Analysis of Nitrating Acids by Near Infrared Spectroscopy

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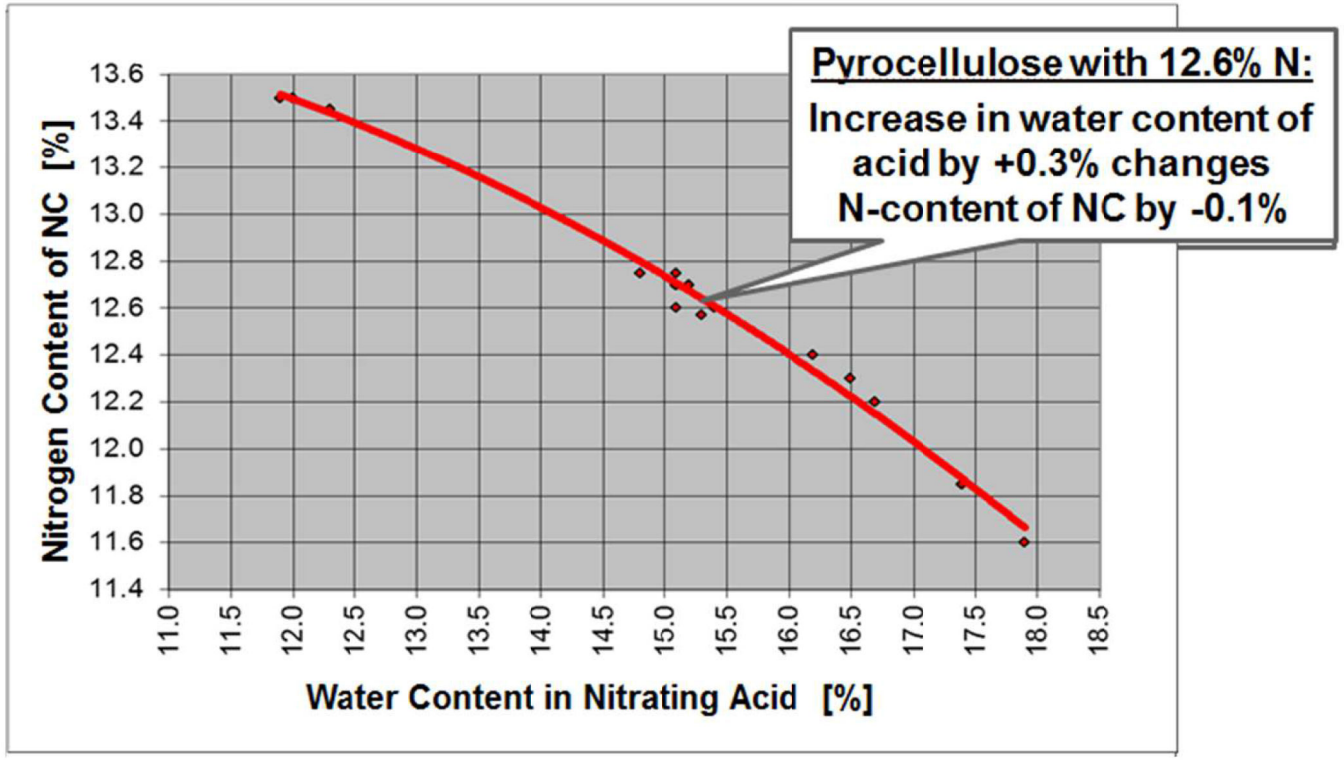
Nitrating Acid Composition - Nitrocellulose

The total nitrogen content of the produced Nitrocellulose is very dependent on the chemical composition of the nitrating acid ➔increasing the water content by 0.3% will reduce the nitrogen content in the final NC by 0.1%



Nitrating Acid Composition - Nitrocellulose

Accurate and reproducible measurement of the nitrating acid content is essential!

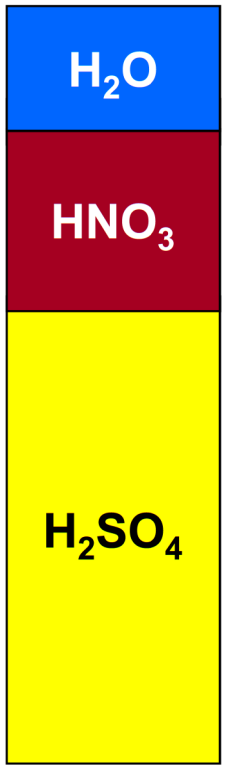
The reproducibility of nitrating acid analysis needs to be within 0.1 to 0.2% water content

➔challenging task using conventional methods

Nitrating Acid Analysis: Lab Method

<u>Traditional nitrating acid analysis</u> is based on duplicate measurements of

- ***total acid*** **content by potentiometric acid-base titration**
- ***sulphuric acid*** **content by evaporation of nitric acid in a sand bath, followed by potentiometric titration**
- **calculation of *nitric acid* from the above results**
- **calculation of *water* content as difference to 100%**

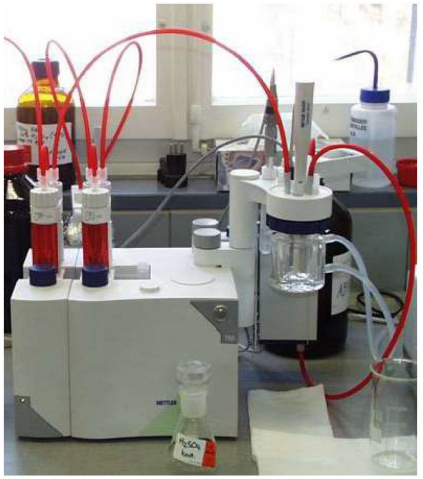


This method is

- **time-consuming (approx. 2 hours)**
- **prone to experimental errors**

Precision in water content determinations: 0.1 % (0.2 to 0.3%)

Nitrating Acid Analysis: Possible Methods



Redox titration (with ferrous ammonium sulphate in concentrated sulphuric acid): determination of the *nitric acid*, in addition to the measurement of *total acid*.

