RHEINMETALL
NITROCHEMIE

Determination of Nitrogen Content in Nitrocellulose by Near Infrared NIR Spectroscopy

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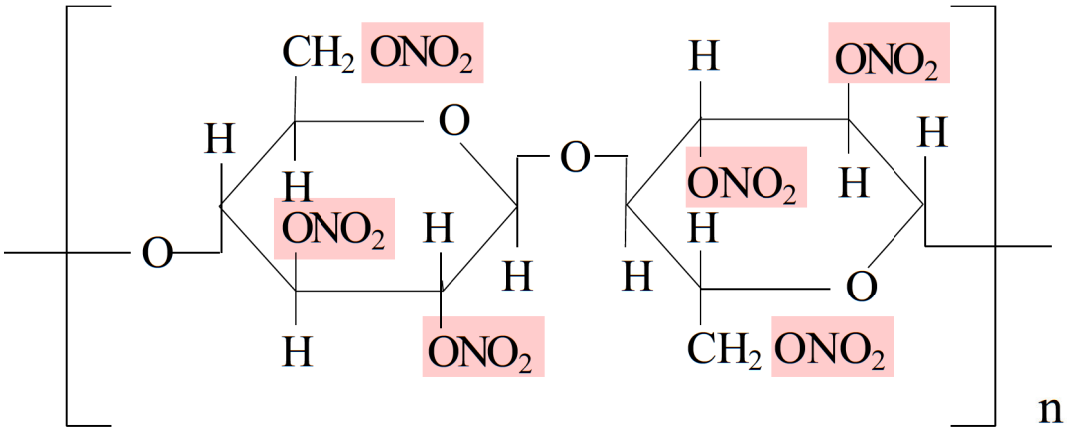
Introduction

Nitrogen-Content of NC



x	N-Content	NC Type
6	14.15%	--- (not achievable)
5.5	13.45%	Guncotton
5	12.75%	Pyrocellulose
4.5	11.96%	Lacquer Grade NC
4	11.11%	
3.5	10.16%	

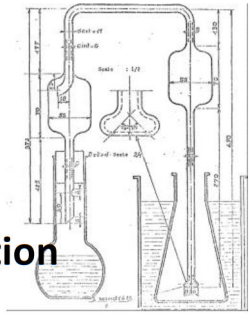
x = number of nitrated hydroxyl groups per structure unit

- **Nitrogen Content (degree of nitration) is the <u>most important attribute of NC</u>; it determines most physical and chemical properties (e.g. energy content, flame temperature, solubility, density, reactivity, ….)**
  - **Nitrogen Content Tests determine the <u>average Nitrogen Content</u> of the NC**

Introduction

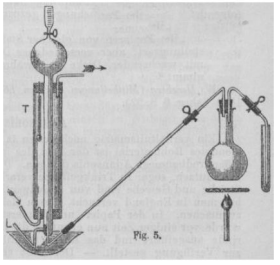
Direct Methods for Determination of N-Content in NC

- **Ferrous Ion Titration Methods (FS/FAS)**
  - Reference Method; very precise and accurate if properly operated
  - Time-consuming, expensive (acid/electrodes), produces waste, …
  - Principle: Dissolving in H_2SO_4 → acidic hydrolysis to NO_3 → redox titration



- **Devarda's Alloy Method**
  - Highest precision / accuracy (if properly operated)
  - Very time-consuming and thus expensive, produces waste, …
  - Principle: Digestion by NaOH → reduction of NO_3 to NH_4 → distillation + titration

- **Nitrogen Combustion Analyzer Method**
  - Lower precision / accuracy → approx. 10 replicates required
  - Highly automated instrument, but time-consuming preparation
  - Principle: Combustion of NC → reduction of NO_x to N_2; removal of other product gases → detection of N_2 by thermal conductivity detector



- **Schulze-Tiemann Method**
  - Intermediate precision / accuracy (if properly operated)
  - Time-consuming, "old-fashioned" method (1890), …
  - Principle: Digestion of NC with $FeCl_2$/HCl → determination of volume of NO

Introduction

Other Methods for Determination of N-Content in NC

- **DuPont Nitrometer Method**
  - Direct method with intermediate precision / accuracy
  - Method is no longer used due to working safety concerns (handling and disposing of large amount of mercury)
  - Principle: Dissolving in H_2SO_4 / Hg → determination of volume of thereby produced NO_x gases

- **Combustion Calorimetry Method**
  - Lower precision / accuracy
  - Advantages: Larger sample amount (4 g) → more representative; no reagents required; no production of waste
  - Main disadvantage: Indirect method; needs to be calibrated by direct method
  - Other disadvantage: Time-consuming and thus expensive
  - Principle: Combustion of NC in calorimeter → so determined heat of combustion is strongly correlated to N-content

Introduction

Problems with Conventional Methods and possible Solution

- **Problems with conventional Methods**
  - Most methods are **very time-consuming** (approx. 2 hours to prepare / calibrate apparatus; then at least 1 hour per NC sample to measure required number of replicates) and thus expensive
  - Most methods are error-prone and not very robust (at least at the required accuracy/precision level of below 0.2% RSD)
    - Small sample mass → loss of only a few fibres influences result
    - Moisture uptake of NC: +0.1% water → –0.01% N-content
    - Presence of agglomerates → error if not fully dissolved in FS/FAS
    - Even small deviation from optimum testing conditions may significantly alter result (e.g. in FAS: Amount and temperature of H_2SO_4 added, ….)

- **Possible Solution = Near Infrared NIR Spectroscopy**
  - Very simple, fast and reproducible method
  - Several other laboratories have reported suitability of NIR method for NC N-content determination

NIR-Results of Other Laboratories

Manuco / Bergerac; France

- Unsatisfactory results with direct NIR measurement of dry NC
- Good results with NIR measurement of wet NC dissolved in acetone
  - Time required for dissolution + NIR measurement is 0.45 h
  - Precision of NIR method is excellent: Repeatability standard deviation s_r = 0.01 % N-content
- To compare with other methods:
  - FAS titration: s_r = 0.015 % N-content (reference method)
  - Devarda's Alloy Method: s_r = 0.01 % N-content (excellent + very precise alternative direct method; but too time-consuming for routine operation)

MANUCO

Bergerac NC GROUPE SNPE

Presented at NC Experts Meeting on STANAG 4178 / MIL-DTL 244; US ARDEC Picatinny ; May 6-7 2009

