Status of NATO-Standard for Nitrocellulose Testing (STANAG/AOP 4178)

Beat Vogelsanger, Michael Ramin, Marc Müller, Patrick Folly

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Contents

- Introduction
- Basis of AOP-4178 Ed. 3
- Main Changes in AOP-4178 Ed. 3
- Summary and Way Ahead

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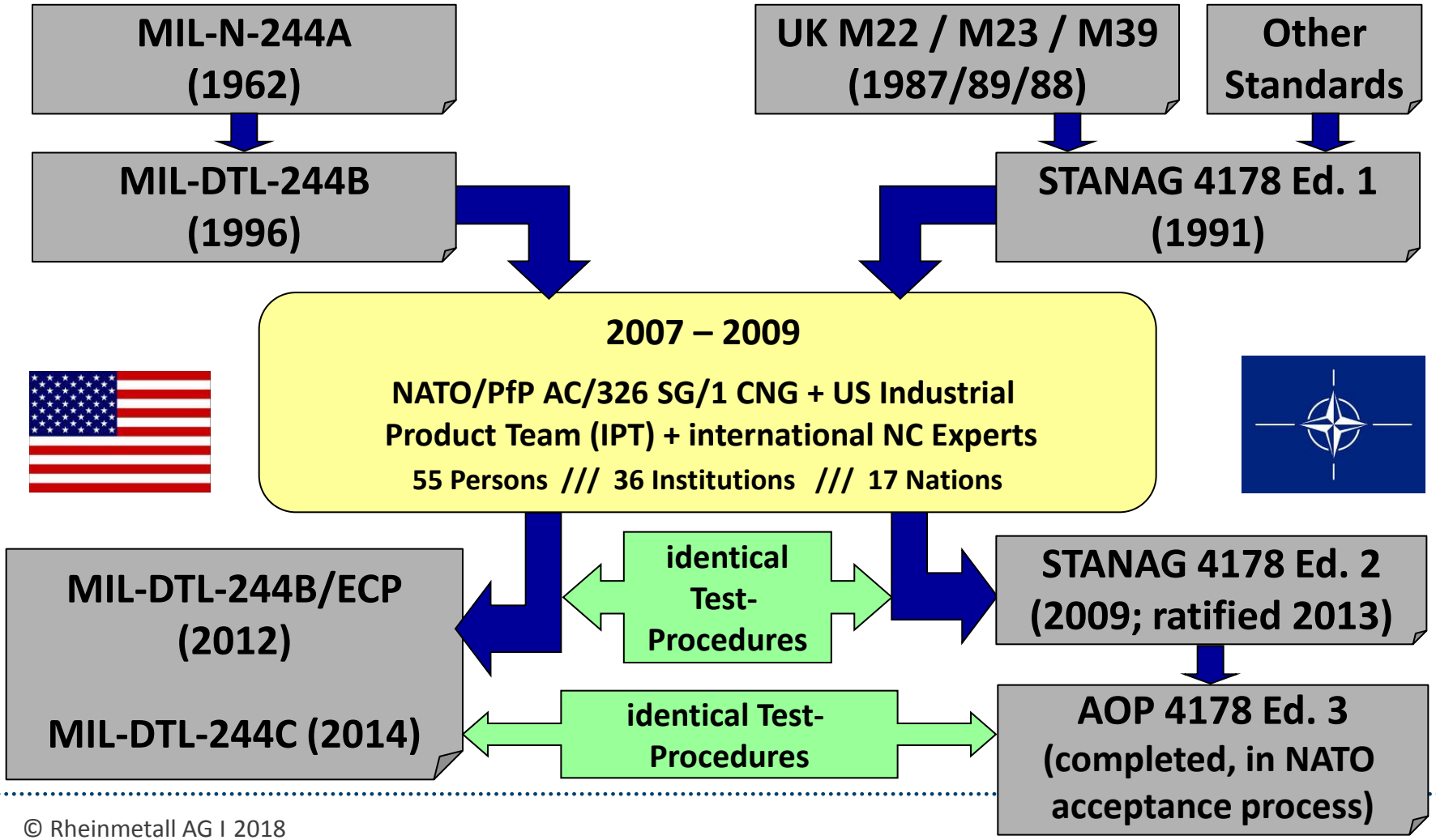
Introduction
Recent History of Standards for NC Testing



<u>Differences between STANAG/AOP-4178 and MIL-DTL-244</u>:

STANAG/AOP-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)

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Test Methods of STANAG/AOP-4178 Ed. 3 / MIL-DTL-244C

