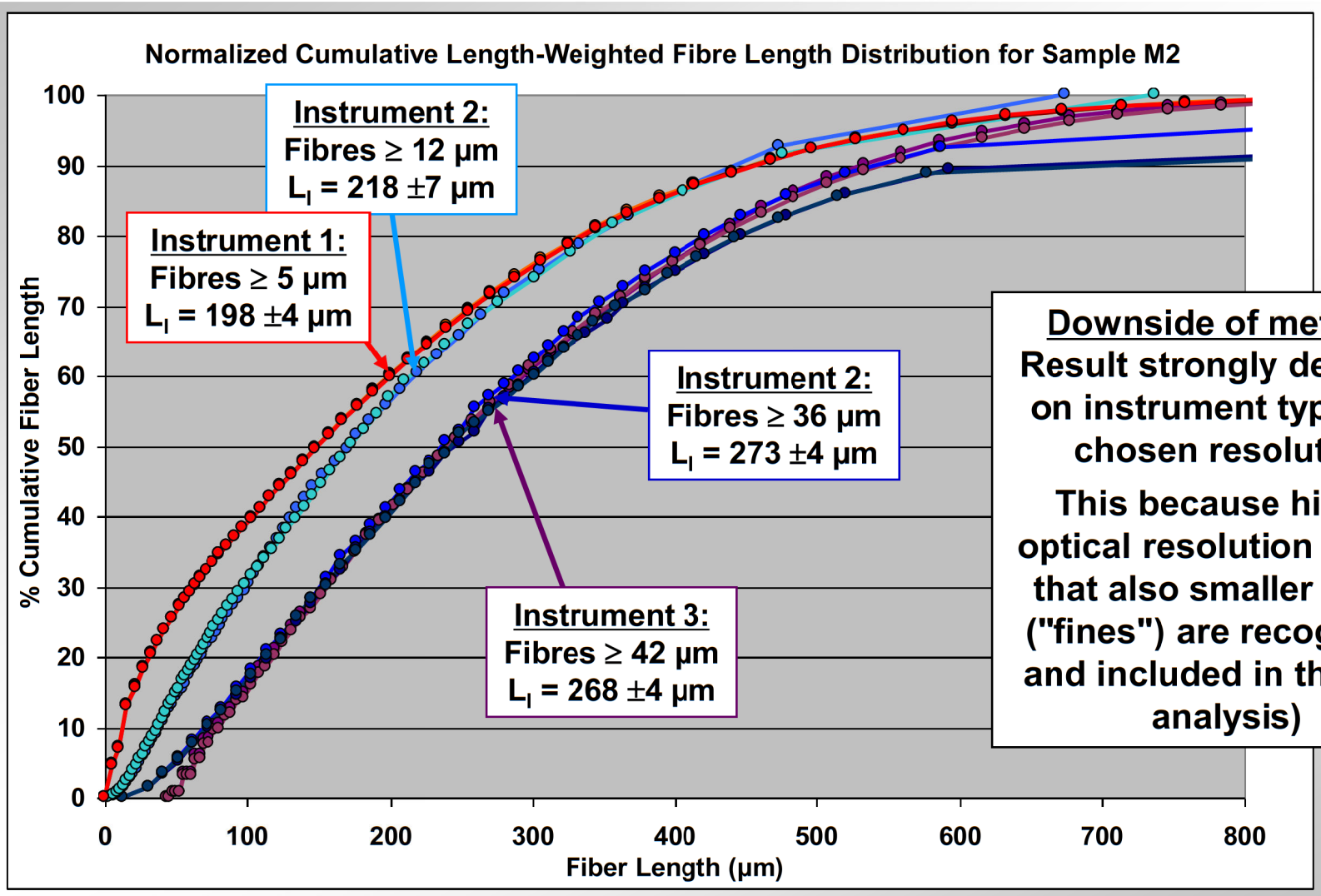
Problem 5: Fibre Quality Analyzer – Influence of Instrument



