Methods for the Determination of Nitrogen Content in Nitrocellulose

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- Direct Methods:
  - Ferrous Ion Titration Methods (FS/FAS)
  - Devarda's Alloy Method
  - Nitrogen Analyzer Method
  - Schulze-Tiemann Method
  - DuPont Nitrometer Method

- Indirect Methods:
  - Combustion Calorimetry Method
  - Near Infrared Spectroscopy Method (NIR)

- Summary and Conclusions
**Introduction**

**Nitrogen-Content of NC**

Nitrogen Content (degree of nitration) is the **most important attribute of NC**

Several test methods possible; all determine the **average Nitrogen Content** of NC

Nitrogen Content should be assessed with:

- **High precision** (standard dev. required $s \leq 0.02\%$ N, preferred $s \leq 0.01\%$ N)
- **High accuracy** (max. deviation from reference method $\leq 0.03\%$ N)

<table>
<thead>
<tr>
<th>$x$</th>
<th>N-Content</th>
<th>NC Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>14.15%</td>
<td>--- (not achievable)</td>
</tr>
<tr>
<td>5.5</td>
<td>13.45%</td>
<td>Guncotton</td>
</tr>
<tr>
<td>5</td>
<td>12.75%</td>
<td>Pyrocellulose</td>
</tr>
<tr>
<td>4.5</td>
<td>11.96%</td>
<td>Lacquer</td>
</tr>
<tr>
<td>4</td>
<td>11.11%</td>
<td>Grade NC</td>
</tr>
<tr>
<td>3.5</td>
<td>10.16%</td>
<td></td>
</tr>
</tbody>
</table>

$x = \text{number of nitrated hydroxyl groups per structure unit}$
Introduction

Methods for Determination of N-Content in NC

Direct Methods:
- **Ferrous Ion Titration Methods (FS/FAS)** → reference method; in STANAG 4178 Ed.2
- **Devarda's Alloy Method** → alternate method; in STANAG 4178 Ed.2
- **Nitrogen Analyzer Method** → alternate method; in STANAG 4178 Ed.2
- **Schulze-Tiemann Method** → alternate method; in STANAG 4178 Ed.2
- **DuPont Nitrometer Method** → alternate method; in STANAG 4178 Ed.2

Indirect Methods:
- **Combustion Calorimetry Method** → alternate method; in STANAG 4178 Ed.2
- **Near Infrared NIR Spectroscopy Method** → altern. method; not yet standardized
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- Summary and Conclusions
FS/FAS Titration Method

Overview

- **Reference method** (STANAG 4178 Ed. 2 / MIL-DTL-244C)
- Potential to be very precise and accurate
- **Principle**: Dissolving of NC in H₂SO₄ → acidic hydrolysis to NO₃⁻ → redox titration

**Issues:**
- Time-consuming, expensive (acid/electrodes), produces waste, ...
- 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!
FAS Titration Method

Strong Influence of Method Parameters

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

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

These effects seen for NC (bubbles → strong sensitivity on H₂SO₄ volume and T as well as on titration T) are almost negligible for KNO₃ calibration standard !!!

- 50 mL H₂SO₄ 0°C max. titration T 30°C  ⇒ N = 12.76%
- 50 mL H₂SO₄ 22°C max. titration T 30°C  ⇒ N = 12.65%
- 50 mL H₂SO₄ 0°C max. titration T 20°C  ⇒ N = 12.76%
- 150 mL H₂SO₄ 0°C  ⇒ N = 12.79%

n = 2
n = 2 - 3
n = 8
n = 28

Nitrogen Content in NC
FAS Titration Method
Optimization of Method Parameters

- **Problem of systematic effects / deviations**
  - Systematic effects are very difficult to identify (FAS result can be highly precise but nevertheless systematically wrong / biased) – how can we be sure that the obtained result is not biased?
  - NC reference materials with certified N-content would solve the problem - but such reference materials are not available!
  - Certified calibration reference material (KNO$_3$) reacts differently to NC in FAS titration (dissolves faster and has different titration curve / end point voltage)

- **Chosen solution: Highest N-content value is regarded as most plausible**
  - This approach is based on the assumption that all systematic effects lower the obtained nitrogen content value; e.g. due to
    - loss of NC fibres during weighing / transfer into the titration beaker
    - incomplete dissolution of NC in the acid
    - loss of formed nitrogen oxides from titrant solution into atmosphere
  - **Method parameters have thus to be optimized for maximum N-content value**
FAS Titration Method
Optimization of Method Parameters – Pyrocellulose 12.7% N