Basic Characterisation

- Nitrogen Content
  - Ferrous Ion Titration
  - NIR Spectroscopy
  - Nitrogen Analyzer Method
  - (Devarda's Alloy Method)
  - (Schulze-Tiemann Method)
  - (Nitrometer Method)
  - (Combustion Calorimetry)
- 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
- Ionic Impurities
  - Ion Chromatography
  - Sulphate Content
  - Residual Acidity
  - Alkalinity
  - Spectroscopy / AAS/ICP
- Oil and Grease Content
- Abel-Type Heat Tests
  - (76.6°C Abel Heat Test)

Polymeric Properties

- Viscosity
  - Falling Ball Viscometer
  - Alternative Method
- Mol. Mass Distribution

Fibre Quality

- Fineness
- Fibre Length Distribution
- (Water Retention Value)
- (Drainability)
- Fiberization Q. / Elutriation

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

Others

- Ignition T / Heat of Explosion

Test method contained in both documents

Test method only in AOP-4178 Ed. 3

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  - All differences between STANAG 4178 Ed. 2 and MIL-DTL-244C eliminated
  - The 16 joint test procedures are now identical
- **International Survey / Questionnaire** (2016)
  - Survey on STANAG 4178 methods (by armasuisse)
  - 12 participating laboratories
  - Findings / conclusions included in revision
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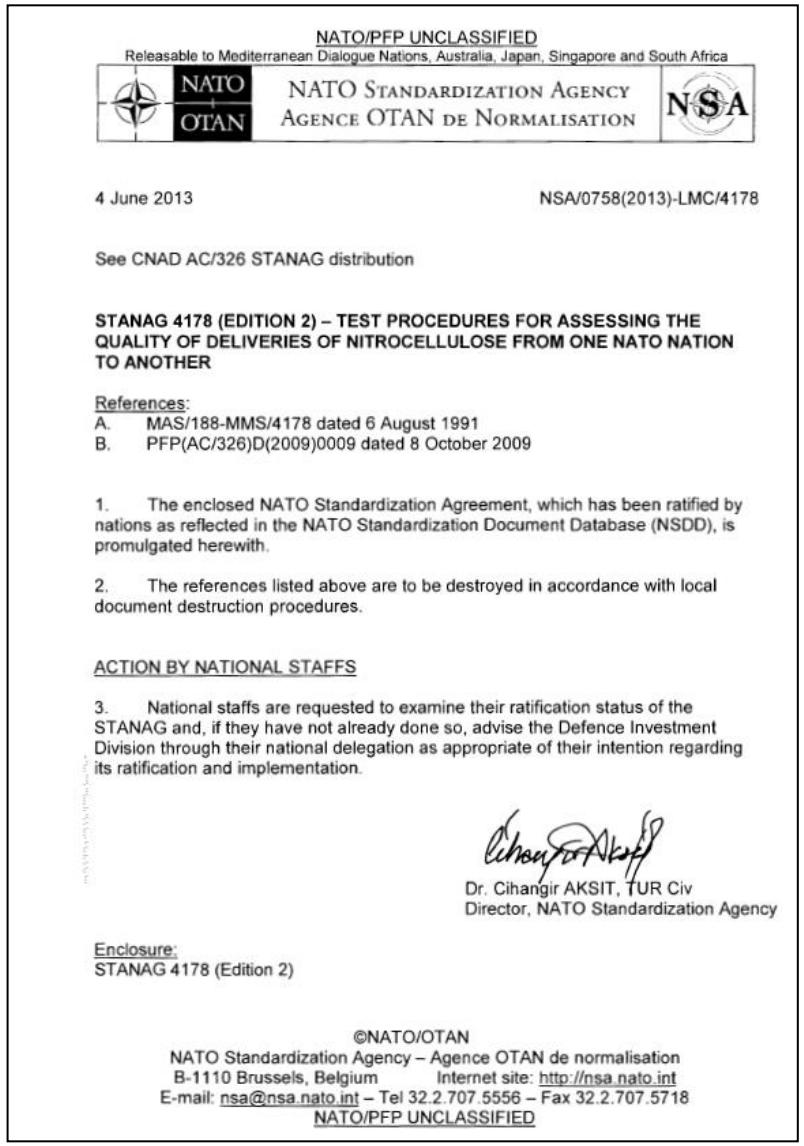

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Releasable to Mediterranean Dialogue Nations, Australia, Japan, Singapore and South Africa

NATO OTAN — NATO Standardization Agency / Agence OTAN de Normalisation — NSA

4 June 2013 NSA/0758(2013)-LMC/4178

See CNAD AC/326 STANAG distribution

STANAG 4178 (EDITION 2) – TEST PROCEDURES FOR ASSESSING THE QUALITY OF DELIVERIES OF NITROCELLULOSE FROM ONE NATO NATION TO ANOTHER

References:
A. MAS/188-MMS/4178 dated 6 August 1991
B. PFP(AC/326)D(2009)0009 dated 8 October 2009

1. The enclosed NATO Standardization Agreement, which has been ratified by nations as reflected in the NATO Standardization Document Database (NSDD), is promulgated herewith.