NIR-Results of Other Laboratories

Thales Australian Munitions; Australia

- Good results with direct NIR measurement of dry NC (fibres)
  - Method is very simple and fast
  - NIR cell is firmly / void-free packed with NC and then measured by NIR
  - Calibration required 50 – 100 samples (different NC grades made from different cellulose raw materials using different process parameters)
  - Different moisture levels included in calibration → water content (as long as below 1.5%) has almost no influence on obtained N-content !
  - **Accuracy of NIR method is equivalent to FAS method** (Precision / repepeatability s_r = 0.01 % N-content; measurement uncertainty = 0.024 % N-content)
  - Nitrogen Analyzer Method has poorer precision (SD = 0.026 % N-content) but slightly better measurement uncertainty (0.019 % N-content)
  - NIR is used as routine method, performance is weekly checked by FAS

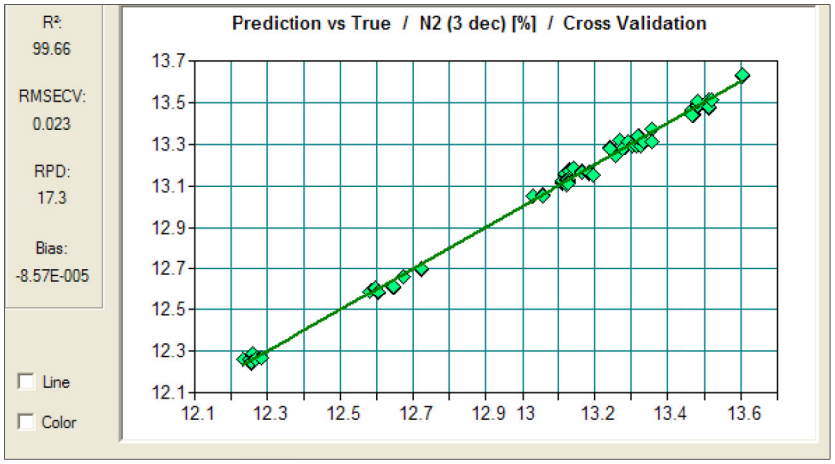
THALES

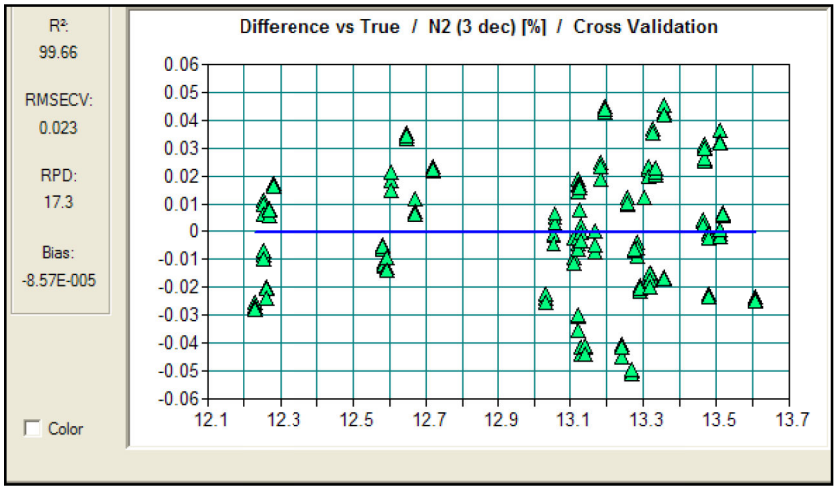
Presented at PARARI Conference, Australia, 2011

NIR-Results of Other Laboratories

ATK Radford; USA

- Good results with direct NIR of NC (fibres)
  - Calibration model made from 150 NC samples measured by FAS and NIR
  - Good correlation between NIR and FAS results; no trends → confirms that **regression model is suitable**
  - Method is not (yet) used for routine analysis of NC N-content
- General considerations regarding NIR:
  - NIR is fast (< 30 sec); often no sample preparation; simple to operate; no reagents required; no waste, no pollution; highly precise and accurate
  - **Continuous monitoring of NIR using primary method is a must !**





Presented at 5th Nitrocellulose Workshop; Switzerland 2012

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NIR-Results of Other Laboratories

Dow Wolff Cellulosics; Germany

- **Manufacturer of Industrial NC also use NIR**
  - **NIR was introduced for routine analysis of NC N-content**
  - **NIR calibration is regularly checked by Schulze-Tiemann Method (which is regarded as being the most reliable / precise direct method)**

Nitrogen Content by NIR

Further developments in instrumental chemical analytics made it possible to reduce the time for analysis drastically. A new method of analysis was sucessfully introduced, the near-infrared spectroscopy (NIR). This method is used today for production control. As the NIR is not an absolute method and requires calibration, the Schlösing-Schulze-Tiemann method is used parallel to it in order to check the calibration of the NIR method.

dowwolff CELLULOSICS DOW

From: http://www.dow.com/scripts/litorder.asp?filepath=/822-00007.pdf

NIR Method

Experimental

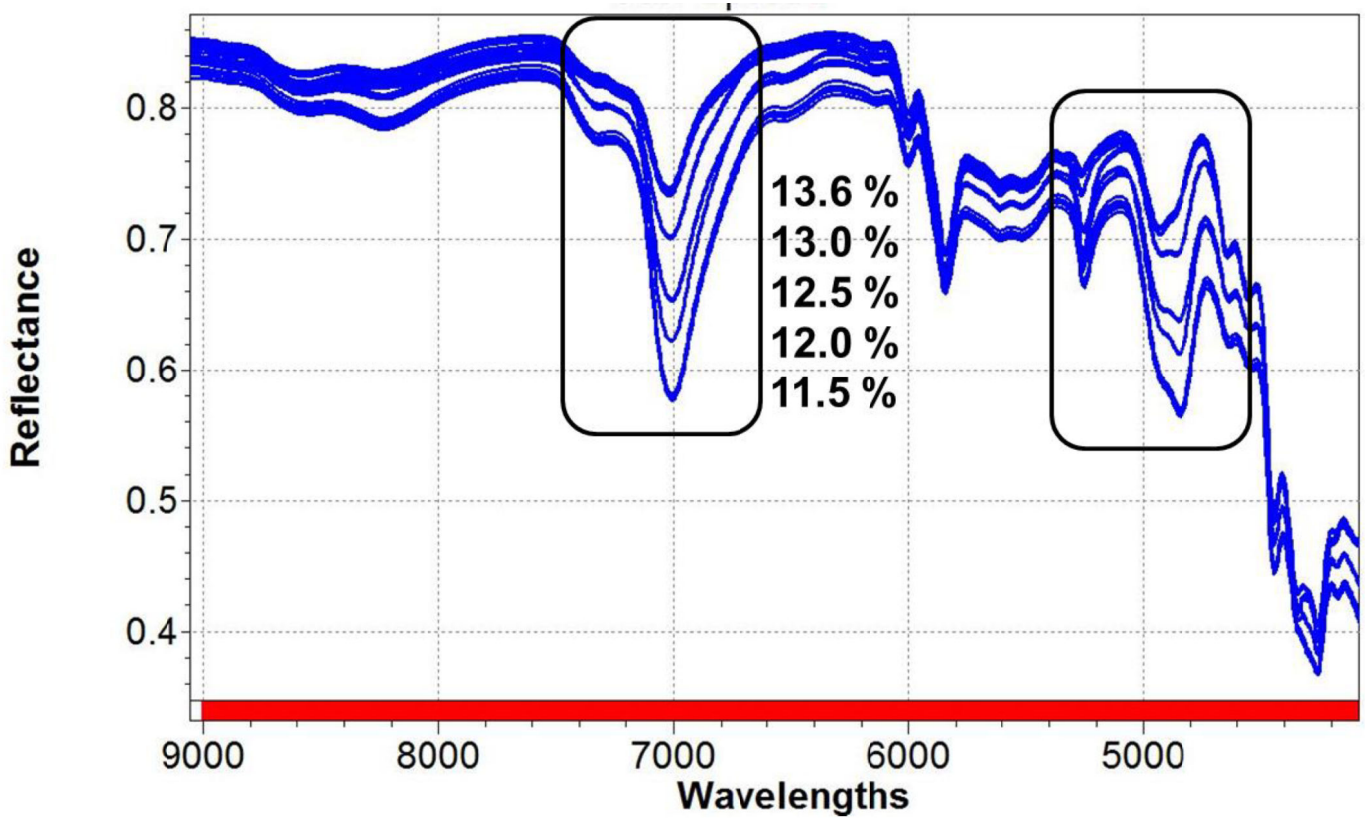
- 1st Step: Drying of NC
  - NC is simply dried in the hot air blower at 60°C (no 2nd dying step in oven at 100°C required)