- Maximum N-content value for $T_{\text{acid/bath}} \leq +5^\circ\text{C}$, $T_{\text{max}} \leq 25^\circ\text{C}$ and $t_{\text{stirring}} \leq 5 \text{ min}$
- Significantly lower N-values for higher temperatures and longer pre-stirring time
- Obviously this NC type dissolves very easily also at low temperatures; reduction in N-content value is dominated by loss of NO$_x$ from solution
FAS Titration Method
Optimization of Method Parameters – Lacquer Grade 11.5% N

- Maximum N-content value for $T_{\text{acid/bath}} = +5^\circ\text{C}$, $T_{\text{max}} \leq 25^\circ\text{C}$ and $t_{\text{stirring}} = 5 - 15$ min
- Significantly lower N-values for higher temperatures due to loss of $\text{NO}_x$
- But also lower N-values for lower temperatures ($T_{\text{acid/bath}} = 0^\circ\text{C} / -5^\circ\text{C}$)
- Obviously this NC type need sufficiently high $T_{\text{acid/bath}}$ and $t_{\text{stirring}}$ to fully dissolve

Influence FAS-Parameters on N-Content Lacquer Grade NC

- Bath $-5^\circ\text{C}$ // max. $20^\circ\text{C}$ (2 mL/min)
- Bath $0^\circ\text{C}$ // max. $24^\circ\text{C}$ (2 mL/min)
- Bath $+5^\circ\text{C}$ // max. $20^\circ\text{C}$ (1 mL/min)
- Bath $+10^\circ\text{C}$ // max. $20^\circ\text{C}$ (0.5 mL/min)
FAS Titration Method
Optimization of Method Parameters – Guncotton 13.5% N

- Maximum N-content value for $T_{acid/bath} = +5^\circ C$ and $T_{max} \leq 25^\circ C$
- Significantly lower N-values for lower temperatures due incomplete dissolution
- Influence if pre-stirring time is marginal; $t_{stirring} = 5$ min seems to be adequate (except for NC sample V3; which need 15 min)
FAS Titration Method

Optimization of Method Parameters – Results and Discussion

- Two main effects of method parameters have been found
  - Dissolution of NC: Higher temperatures and longer duration of stirring assist dissolution of NC
  - Loss of NO\textsubscript{x}: Larger amounts of sulfuric acid, lower temperatures of acid and cooling bath, lower maximum temperature during titration and shorter duration of stirring reduce loss of NO\textsubscript{x} from titrant solution into atmosphere

- Mainly due to differences in solubility, optimum range of parameters might differ for the individual NC grades / types

- With the existing FAS equipment, the following parameters appeared suitable
  - Volume of sulphuric acid 98% = 90 mL (150 mL favoured but not possible)
  - Temperature of sulphuric acid = 0 – 5°C
  - Temperature of cooling bath / thermostat = 0 – 5°C
  - Pre-stirring time = 2' (pyrocellulose), 5' (guncotton/blends/lacquer grades)
  - Titrant temperature during titration = 5°C to 20°C (not exceeding 22°C)
  - Resulting analysis time (stirring + titration) = 25' for guncotton/blends

- So obtained N-values are plausible and coincide well with results of other labs
Devarda's Alloy Method

Overview

- **Alternate direct method** (STANAG 4178 Ed. 2; refers to STANAG 4178 Ed. 1 and UK Laboratory Method M39)

- **Principle**: Digestion of NC by NaOH → reduction of NO₃⁻ to NH₃ using Devarda's alloy → water vapour distillation into acid → back-titration

- Method is reported to be **very precise and accurate** if very carefully performed (by hand)

- **Issues**: Very time-consuming (several hours) and thus expensive, needs chemicals, produces waste, ...