2. The references listed above are to be destroyed in accordance with local document destruction procedures.

ACTION BY NATIONAL STAFFS

3. National staffs are requested to examine their ratification status of the STANAG and, if they have not already done so, advise the Defence Investment Division through their national delegation as appropriate of their intention regarding its ratification and implementation.

Dr. Cihangir AKSIT, TUR Civ
Director, NATO Standardization Agency

Enclosure:
STANAG 4178 (Edition 2)

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NATO Standardization Agency – Agence OTAN de normalisation
B-1110 Brussels, Belgium Internet site: http://nsa.nato.int
E-mail: nsa@nsa.nato.int – Tel 32.2.707.5556 – Fax 32.2.707.5718
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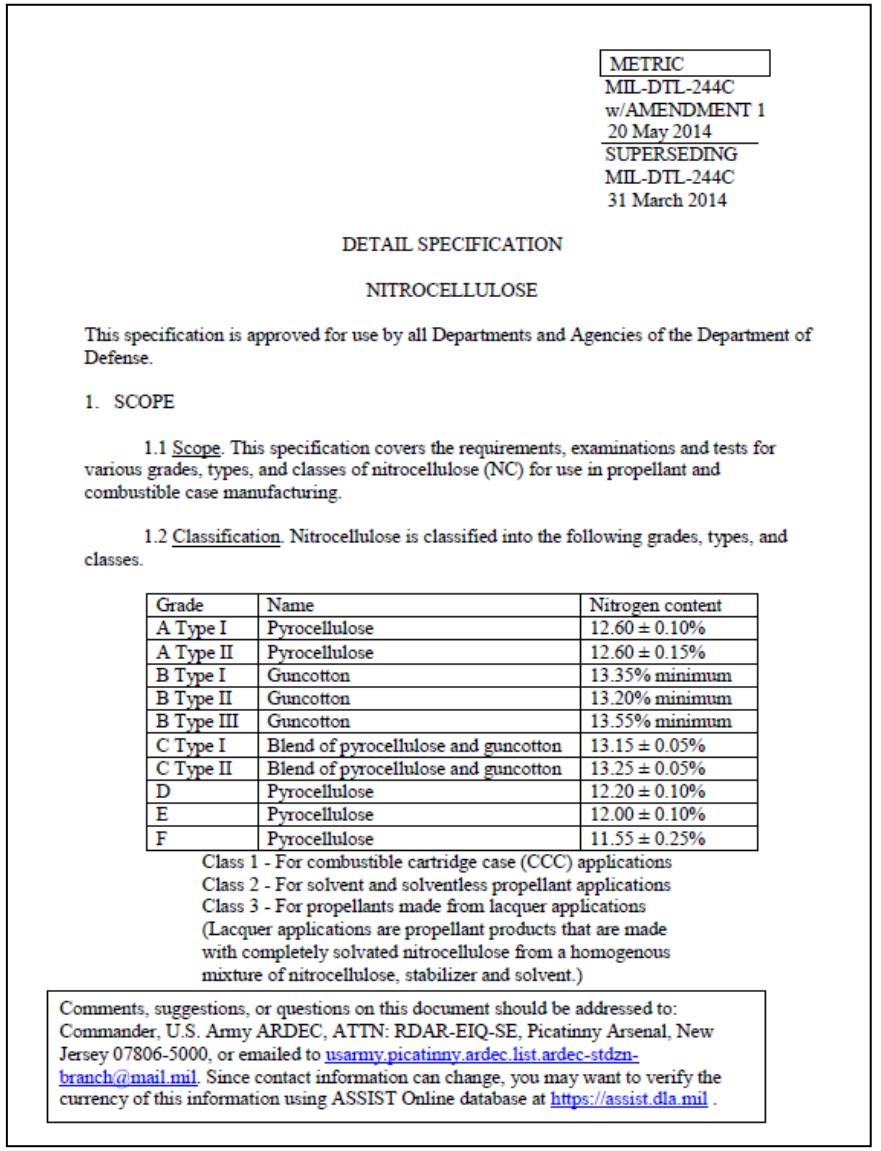

METRIC
MIL-DTL-244C
w/AMENDMENT 1
20 May 2014
SUPERSEDING
MIL-DTL-244C
31 March 2014

DETAIL SPECIFICATION

NITROCELLULOSE

This specification is approved for use by all Departments and Agencies of the Department of Defense.