- 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
  - Filling the cell and measuring is repeated
  - The N-content of the NC is then automatically calculated from the recorded 6 NIR spectra

NIR Method

The Spectrum



- **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 2nd overtone)**
  - **Around 7'000 cm^{-1} (H_2O and R-OH 1st overtone)**

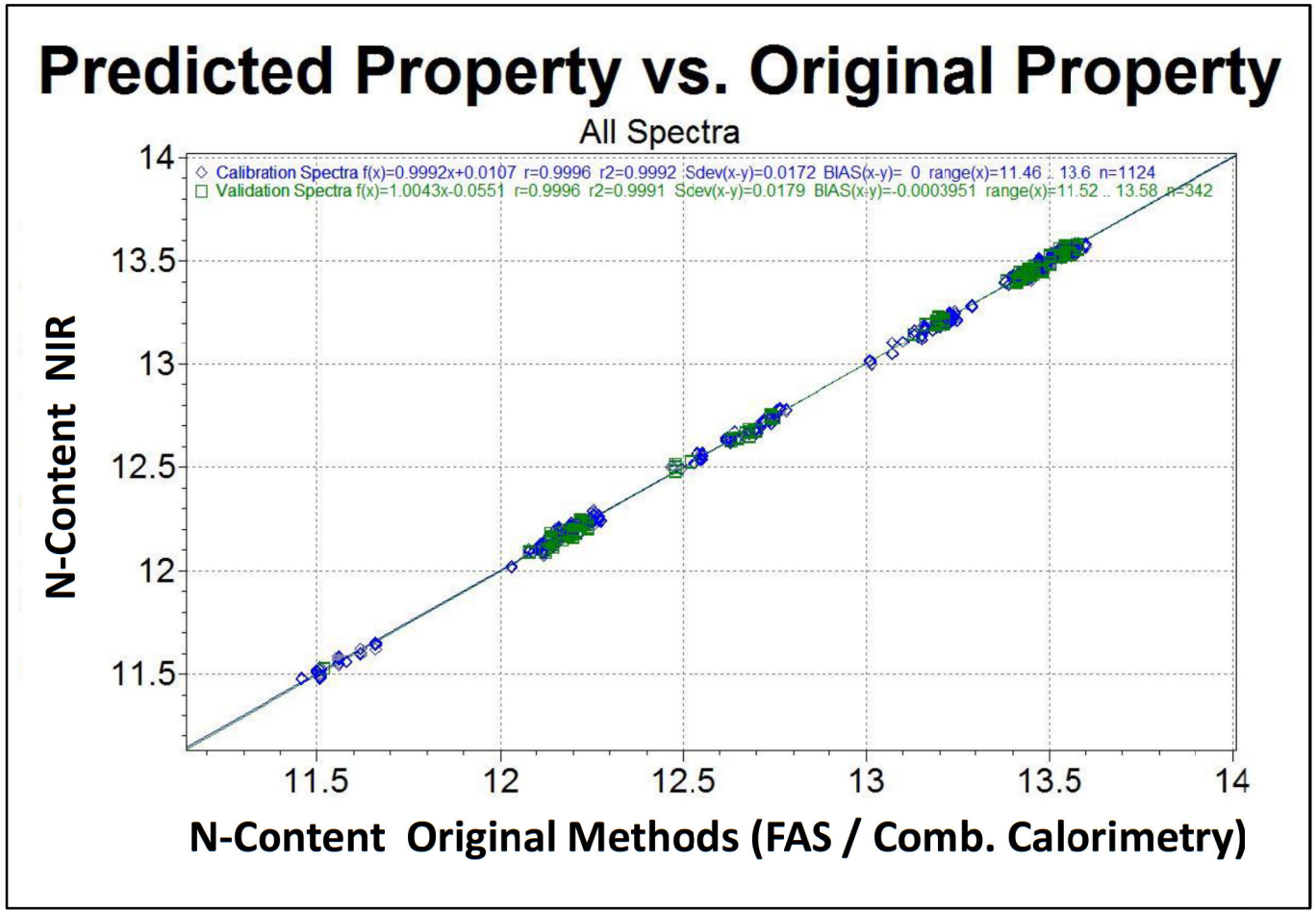
NIR Method

The Calibration

- NIR calibration model based on **251 different NC samples** (N-content 11.4% – 13.6%)
  - Most samples from recent production; different NC grades produced from different linters types using different process parameters
  - **83** samples analysed by **FAS** titration as reference method
  - **154** samples analysed by **combustion calorimetry** as reference method
  - **14** samples (from own production and other suppliers) with **additional nitrogen content results** obtained by own and other laboratories using FAS titration, Devarda's alloy method, Schulze-Tiemann and nitrogen analyzer
  - All 251 samples were first measured after drying in hot air-blower; **113** of these samples were then **re-measured with different water contents** (additional drying in oven at 100°C or vacuum oven at 60°C; equilibration at ambient)
- Using only the FAS samples would give a significantly better model, but inclusion of the less accurately determined combustion calorimetry samples turned out to be necessary in order to obtain a more robust model (also because the FAS method gave inconsistent results for two specific NC grades)