Downside of method:
Result strongly depends on instrument type and chosen resolution

This because higher optical resolution means that also smaller fibres ("fines") are recognised and included in the data analysis)

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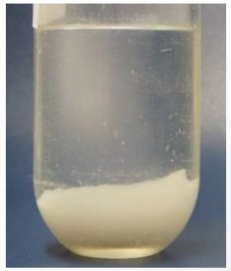
Further Potential for Improvements

- **More Modern Test methods:**
  - Many NC tests are still "old-fashioned" wet-chemistry methods (time-consuming, difficult to automatize, yield little information)

- **Distribution of Nitrogen Content of NC:**
  - Distribution of Nitrogen Content is determined indirectly (by Ether-Alcohol / Acetone Solubility)
  - No standardized method for direct determination is currently available
  - ATK has developed / patented HPLC Method which provides some insight into distribution of N-Content



- **Test for NC Processability:**
  - "Processability" of the NC (ability to make "good" propellants / explosives) is one of the most important properties of the NC
  - Actually, final product (propellant) needs to be produced and tested
  - No easy / cheap test for characterisation of NC processability is currently available

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Round Robin Test (RRT) on Nitrocellulose Analysis

- **Background / History:**
  - Idea for Round Robin Test (RRT) on Nitrocellulose Analysis arose 2011
  - Goal: Assist implementation of new standards (STANAG 4178 Ed.2 / MIL-DTL-244B/ECP)
  - Initially under mandate of NATO/PfP AC/326 SG1 CNG and US DoD, ARDEC
  - Proposed procedure: 6 NC samples to be supplied; testing for N-Content, EA-Solubility, Acetone Insol., 134.5°C Heat Test, 132°C Stability Test, Fineness, Viscosity

  Preliminary testing of RRT samples performed by 3 labs (2013; GD-OTS + Manuco + NCW)

- **Actual Status: Work on RRT has been stopped**; main reasons are:
  - RRT is no longer supported by NATO AC/326 SG/A !
  - Test procedures are no longer clearly defined (differences between STANAG 4178 Ed.2 and MIL-DTL-244C; FS/FAS method for N-content not yet robust enough)
  - High workload for the organisers (actually: GD-OTS Valleyfield + Nitrochemie)

- **Future of RRT:** What needs to be done to re-start RRT:
  - RRT needs clear support / patronage from NATO AC/326 SG/A + U.S. DoD, PM-CAS!
  - Test procedures need to be defined (→ MIL-DTL-244C / STANAG 4178 Ed.3)
  - Work-share and possibly funding need to be discussed / agreed on
    (GD-OTS Valleyfield + Nitrochemie Wimmis are still prepared to contribute to this effort)

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Summary and Outlook

- STANAG 4178 Ed. 2 and MIL-DTL-244 B/ECP, which have been revised / established 2007 – 2010, provided an internationally accepted set of NC testing methods
  - But: Several errors / problems have been detected in these test methods
  - Improvements have been found (and already implemented in the labs !)
  - New / better test methods have been developed (and already introduced !)
- In the meantime, MIL-DTL-244 has been further revised – thereby errors in existing tests have been corrected and new test methods have been included
  - Several test are no longer identical in MIL-DTL-244 C and STANAG 4178 Ed. 2
  - STANAG 4178 Ed. 2 also needs to be revised in the next few years (→ Ed. 3); tests need to be harmonized with MIL-DTL-244 C; new / superior test methods need to be added (start of revision is planned for 2015)
- A lot of work is going on to improve NC test procedures, e.g.:
  - NIR spectroscopy for N-Content / E/A-Solubility and Viscosity testing
  - New methods to assess Fibre Quality, Microstructure/Crystallinity, Distribution of Nitrogen Content, …
- This effort will continue, and we can look forward to have even better NC test methods in the near future !

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Thanks very much for your attention !

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PROJECT MANAGER COMBAT AMMUNITION SYSTEMS
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