This method is:

- faster,
- requires additional titration equipment
- still prone to imprecision due to experimental error

Attempts by either non-aqueous titration or by ion chromatography could not meet the precision requirements.

Direct Karl-Fischer titration produces systematic errors of up to 6% for *water* due to the esterification of the Karl-Fischer solvent with *sulphuric acid* for which water is a by-product.

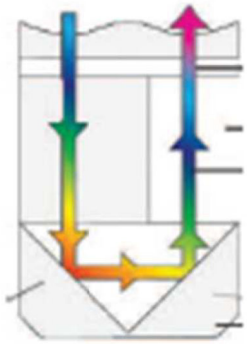
Nitrating Acid Analysis: NIR Method

A Near InfraRed method for fast and simultaneous analysis of all three components in nitrating acid has been developed

The method is based on direct measurement of acids with

BUCHI NIRFlex N-500

Hellma all-quartz Probe

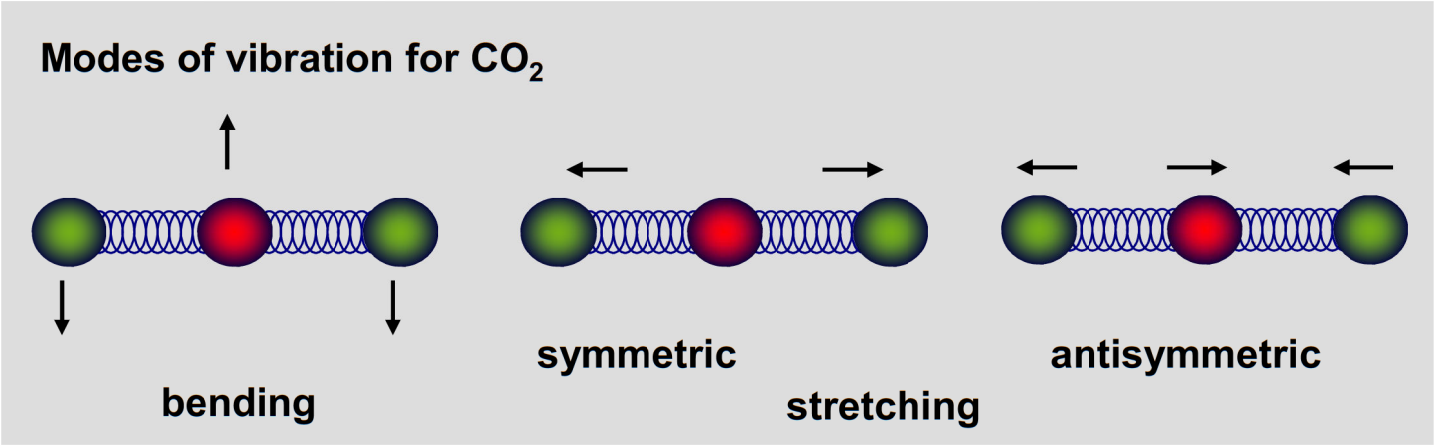


Thickness: 1 mm

Transmittance

Near Infrared Spectroscopy

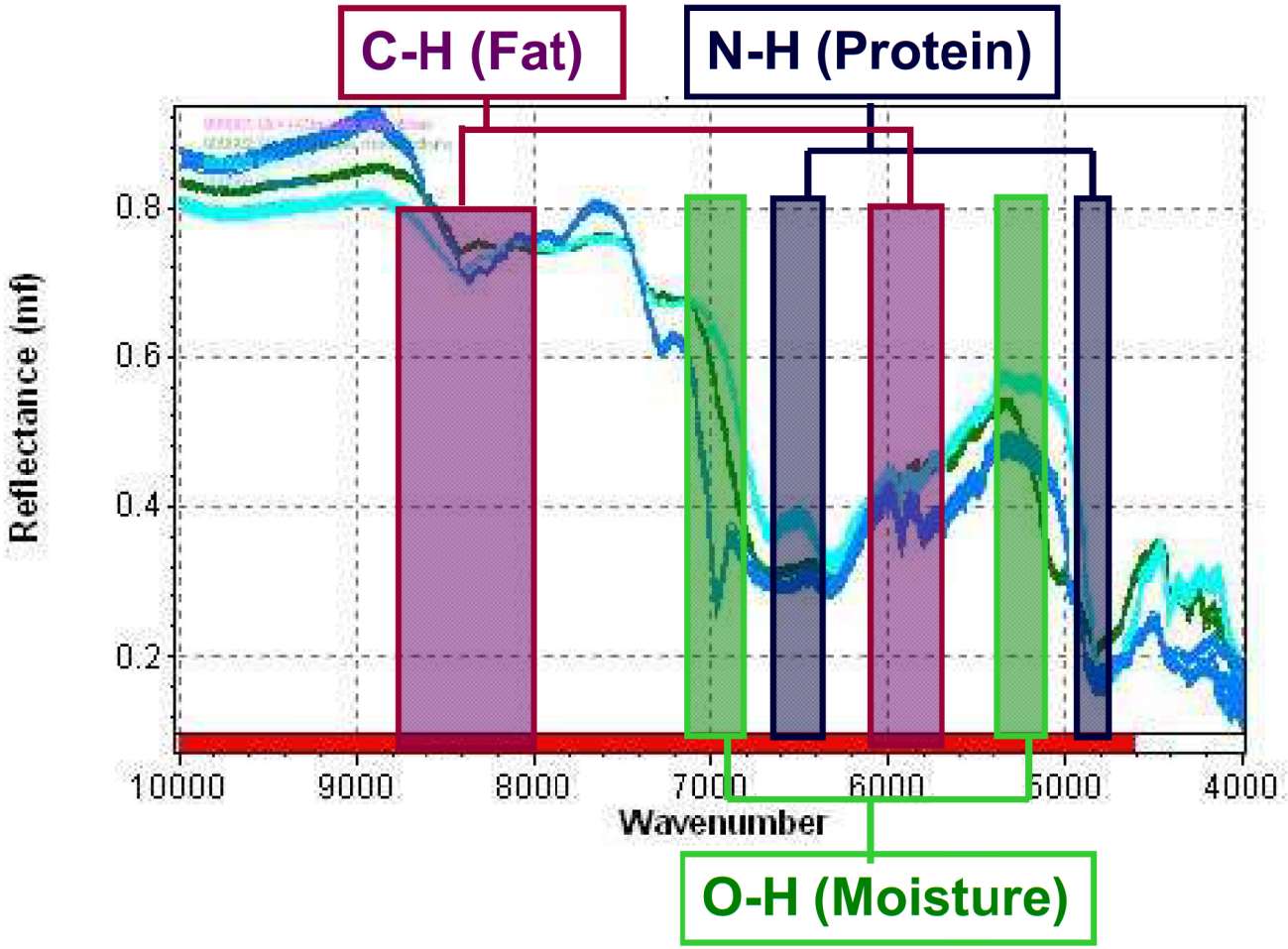
Near Infrared spectroscopy is a form of vibrational spectroscopy