NIR Method

The Model



- **Regression coefficient R^2 = 0.9992**
- **Standard error of calibration SEC = 0.017%**
- **Standard error of prediction SEP = 0.018%**

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NIR Method

The Precision

Examiner	Prec. Type	n =	FAS	Devar-da	Schulze-Tiem.	N-Ana-lyzer	Comb. Calori.	NIR
NCW CHE	s_r	≥10	0.005	--	0.015	0.020	0.022	0.005
NCW CHE	s_r	≥40	0.007	--	--	--	0.025	0.009
NCW CHE	s_{zi}		0.006	--	--	--	0.020	0.007
Manuco FRA	s_r	?	0.015	0.010	--	--	--	0.010
Thales AUS	s_r	?	0.010	--	--	0.026	--	0.011
GD-OTS CAN	s_r	14	0.010	--	--	--	--	--
Assessment			XXXX	XXXX	XX	X	X	XXX

s_r = repeatability; sample measured n times by 1 operator within short time period (usually 1-3 d)

s_{zi} = intermediate precision; sample is regularly re-measured by different operators (over months)

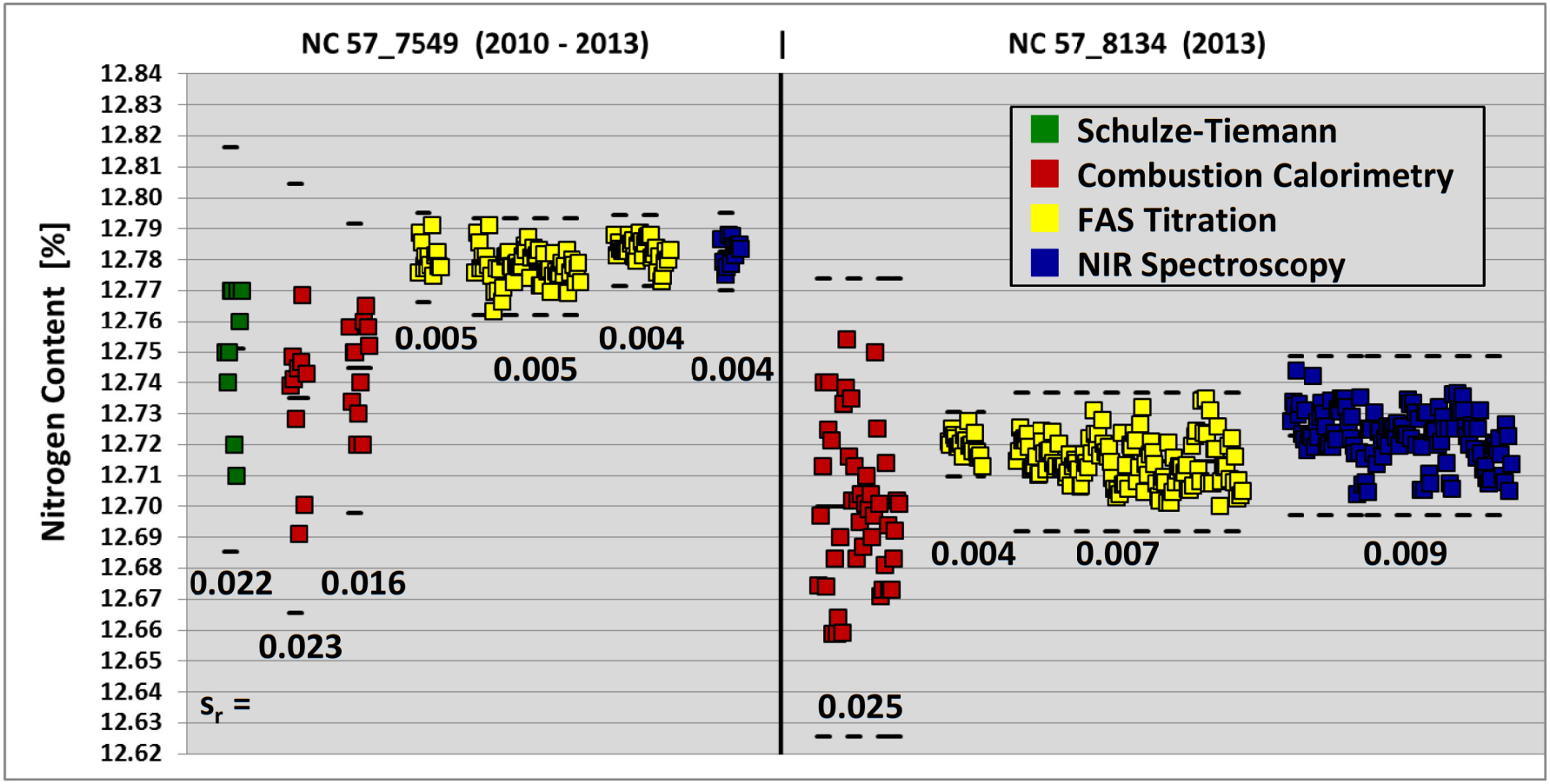
GD-OTS CAN: 8 x 14-replicates (FAS / FS; diff. electrodes; 2 operators) → s_r 0.009% – 0.014%

STANAG 4178 Ed.2: s_r (n=12) 0.010% = excellent; 0.015 = acceptable and 0.020 = marginal

Table is meant to compare methods and not labs; detailed set-up of other labs unknown