- **Automated Kjeldahl / Devarda apparatus**: Is very fast and easy to operate, but does not meet the extremely high precision and accuracy requirements of this demanding application!
Devarda's Alloy Method
Automated Kjeldahl / Devarda Apparatus – Results

- Already calibration with KNO₃ using automated Kjeldahl / Devarda apparatus gave insufficient precision and accuracy (for this specific application):
  - Standard dev. s = 0.05% N for KNO₃, which corresponds to s = 0.04% as reported for NaNO₃ in application note; this is inferior by factor 10 if compared to FAS (s = 0.005% N)
  - Recovery of nitrogen of only 97%-99%

- Reason is that automated Devarda reaction / distillation is performed much much faster and thus less carefully than "by hand"
Nitrogen Analyzer Method

Overview

- **Alternate direct method** *(STANAG 4178 Ed. 2)*
- **Principle:** Combustion of NC → reduction of NO\(_x\) to N\(_2\); removal of other product gases → detection of N\(_2\) by thermal conductivity detector
- **Highly automated instruments**, e.g. from LECO, Büchi, Gerhardt, Eltra, ....
- **Precision** markedly lower than FAS → approx. 10 replicates required → more elaborate sample preparation ruins the advantage of automated analysis
- **Several accuracy-related issues:**
  - Already the uncertainty in N-content of specified calibration samples *(EDTA: 9.58±0.03% N; carbanilide: 13.20±0.05% N)* "eats up" the entire accuracy budget
  - Shifts in result of up to 0.07% N per day have been found with some instruments
  - Obtained results depend to some extent on instrument parameter settings (e.g. difference up to 0.08% N for NC depending on oxygen dosing settings)
  - Obtained results depend on sample combustion rate *(NC burns much faster than inert calibration sample → much higher/shorter N-peak; a defined amount of methyl alcohol needs to be added to NC to slow down decomposition rate)* ⇒ if no methyl alcohol is added, obtained N-content is too low by >1.0% N !!!
Nitrogen Analyzer Method

Results (Precision)

- Calibration of Nitrogen Analyzer with EDTA (Ethylenediaminetetraacetic acid):
  Stand. dev. $s = 0.020\%$; coinciding with $s = 0.026\%$ as reported by Thales Australia using another instrument

($= 4 - 5$ times higher standard dev. than for FAS calibration with $\text{KNO}_3$; $s = 0.005\%$)
Nitrogen Analyzer Method

Results (Accuracy / Bias)

- Analysis of NC sample did, in addition to the lower precision, also show variation of obtained N-content values depending on sample preparation and instrument set-up (results N-Analyser 1-3 obtained with instrument settings optimized for NC; N-Analyser 4 with standard set-up)

![Graph showing nitrogen content results for different methods and settings]
Nitrogen Content in NC

Nitrogen Analyzer Method

Results (Accuracy / Bias)

- Obtained N-content values depend on sample preparation and instrument set-up!
  If no methyl alcohol is added to the NC sample prior to packing into foil, sample burning rate is so high that a very high peak with very steep slope is obtained in the instrument, resulting in a false low reading of obtained nitrogen content value!!!

- But also amount of methyl alcohol and residence time has significant influence on peak shape and thus also on obtained nitrogen content value.

<table>
<thead>
<tr>
<th>Sample Weight</th>
<th>Obtained N-content [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>50 – 100 mg</td>
<td>12.72</td>
</tr>
<tr>
<td>150 – 200 mg</td>
<td>12.72</td>
</tr>
<tr>
<td>150 – 200 mg</td>
<td>12.72</td>
</tr>
<tr>
<td>150 – 200 mg</td>
<td>12.70</td>
</tr>
<tr>
<td>150 – 200 mg</td>
<td>12.71</td>
</tr>
<tr>
<td>150 – 200 mg</td>
<td>12.75</td>
</tr>
<tr>
<td>150 – 200 mg</td>
<td>12.67</td>
</tr>
<tr>
<td>150 – 200 mg</td>
<td>11.24</td>
</tr>
</tbody>
</table>

No desensitiser added

FAS 2013 (n=150)
FAS 2014 (n=2)
FAS other Lab (n=5)
NIR (n=195)
N-Analyzer 1 (n=14)
N-Analyzer 2 (n=9)
N-Analyzer 3 (n=14)
N-Analyzer 4 (n=14)
N-Analyzer; no MeOH added
Schulze-Tiemann Method

Overview

- **Alternate direct method**
  (STANAG 4178 Ed. 2; refers to German Standard TL 1376-589)

- **Principle**: Digestion of NC with FeCl₂/HCl → determination of volume of NO

- Time-consuming, "old-fashioned" method (1890), ...