- **The NIR method is very selective and specific**
- **Spectra can be regarded as a „fingerprint“ of the molecules**

Near Infrared Spectrum

NIR	λ = 780 to 2500 nm	(12.800 to 4.000 cm^{-1})
NIRFlex	λ = 1000 to 2500 nm	(10.000 to 4.000 cm^{-1})



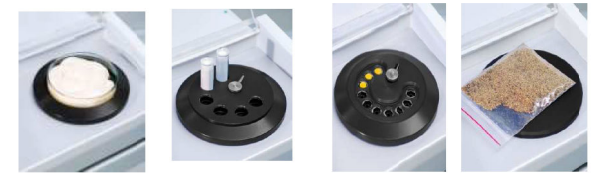
Advantages of NIR Spectroscopy

- Easy sample prep
- No specific qualitative information
- Weak molecular ID ability
- Water is non interfering
- Strong quantitative ability
- Good fiber optics interface

- Easy sample prep
- Specific qualitative information
- Strong molecular ID ability
- Water is non interfering
- Strong quantitative ability
- Good fiber optics interface

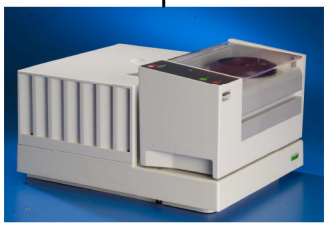
- Difficult sample prep
- Specific qualitative information
- Strong molecular ID ability
- Water interferes
- Moderate quantitative ability
- Difficult fiber optics interface

NIRFlex N-500 Polarisation Interferometer



Petri Dish Vials Tablets XL (e.g. bags)