1. SCOPE

1.1 Scope. This specification covers the requirements, examinations and tests for various grades, types, and classes of nitrocellulose (NC) for use in propellant and combustible case manufacturing.

1.2 Classification. Nitrocellulose is classified into the following grades, types, and classes.

Grade	Name	Nitrogen content
A Type I	Pyrocellulose	12.60 ± 0.10%
A Type II	Pyrocellulose	12.60 ± 0.15%
B Type I	Guncotton	13.35% minimum
B Type II	Guncotton	13.20% minimum
B Type III	Guncotton	13.55% minimum
C Type I	Blend of pyrocellulose and guncotton	13.15 ± 0.05%
C Type II	Blend of pyrocellulose and guncotton	13.25 ± 0.05%
D	Pyrocellulose	12.20 ± 0.10%
E	Pyrocellulose	12.00 ± 0.10%
F	Pyrocellulose	11.55 ± 0.25%

Class 1 - For combustible cartridge case (CCC) applications
Class 2 - For solvent and solventless propellant applications
Class 3 - For propellants made from lacquer applications
(Lacquer applications are propellant products that are made with completely solvated nitrocellulose from a homogenous mixture of nitrocellulose, stabilizer and solvent.)

Comments, suggestions, or questions on this document should be addressed to: Commander, U.S. Army ARDEC, ATTN: RDAR-EIQ-SE, Picatinny Arsenal, New Jersey 07806-5000, or emailed to usarmy.picatinny.ardec.list.ardec-stdzn-branch@mail.mil. Since contact information can change, you may want to verify the currency of this information using ASSIST Online database at https://assist.dla.mil .

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Even when test parameters had to be further restricted (e.g. for Nitrogen Content with FS/FAS Titration), this was done by adding a note rather than by changing the test procedure to maintain equality with MIL-DTL-244C

NOTE 7: Results of FS/FAS titration strongly depend on several experimental parameters. In particular volume and initial temperature of the sulphuric acid as well as maximum temperature during titration significantly influence the result. Main reason is that sensitivity toward these parameters is different between potassium nitrate calibration and nitrocellulose titration. Even if all parameters are kept within the range given above, not tolerable systematic deviations of obtained nitrogen content values may appear, often together with excellent precision which makes it difficult to recognize such effects. Investigations have shown that most relevant systematic effects lower the obtained nitrogen content value; e.g. due to loss of NC fibres during preparation, due to incomplete dissolution of NC in the acid, and due to loss of formed nitrogen oxides from the solution by small gas bubbles. Therefore test parameters can be optimized by targeting the maximum nitrogen content value (as the maximum value obtained is the most plausible one). Thus it was found that: (i) Adding the nitrocellulose into the dry beaker and spilling the beaker walls with sulphuric acid prevents the loss of fibres which otherwise tend to stick on acid droplets on the beaker wall above the solution. (ii) A larger amount of sulphuric acid reduces loss of formed nitrogen oxides from the solution and assists dissolving the sample; it is recommended to use 100 ml at least, better 150 ml for 300 mg of sample. (iii) Temperature of added sulphuric acid is relevant, lower temperature reduces loss of formed nitrogen oxides but slows down dissolution of sample; 5°C sulphuric acid temperature is a good compromise. (iv) Long duration of stirring ensures completeness of sample dissolution but increases loss of formed nitrogen oxides; different nitrocellulose grades might require different stirring times, typically 5 minutes to max. 30 minutes of stirring at around 5°C. (v) Maximum temperature during titration has a strong systematic influence on result due to loss of formed nitrogen oxides if temperature is too high; it is therefore strongly recommended to not exceed 25°C during entire sample dissolution and titration although both this standard and MIL-DTL-244C would allow to go up to 40°C.