NIR Method

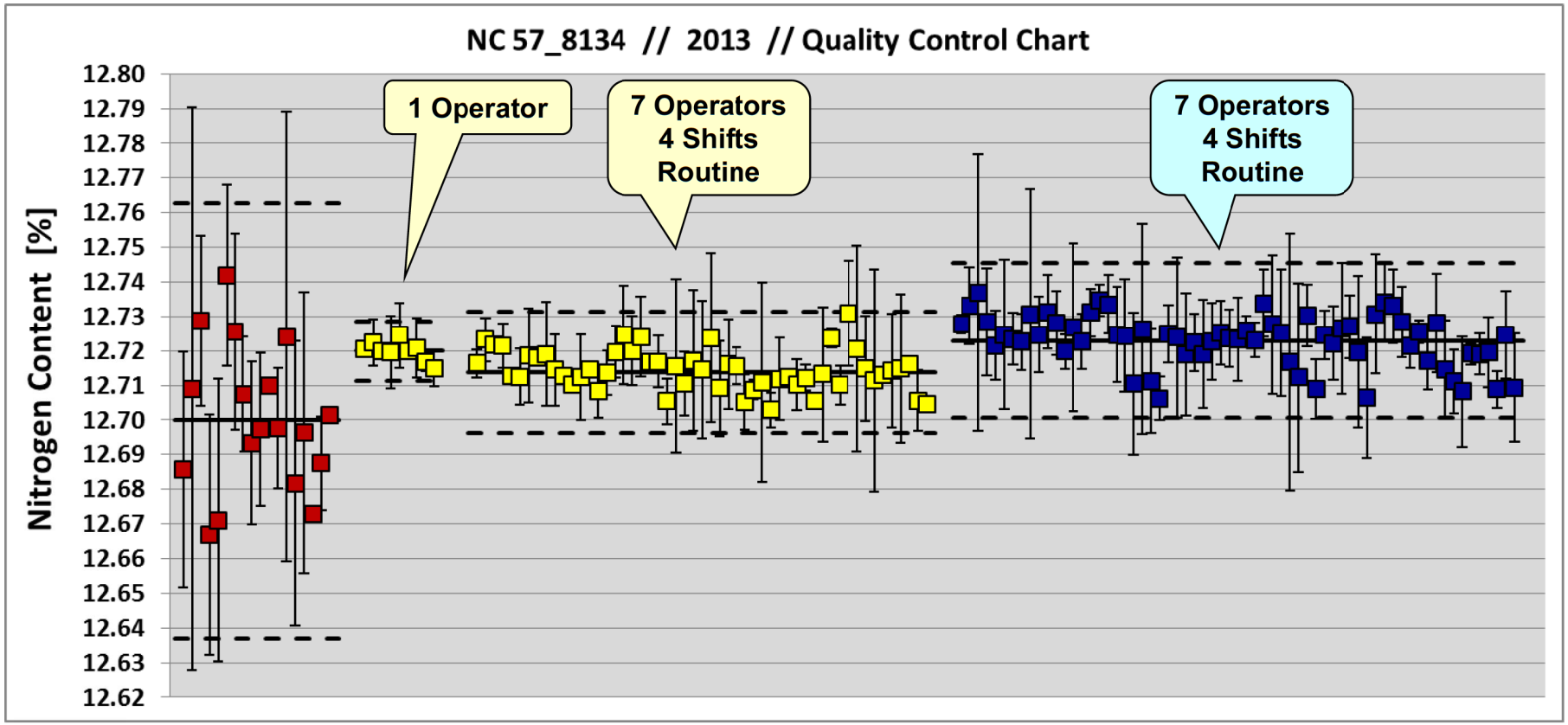
The Precision (Repeatability Precision - Quality Control Chart)



Replicates n	=	10	10	12	14	58	34	12	46	20	130	127
Operators	=	1	1	1	1	1	2	1	6	1	7	8
Period month	=	-	-	-	-	5	4	-	4	1	5	4

NIR Method

The Precision (Laboratory Precision - Quality Control Chart)

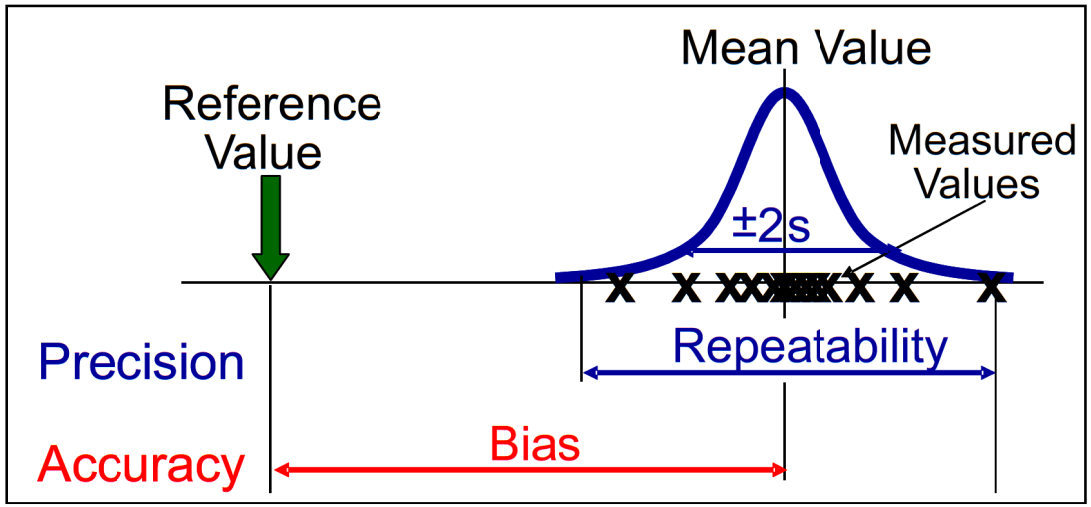


Combustion Calorimetry		FAS Method	NIR Spectroscopy
N-Content	= 12.70	12.72	12.71	12.72
s_{zi}	= 0.020	0.003	0.006	0.007
n	= 18	9	54	65

NIR Method

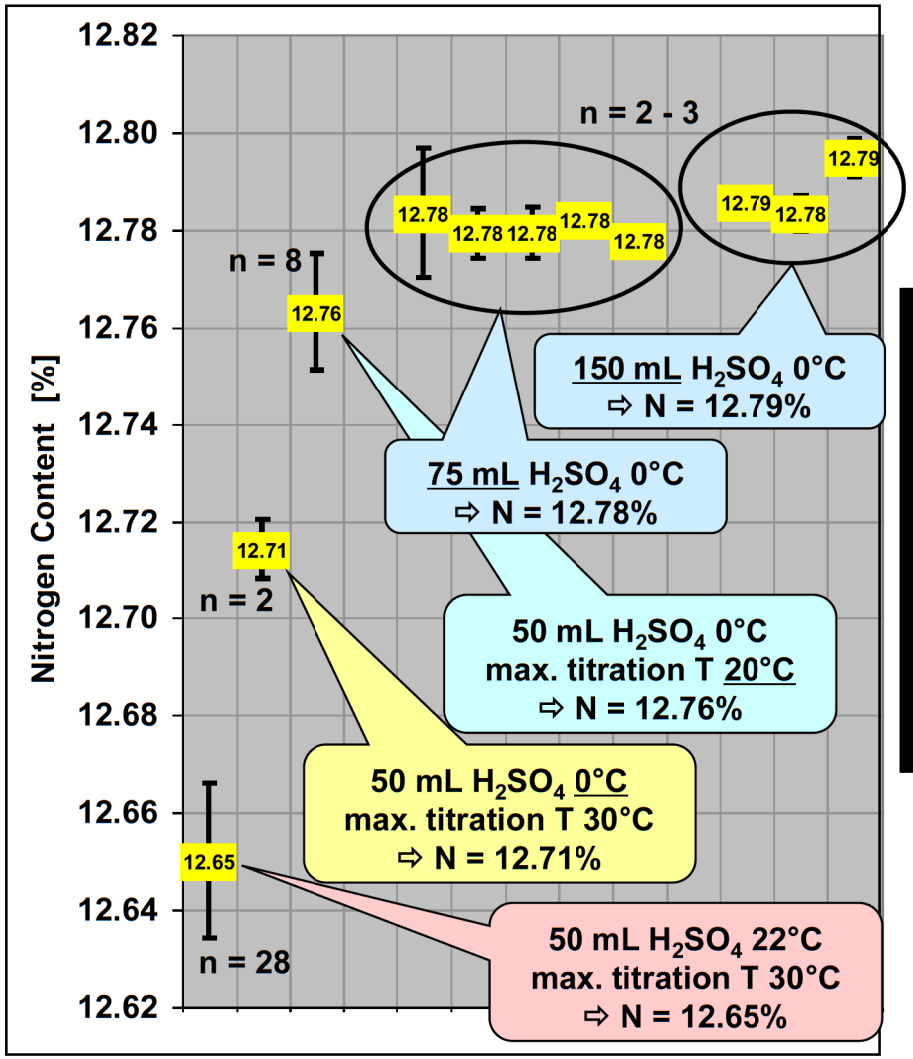
Problem of Calibration / Validation: Finding Reference Values