NIRFlex N-500



Solids

Fiber Optic Solids

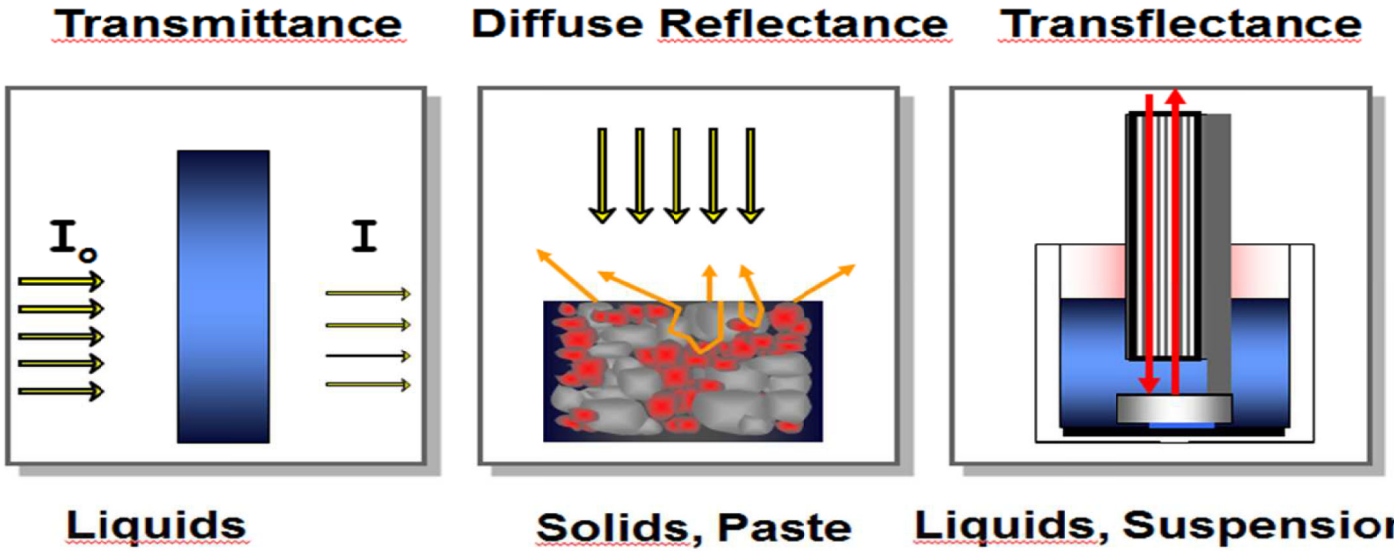
Fiber Optic Liquids

Liquids

Fiber Optic SMA

NIR Spectroscopy

- Easy measurement of Solids/ Liquids / Suspension



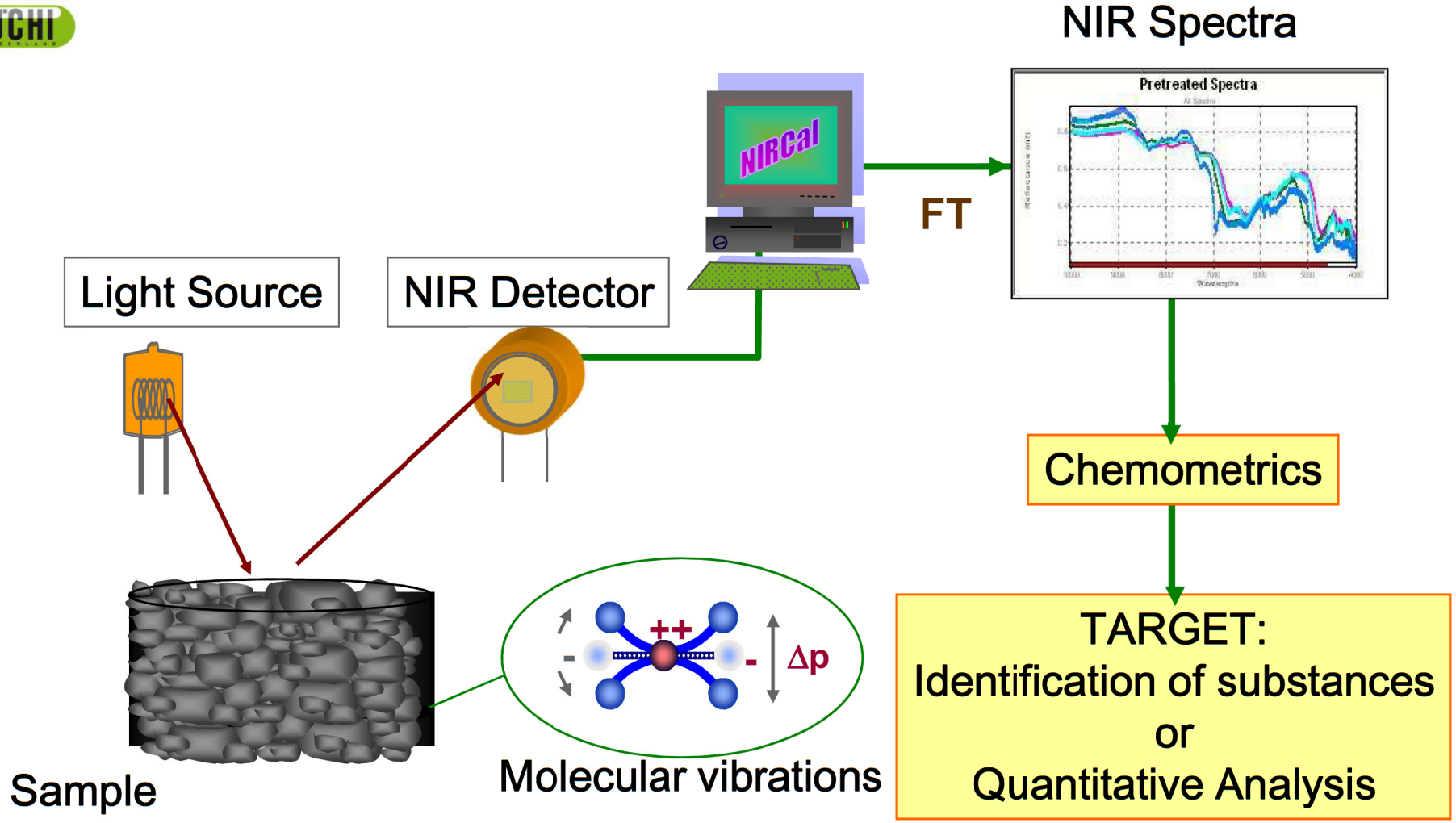
- The absorption bands are very broad and often overlapping