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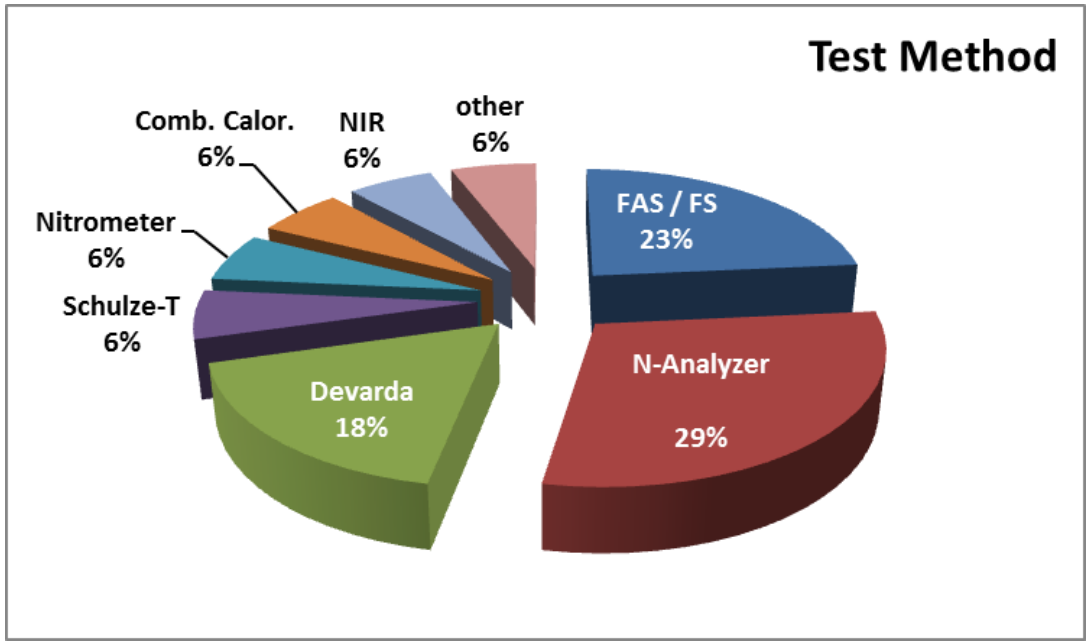
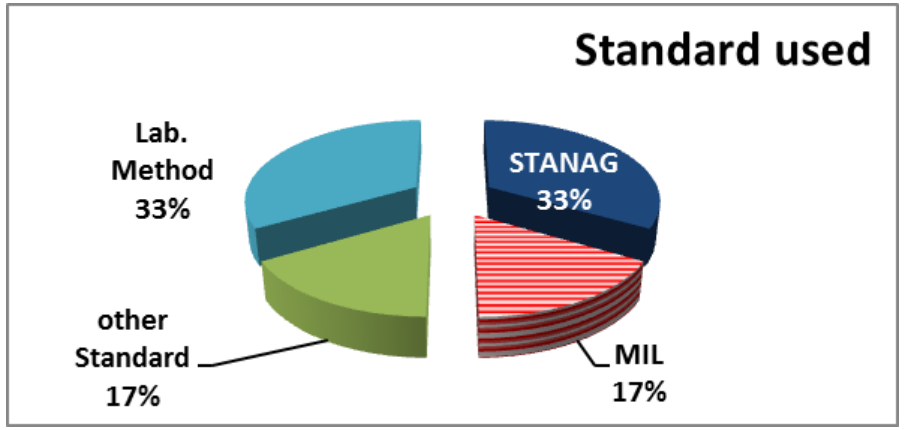
Test 2: Nitrogen Content





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Main Changes in AOP-4178 Ed. 3 (Compared to STANAG 4178 Ed. 2)

- Procedure for **Sampling of NC** added
- Determination of **Nitrogen Content**:
  - **FAS/FS Titration**-Method improved
  - Near Infrared Spectroscopy **NIR-Method** included
  - No longer used test procedures omitted
- **65.5°C Abel Heat Test** and **Grit Test** omitted
- **Viscosity**: Alternative Viscosity Test method which is also suitable for low viscosity NC grades added
- Method for **Fibre Length Distribution** improved
- **Fiberization Quality / Agglomerates**: **Wet Sieving Method** replaced by **Elutriation Method**
- Clearly stated that some methods are only suitable for comparative testing