- **Intermediate precision / accuracy** achievable if properly operated

- Several parameters may produce systematic errors and thus reduce accuracy:
  - Mismeasurement of eudoimeter temperature by +1°C → systematic error of -0.06% N
  - Mismeasurement of atmospheric pressure by +1 mbar (+1 hPa) → systematic error of +0.01% N
  - Mismeasurement of gas volume by +0.1 mL → systematic error of +0.01% N
DuPont Nitrometer Method

Overview

- **Alternate direct method** (STANAG 4178 Ed. 2; refers to STANAG 4178 Ed. 1 and UK Laboratory Method M39)

- **Principle:** Dissolving of NC in H₂SO₄ / Hg → determination of volume of thereby produced NOₓ gases

- Method is reported to be of *intermediate precision and accuracy*

- Method should no longer be used due to working safety concerns (handling and disposing of large amount of mercury)
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Combustion Calorimetry Method

Overview

- Alternate **indirect method** (STANAG 4178 Ed. 2)

- **Principle:** Combustion of NC in calorimeter → so determined heat of combustion is strongly correlated to N-content

- **Advantages:** Larger sample amount (4 g) → more representative sample; no reagents required; no production of waste

- **Issues:**
  - Only **intermediate precision and accuracy** (Standard dev. s ≈ 0.02% N; just meets requirement of STANAG 4178 Ed. 2 but is inferior by at least factor 4 if compared to standard dev. attainable with FAS)
  - Indirect method; needs to be calibrated by direct method
  - Time-consuming and thus expensive
Near Infrared NIR Spectroscopy Method

Overview

- Alternate *indirect method* (not yet standardized)

- **Principle:** Recording of NIR spectrum
  (NIR spectrum changes significantly with N-content of the NC)

- Method is very precise and accurate if thoroughly calibrated

- **Further Advantages:**
  - Much shorter analysis time (10 minutes for duplicate analysis !)
  - Larger sample mass (approx. 10 g) and thus more representative sample
  - Result remains unaffected by changing moisture level (within calibrated range)
  - High robustness of the method ("difficult to produce errors / wrong results")
  - No reagents required; no production of waste; no pollution

- **Disadvantages of NIR method**
  - Indirect method; needs to be calibrated by a direct method
  - Method not yet standardized
Near Infrared NIR Spectroscopy Method

Experimental

1st Step: Drying of NC
- NC is simply dried in the hot air blower at 60°C (no 2nd dying step in oven at 100°C required)

2nd Step: Filling the NC into solids cell
- Approx. 10 g of NC is void-free filled into the Büchi NIRFlex-Solids-Cell; the NC is then compressed by inserting a piston

3rd Step: Recording NIR spectrum
- The NIR spectrum is recorded for 16 s each at 3 different positions of the cell
- The N-content of the NC is then automatically calculated from the recorded 3 NIR spectra
The NIR spectrum changes significantly with N-content of the NC:
- Between 4'500 cm\(^{-1}\) and 5'100 cm\(^{-1}\) (R-OH combination bands, R-N-O 2\(^{nd}\) overtone)
- Around 7'000 cm\(^{-1}\) (H\(_2\)O and R-OH 1\(^{st}\) overtone)
NIR Method

Improved Calibration Model 2015 (first Model implemented 2013)

- Number of calibration samples = 692; number of validation samples = 1040
- Regression coefficient $R^2 = 0.9994$
- Standard error of calibration SEC = 0.016%
- Standard error of prediction SEP = 0.013%
NIR Method

The Precision (Laboratory Precision - Quality Control Chart)

NC 57_8134 // 2013 // Quality Control Chart

Combustion Calorimetry
N = 12.70%
s_{zi} = 0.020%; n = 18

FAS Titration
N = 12.72%
s_{zi} = 0.006%; n = 63

NIR Spectroscopy
N = 12.73%
s_{zi} = 0.006%; n = 63
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Summary and Conclusions

- For NC N-content analysis, requirements regarding precision / accuracy are very strict – very close to or even beyond the limits of feasibility for most analytical methods.

- The reference method FAS/FS is highly precise but requires a tremendous effort to ensure also high accuracy (= elimination of systematic errors).

- Devarda's Alloy Method is reported to also achieve high precision / accuracy if carefully performed (manually) but is very time-consuming.

- Other tested methods, such as automated Devarda/Kjeldahl, Nitrogen Analyzer, Schulze-Tiemann, Nitrometer and Combustion Calorimetry, suffer from at least one severe drawback and cannot match precision/accuracy level of FAS/FS/Devarda.

- Once thoroughly calibrated, the indirect NIR Method has proven to be very robust, precise and accurate. Furthermore, NIR is very fast and does neither require reagents nor produce any waste or pollution. NIR has the potential to become the most important method for routine NC N-content analysis upon being included in the relevant standards / specifications.
Thanks very much for your attention!