➔ Problems with direct interpretation of the spectra

- Solution: Chemometrics

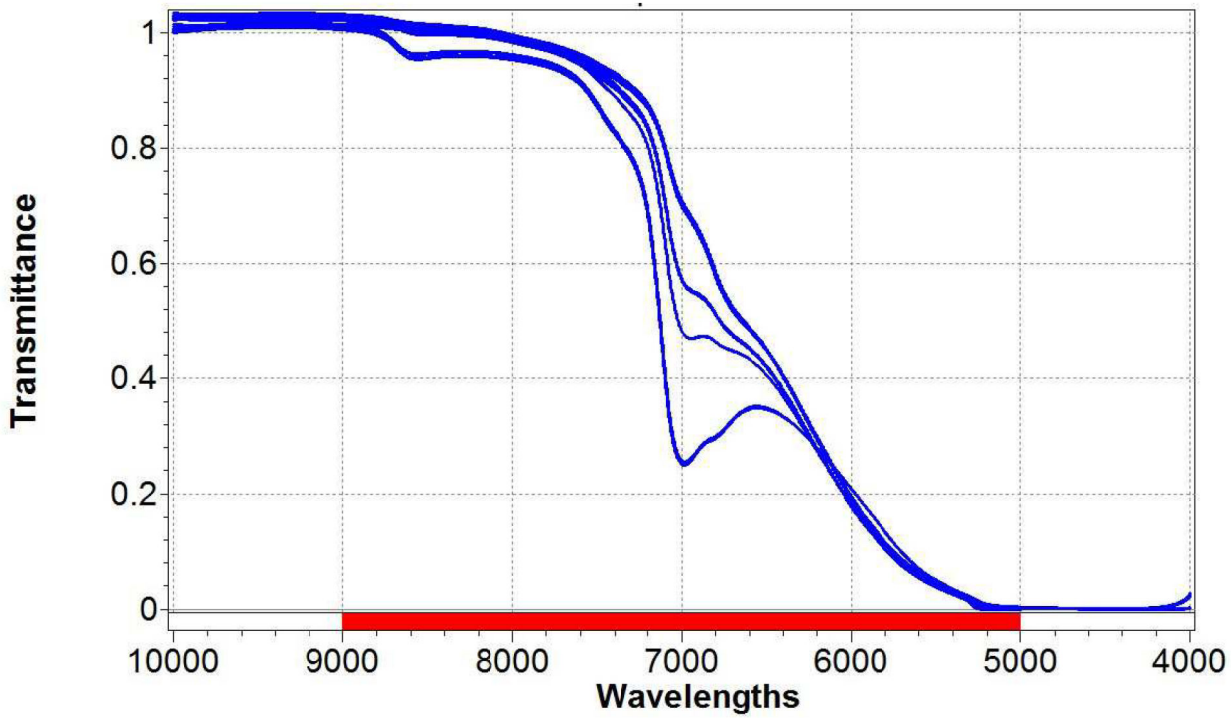
- NIR is a secondary method ➔ calibration is necessary

Near Infrared Measurements



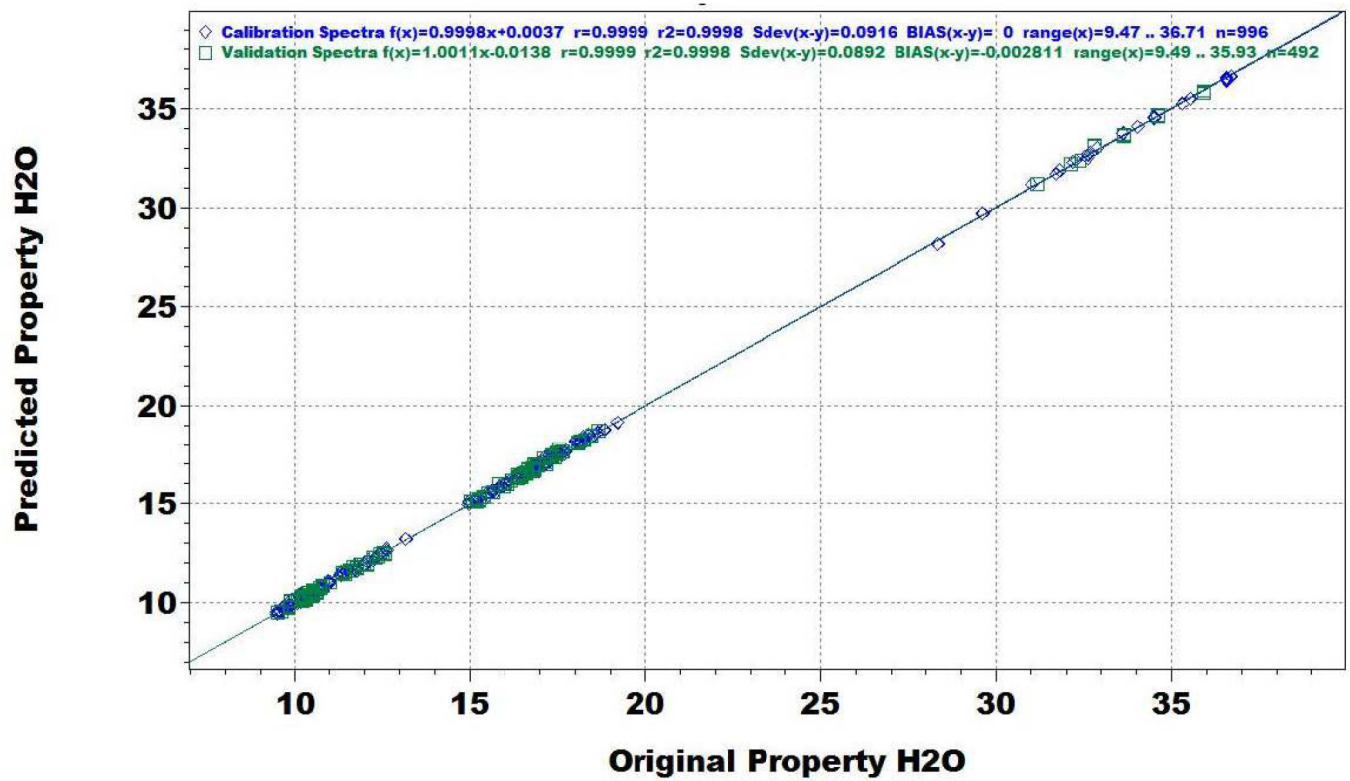
NIR Measurement: Water Content

Nitrating acids were measured by both the classic titration method and NIR during 3 months ➔ NIR Spectra