4.1.1. Sampling of Nitrocellulose

1. Nitrocellulose may be sampled at various stages of its manufacture. The samples shall be taken in their original form (e.g. as nitrocellulose slurry, as water-wet or as alcohol-wet nitrocellulose) and will require preliminary treatment before analysis can begin.
2. The sample must be representative for the respective lot to be tested. The following guidelines apply (based on MIL-DTL-244C):
   a. Sampling from process vessels (before pack-out): To ensure homogeneity of the material, the process vessel shall be stirred or vigorously agitated for an adequate time before sampling, and the slurry sample shall be obtained from the process vessel while stirring or being agitated, by a means that ensures the sample is representative of the total contents. Recommended minimum sample size for complete analysis is 500 g.
   b. Sampling during pack-out (e.g. for visual purity test and for verification of total volatile, water or alcohol content, of oil and grease content, or of fiberization quality): At th
   container, one grab s
   containers or less. In ca
   less than 30, a minimun
   beginning (first transpor
   third of the batch) and
   packed. In most case
   individually. Recommen
   c. Sampling after pack-ou
   shall be selected for sa
   of 10 containers might b
   of 3 containers should
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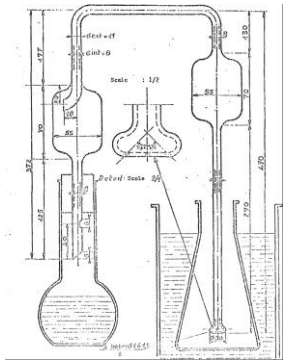
FAS/FS Titration is reference method, NIR and N-Analyzer are alternate methods; all are described in AOP-4178 Ed. 3



Devarda's Alloy, Schulze-Tiemann, Nitrometer and Combustion Calorimetry Methods are listed but not described in Ed. 3; they still may be used (Reference to Ed. 1 / Ed. 2)

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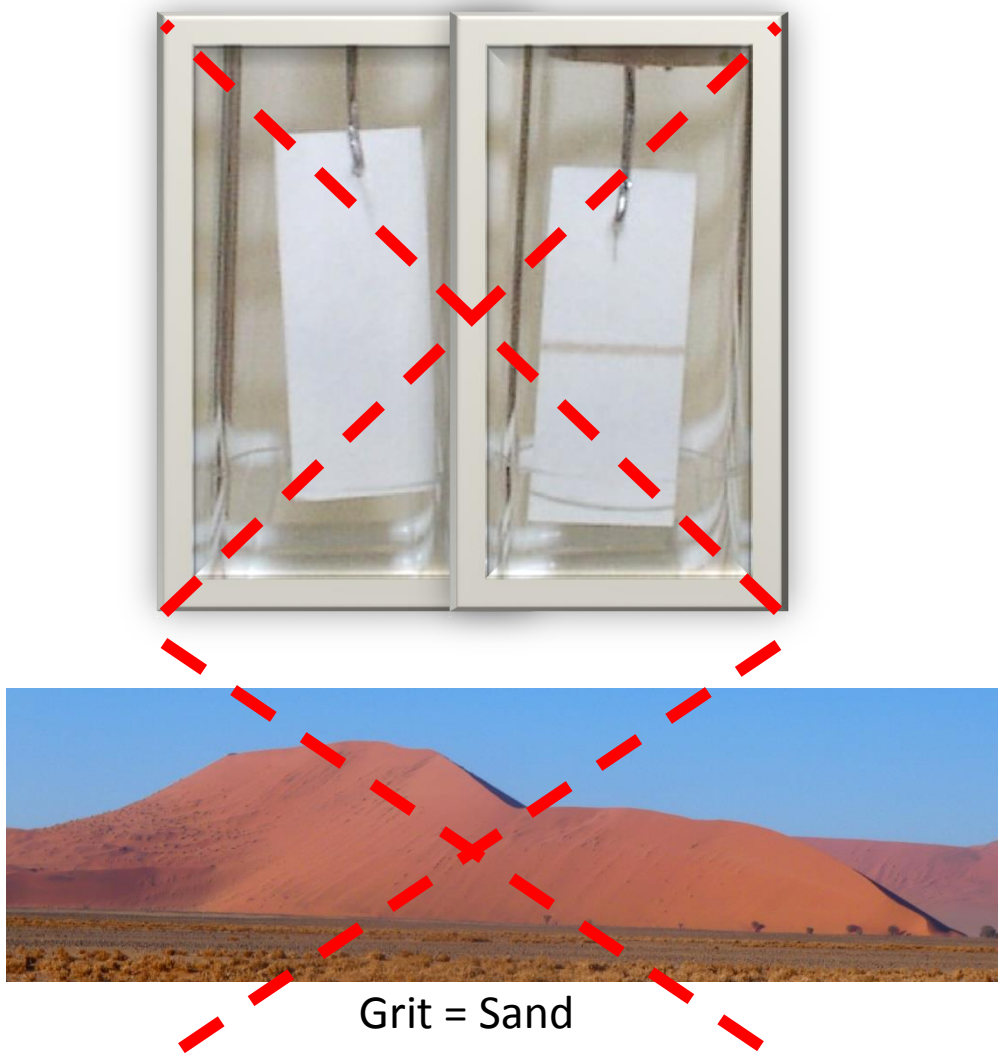