- **Main problem of calibration / validation is definition of N-content reference values !**
  - **NC reference material with certified nitrogen content is not available**
  - **Certified calibration reference materials are available at least for the direct methods; but these materials react differently to NC in N-content analysis**
    - **KNO_3 dissolves faster and has different titration curve / end point voltage than NC in FAS**
    - **EDTA / nicotinamide / … burn totally different to NC in Nitrogen Combustion Analyzer**
  - **Interlaboratory comparison yields differences of up to 0.10% regarding N-content**
  - **Within laboratory, different methods often differ by up to 0.05% in NC N-content**
  - **STANG 4178 Ed. 2: Alternative methods should not differ >±0.03% N from FAS/FS reference methods**
- **"Most plausible N-content" values need to be assessed for calibration / validation NC samples using all available information**

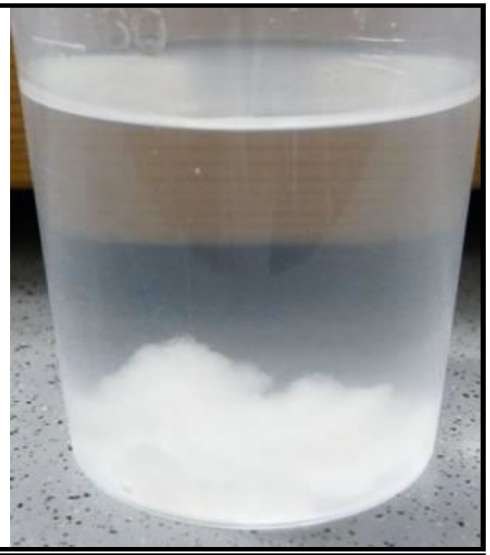


NIR Method

Problem of Validation: Uncertainty of FAS Reference Method



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

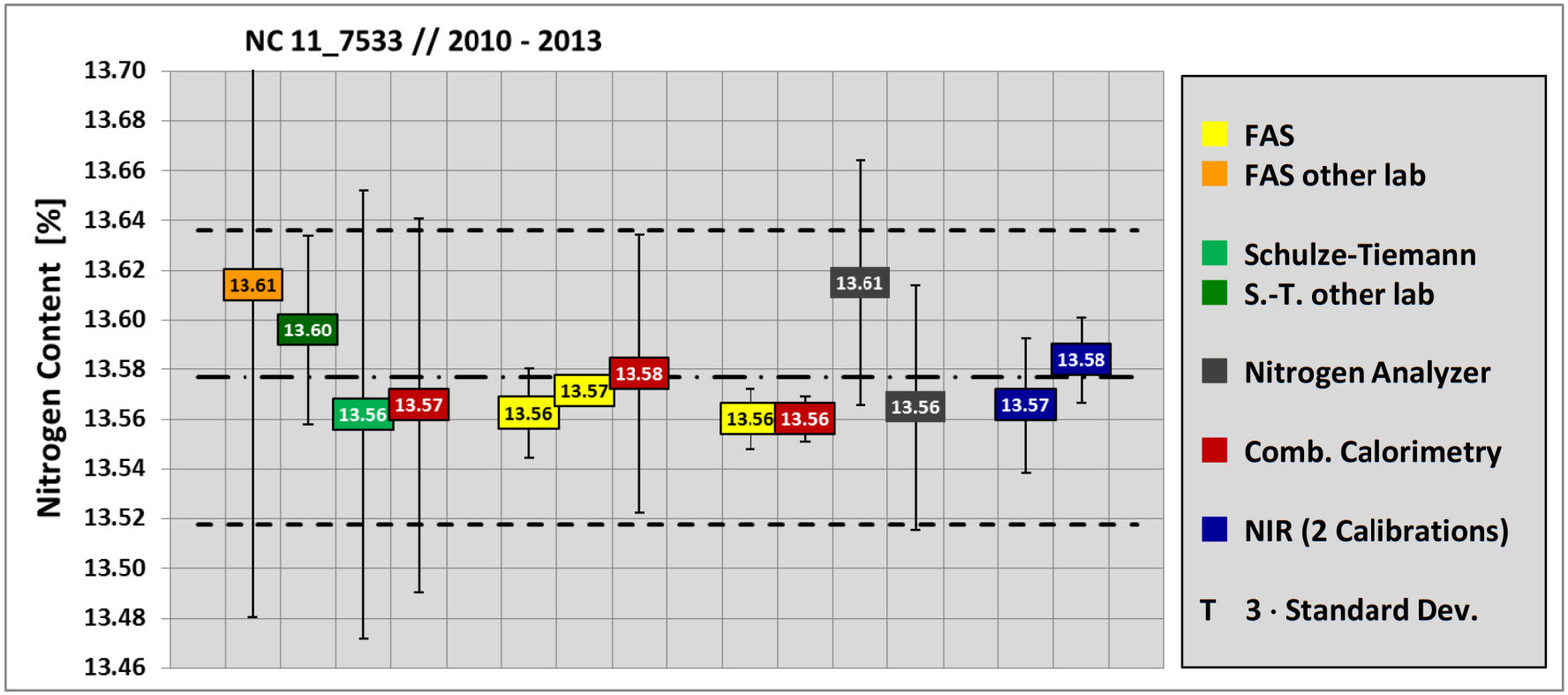


These effects seen for NC (bubbles → strong sensitivity on H_2SO_4 volume and T as well as on titration T) are almost negligible for KNO_3 calibration standard !!!