The absorption band at 6.897 cm^{-1} (–OH st. first overtone) had the greatest contribution to the water content (10-15-20-35 %)

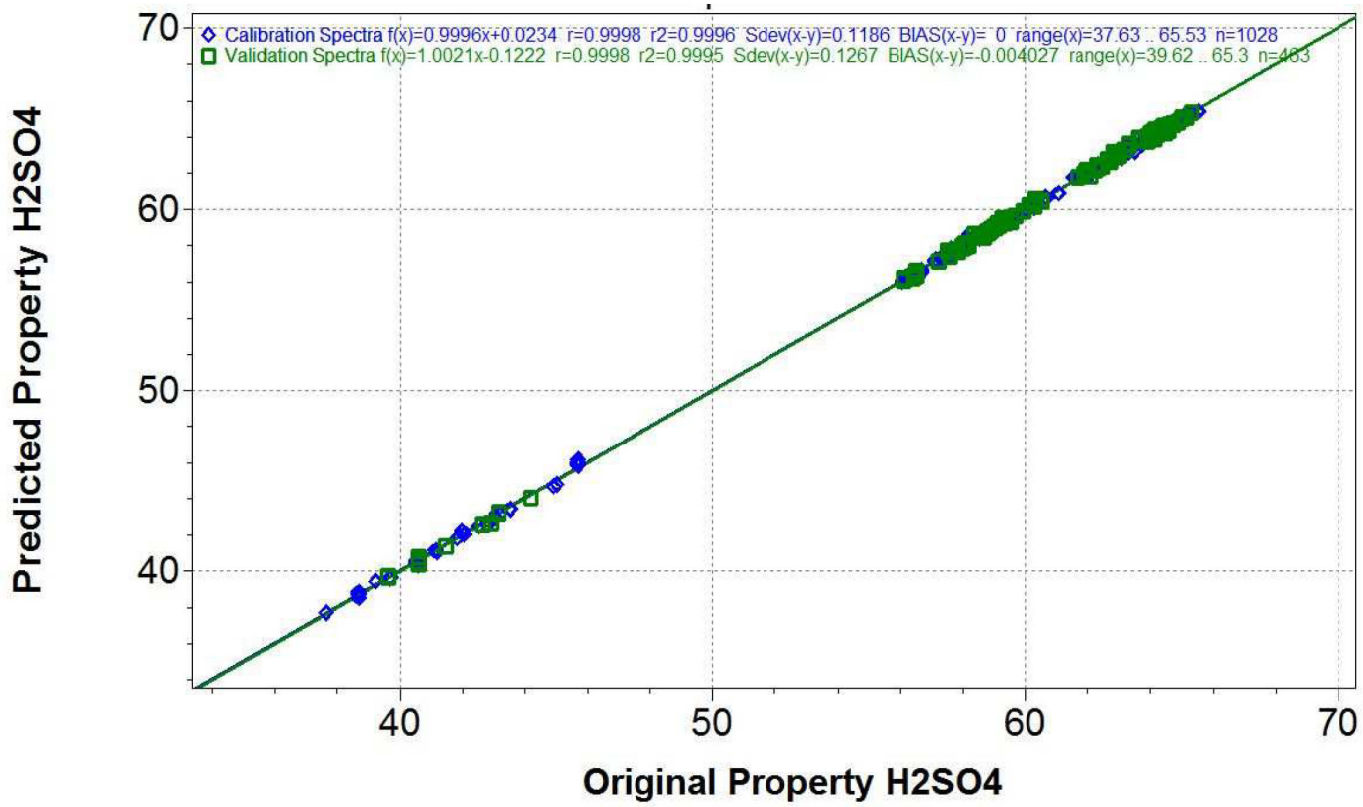
NIR Calibration: Water Content



Regression Coefficients: **0.99**

Standard deviations: **0.1 %**

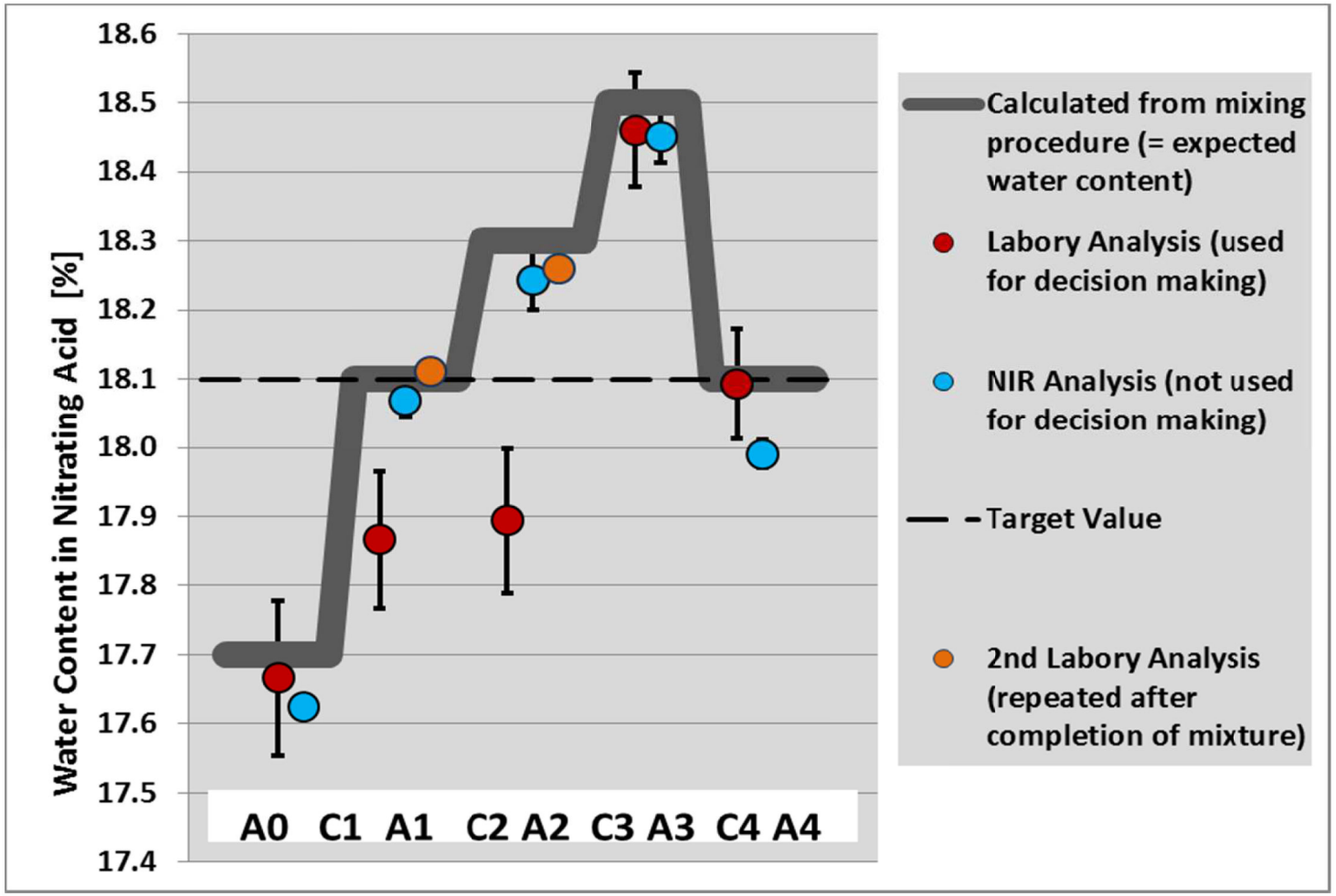
NIR Calibration: Sulphuric Acid Content