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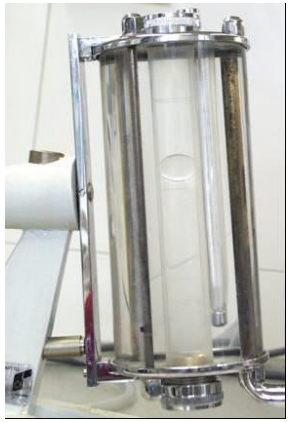
"MIL Viscosity" (falling sphere viscometer / 10% NC solution) remains standard viscosity method

Alternate viscosity method based on German TL 1376-589 (3% NC solution in acetone) allows using different viscometer types such as Hoeppler, Ubbelohde, or rotational viscometer; all viscometers give equivalent results



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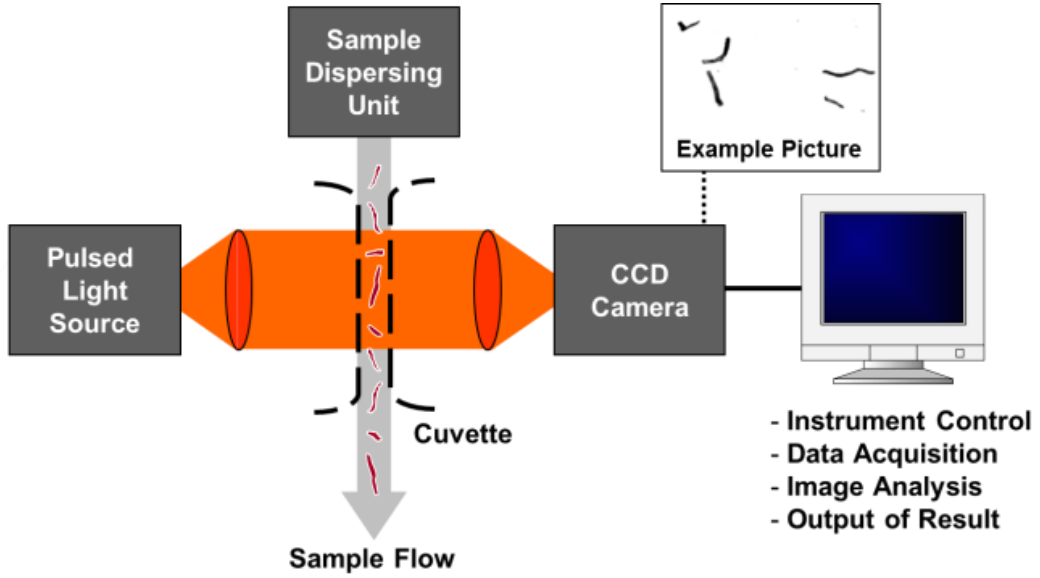
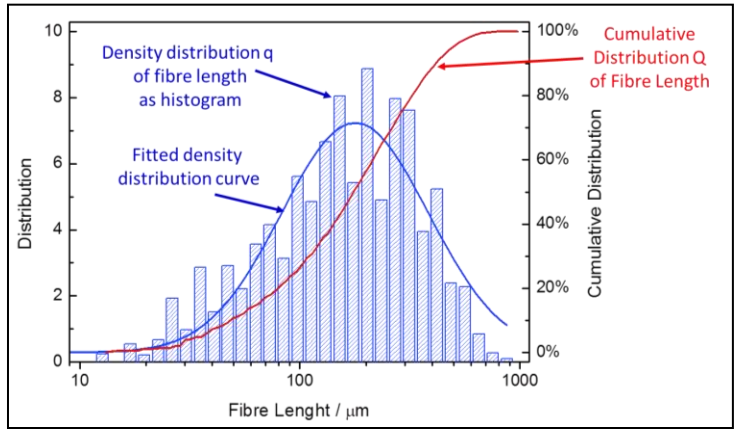


Test method fully rewritten + considerably improved; automated calculation of fibre length distribution; …



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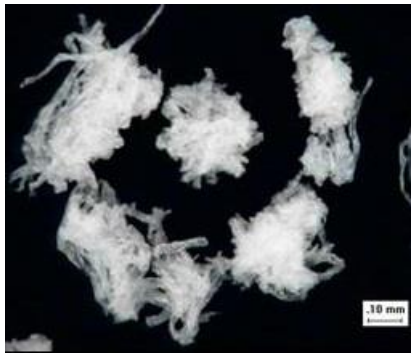
Wet Sieving Method as described in Ed. 2 is not suitable for NC with low agglomerate contents and cumbersome for certain NC types