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

NIR Method

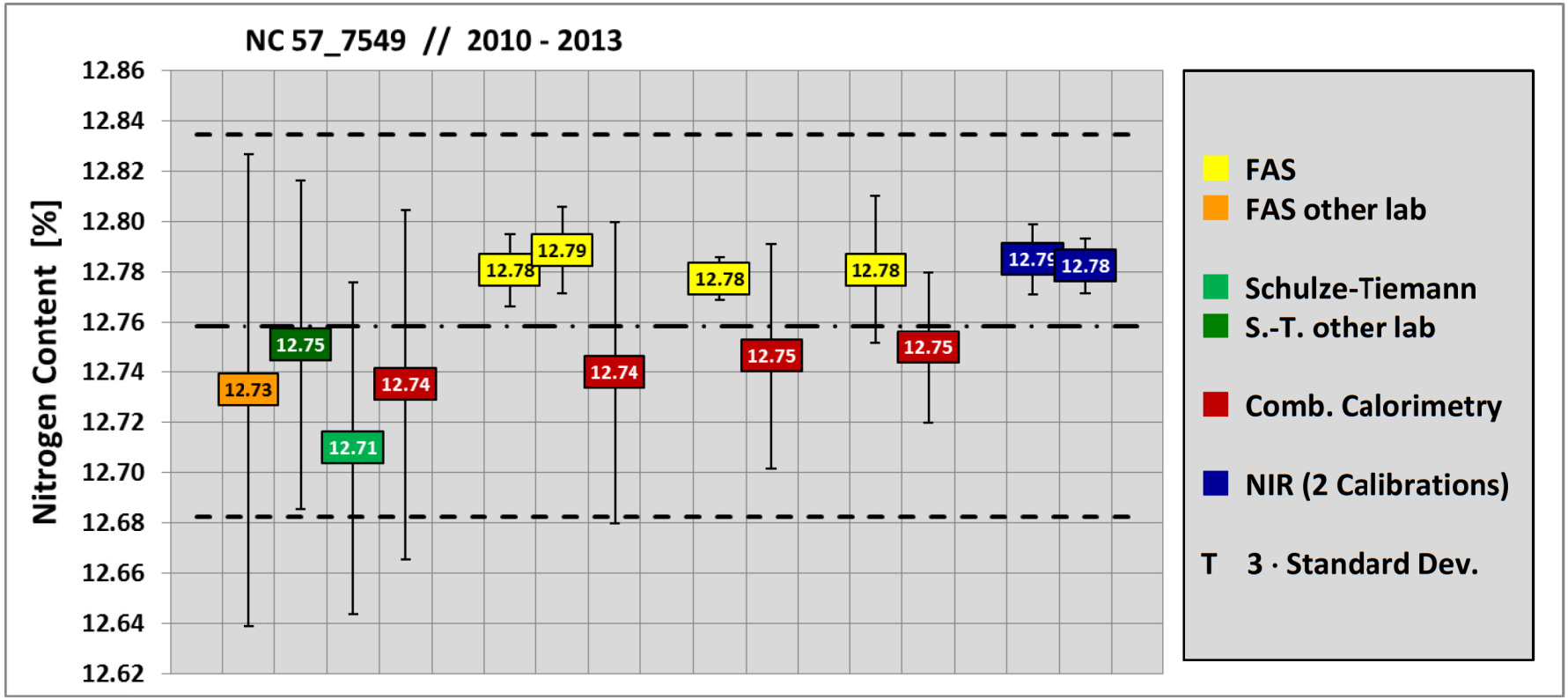
Validation – Assessing Most Plausible N-Content Value



- **Most plausible N-content values need to be assessed for validation NC samples**
  - **In this example: Mean of all test methods is 13.58% N-content; most precise FAS results are 13.56% - 13.57%; highest obtained FAS values are likely to be "true" since almost all mistakes in FAS procedure give lower N-content → most plausible N-content value is around 13.57%**

NIR Method

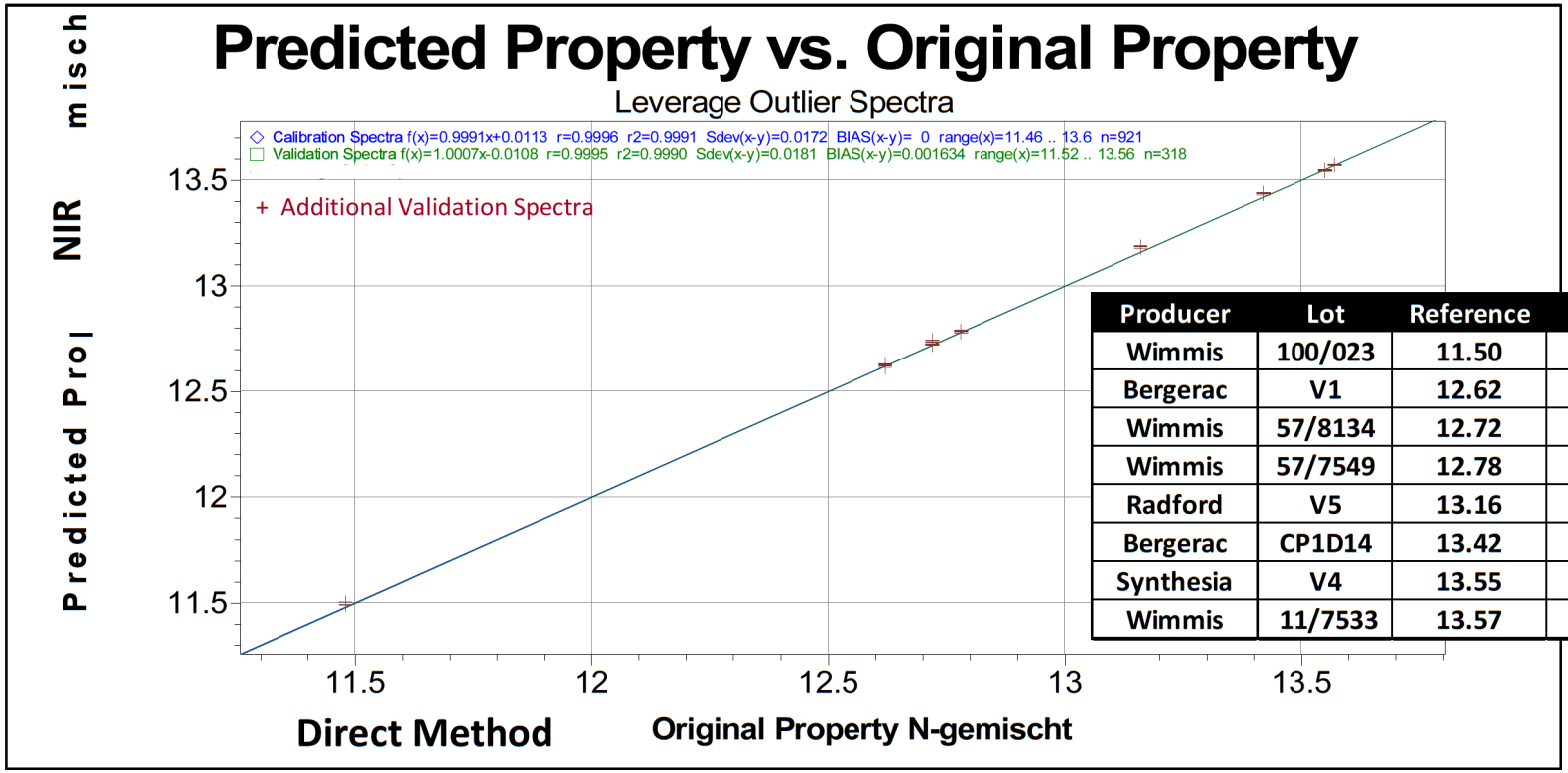
Validation – Assessing Most Plausible N-Content Value