Regression Coefficients: **0.99**

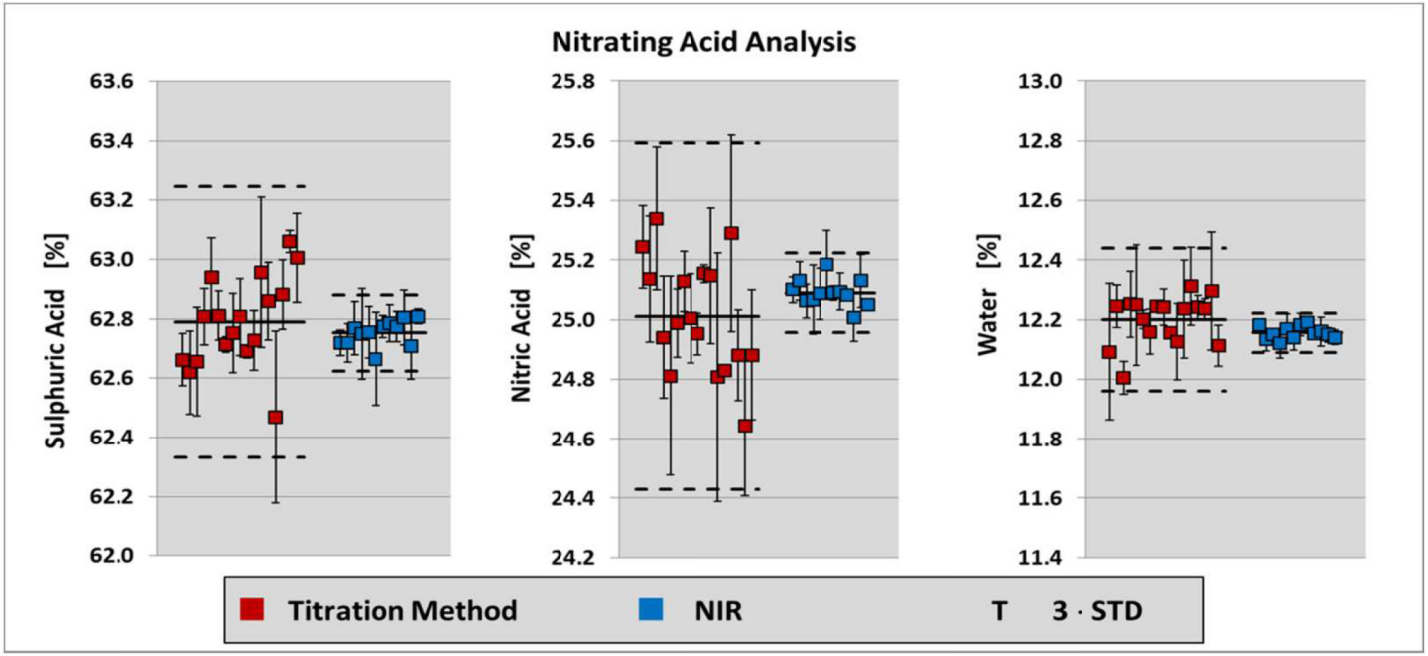
Standard deviations: **0.13 %**

Lab vs. NIR Results –Test Period



Target value: 18.1 % water

Reproducibility of Lab vs. NIR Method



Titration: 17 analyses by 8 different operators
NIR: 12 analyses by 6 different operators
Each analysis was performed in duplicate