New Fiberization Quality Test / Elutriation Method is more robust and also applicable for NC with low agglomerate contents; on the other hand, precision is inferior for NC with extremely high agglomerate contents

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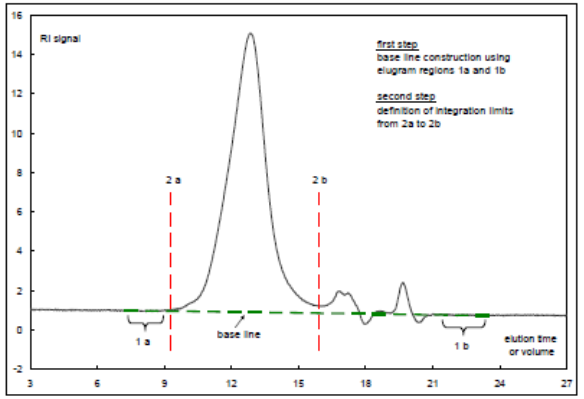

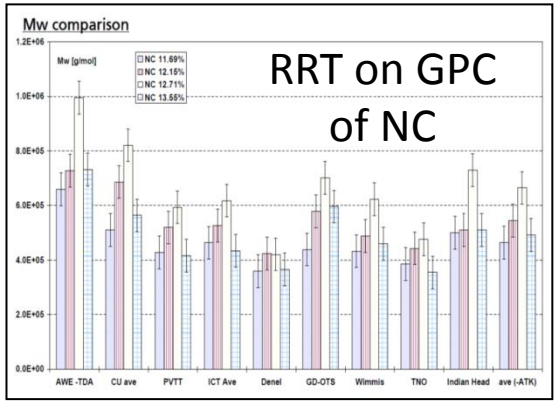

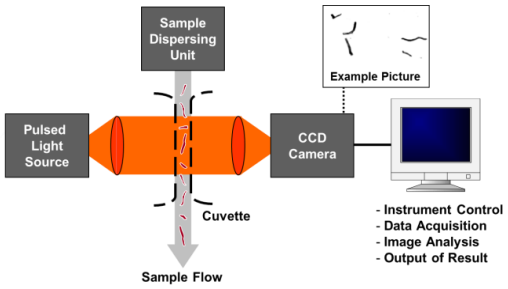

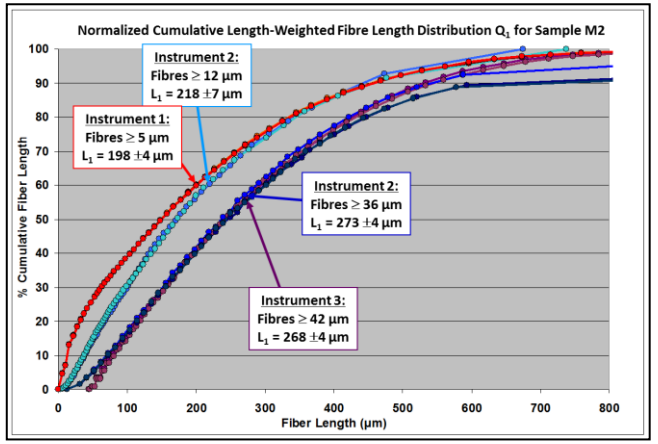

Molecular Mass and Fibre Length Distribution Tests yield valuable information; their numerical results, however, strongly depend on instrument type and/or experimental conditions → only suitable for comparative testing

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Summary and Way Ahead

- Numerous corrections and improvements have been implemented in AOP-4178 Ed. 3
- The document is now consistent within itself and harmonised with MIL-DTL-244C
- Many persons / laboratories / agencies / institutes / companies have contributed to this revision - directly or by participating in the survey / questionnaire or NC testing workshop - this is greatly appreciated

- The final draft of AOP-4178 Ed. 3 has been submitted for NATO acceptance process

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NATO STANDARD

AOP-4178

TEST PROCEDURES FOR ASSESSING THE QUALITY OF DELIVERIES OF NITROCELLULOSE FROM ONE NATO NATION TO ANOTHER

Edition 3 Version 1
Final Draft / February 2017

NORTH ATLANTIC TREATY ORGANIZATION

ALLIED ORDNANCE PUBLICATION

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