- **Most plausible N-content values need to be assessed for validation NC samples**
  - **In this example: FAS was performed in 4 series over 3 years, >100 replicates have been measured, all of them resulting N-content around 12.78% - 12.79% → this value is most plausible, although other (less precise) methods give slightly lower N-content values**

NIR Method

The Validation



Producer	Lot	Reference	NIR	Difference
Wimmis	100/023	11.50	11.50	0.00
Bergerac	V1	12.62	12.62	0.00
Wimmis	57/8134	12.72	12.72	0.00
Wimmis	57/7549	12.78	12.79	0.01
Radford	V5	13.16	13.19	0.03
Bergerac	CP1D14	13.42	13.44	0.02
Synthesia	V4	13.55	13.55	0.00
Wimmis	11/7533	13.57	13.57	0.00

- **Excellent agreement between NIR result and "most plausible N-content" values as obtained using several different methods" is found; this for all validation samples**

NIR Method

The Quality Control Protocol

Quality Control Protocol to verify NIR performance:

- **Daily NIR performance check:**
  - **A known NC sample is measured prior to each series of measurements; N-content value of this sample is monitored by means of a quality chart**
- **Weekly NIR performance check:**
  - **Once per week, at least 2 different NC samples from actual production are subjected to parallel analysis by NIR and primary method (FAS titration)**
- **Additional NIR performance check after changes in raw material or process:**
  - **Each NC type with potentially different properties / fibre texture (e.g. NC produced from new grade / new lot of cellulose; alterations of production process; …) needs to be parallel analysed by NIR and primary method, followed by adding to the NIR model, before being cleared for routine NIR analysis**

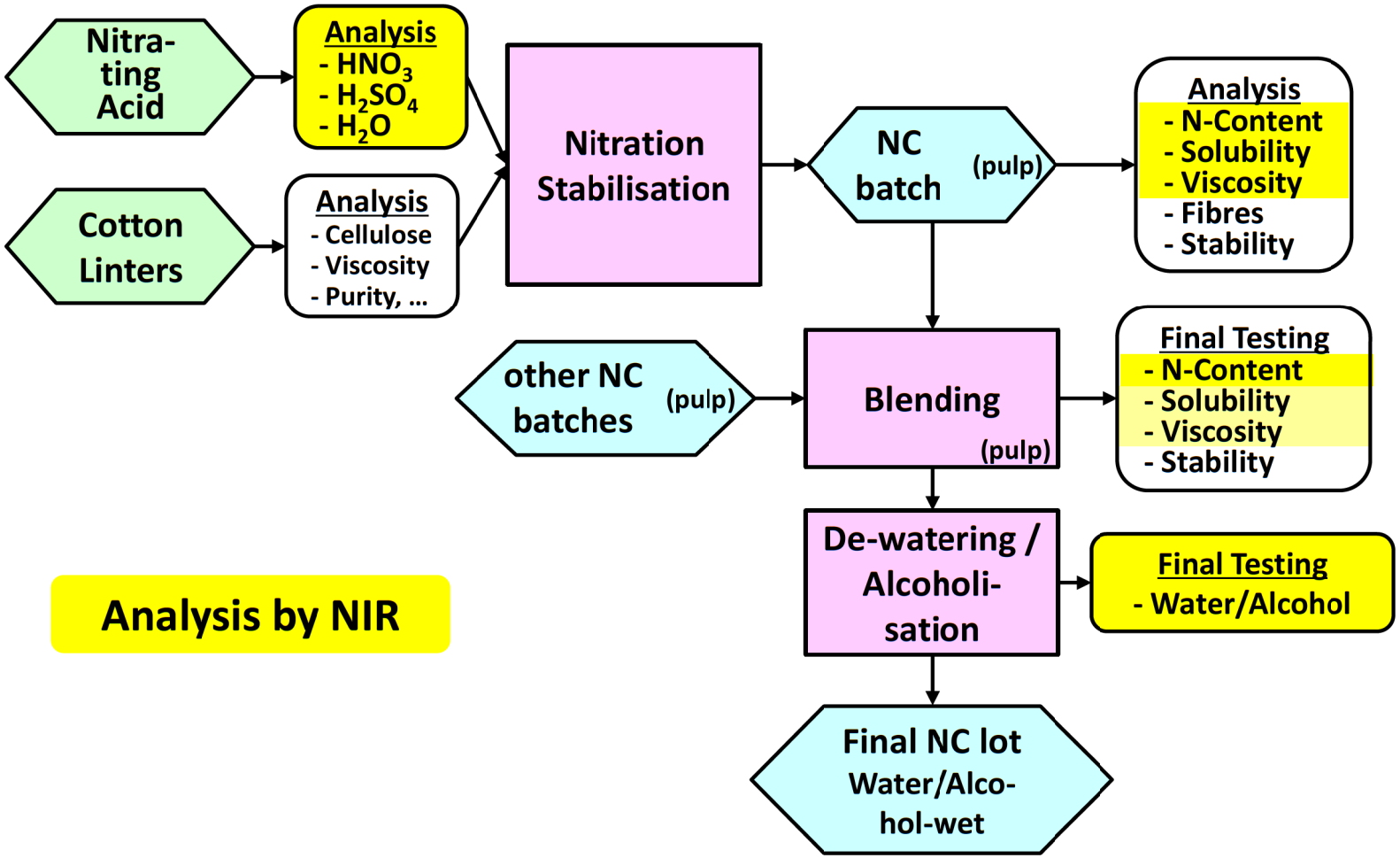
NIR Method

Summary and Conclusions

- **Advantages of NIR method**
  - Much shorter analysis time (10 minutes for duplicate analysis !)
  - High precision and reproducibility of results → more stable NC production
  - 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
  - Other features of the NC such as fibre texture or surface constitution might influence result unless included in calibration
  - Method not yet standardized
- **The suitability of the NIR method for NC N-content determination is thus verified**
  - NIR method needs to be added to STANAG 4178 at the next revision

NIR Method

Outlook – Further Applications of NIR in Nitrocellulose Production



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Thanks very much for your attention !