➔ **Better reproducibility of the NIR method is evident**

NIRFlex for Nitrating Acid Analyses

Advantages of the NIR

- **Fast:** almost no sample preparation - results obtained within seconds
- **Versatile:** simultaneous determination of several parameters
- **Easy:** extremely user-friendly routine
- **Economical:** reduces operating expenses
- **Efficient:** more analyses from a batch per time
- **Safe:** no chemical reactions, no chemical waste

NIR Analysis of Acids by Nitrochemie Wimmis

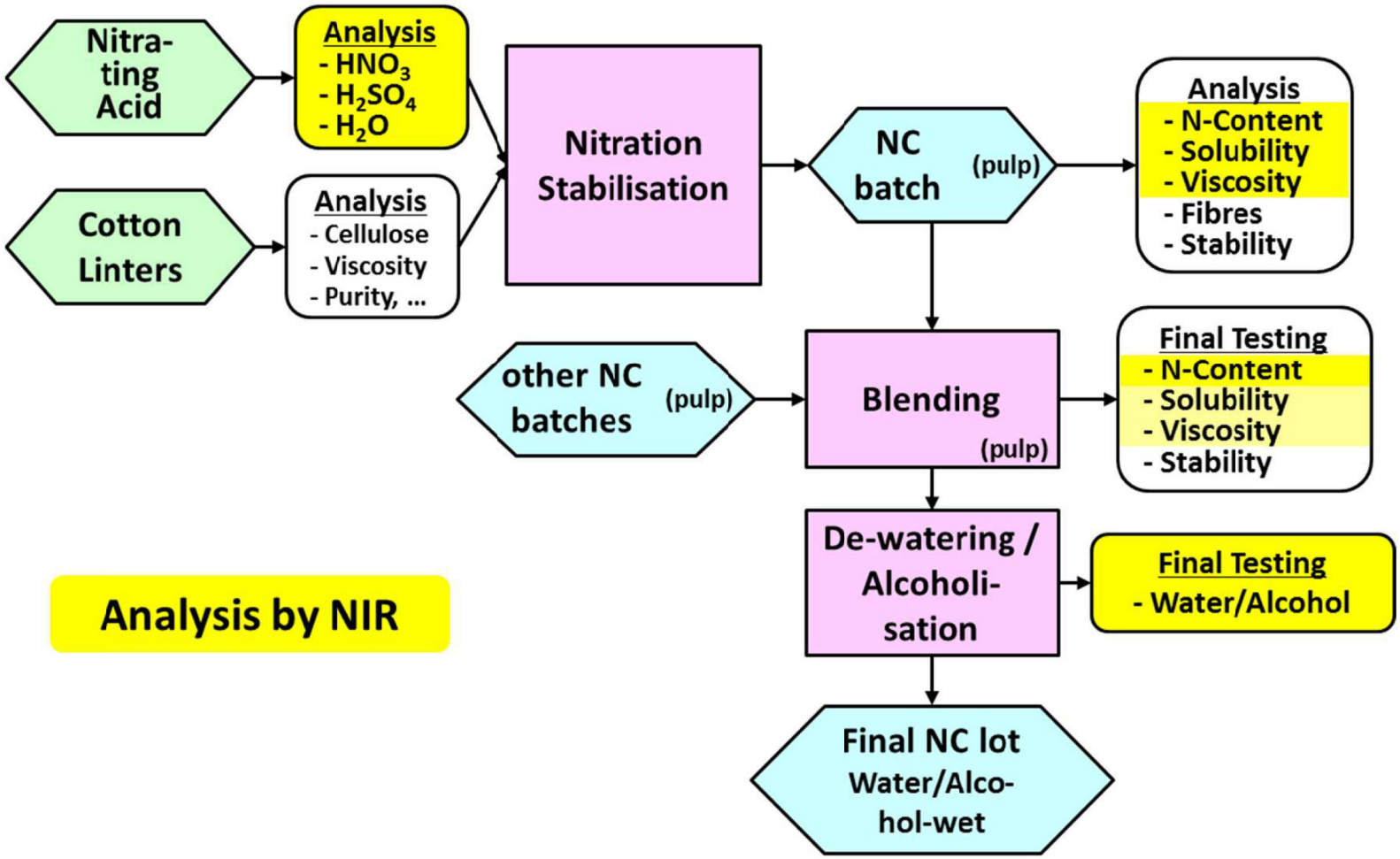
The NIR acid analysis method resulted (routine over 9 months):

- **shorter response times and more analyses from a batch**
- **significant reduction of workload for laboratory technicians**

➔ better process and product control in the nitration plant

A quality control protocol consisting of at least weekly parallel analysis of several nitrating acids by NIR and classic titration method ensured constant NIR performance

Further NIR Applications in NC Production Process



Thank you for your attention!

MERCI!

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Marc Müller