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# Stability Testing of Nitrocellulose

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- Introduction / Established stability tests
- Correlation of the different stability tests
- Possible new methods
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# Introduction

Stability testing of nitrocellulose is essential in order to avoid or at least to reduce safety-relevant incidents during storage and use of this energetic compound.

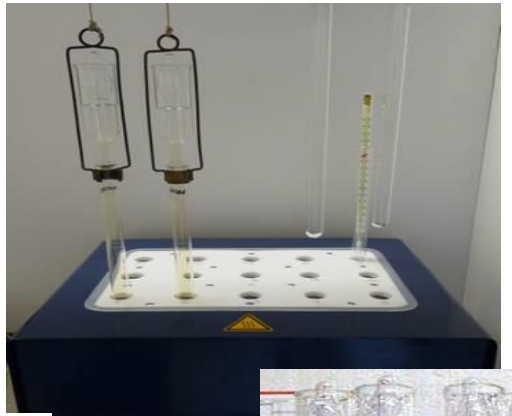
According to NATO Standard STANAG/AOP-4178, stability of nitrocellulose can be tested by any of the three following methods:

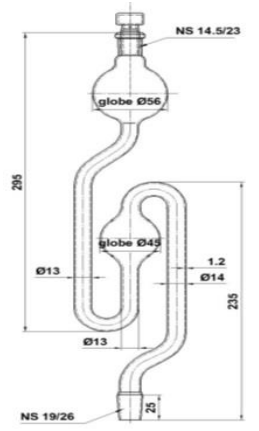
- 132°C Bergmann-Junk Test (BJ)
- 132°C Bergmann-Junk-Siebert Test (BJS)
- 134.5°C Heat Test (‘Methyl Violet Test’ MV)

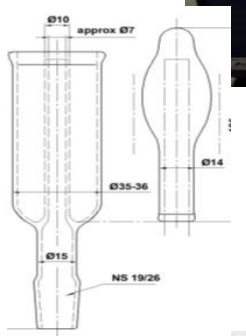
# 132 °C Bergmann-Junk Stability Test and Bergmann-Junk-Siebert Test

In the 132 °C Bergmann-Junk Stability Test, the sample is heated for 2 hours at 132 °C, followed by assessment of the evolved and collected nitrogen oxides by acid/base titration

- **Test 5A:** Direct Titration Method; easier and more precise variant, not applicable to chalked nitrocellulose
- **Test 5B:** Back Titration Method; more elaborate variant, corrects for influence of chalk; thus applicable to all types of nitrocellulose
- **Test 5C:** ***Bergmann-Junk-Siebert Test*** variant (German variant); similar to Test 5A, but uses different set-up (e.g. globes filled with $H_2O_2$ solution instead of cups filled with water to collect the nitrogen oxides)






# 134.5°C Heat Test ("Methyl Violet Paper Test")

**Test procedure**:

- NC sample is filled into test tube
- A piece of methyl violet test paper is attached at top of tube
- Tube is heated to 134.5°C
- Nitrogen oxides released from heated sample react with paper
- The time until the color of the paper has changed completely into salmon pink gives an indication of the stability of the NC
- Time to discoloration should be ≥ 30 minutes

**Test method is easy to perform and fast**

# 134.5°C Heat Test ("Methyl Violet Paper Test")

Test results are only semi-quantitative, because

- observation of discoloration of test paper is subjective
- quality of heat test paper varies between different suppliers and changes over storage time
  (this problem has been reduced as MIL-DTL-244C contains a procedure to prepare and certify heat test papers)

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# Comparison measurement of 132 °C BJ , 132 °C BJS, and 134.5 °C MV

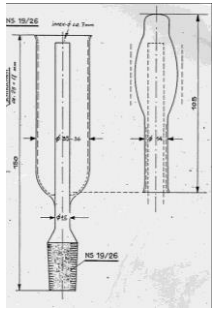
- **Certified test papers** according to MIL-DTL-244C have been used *(produced and generously offered by GD-OTS Canada to support this study)*
- **Parallel measurements of different NC types** have been performed
- **Good correlation** of all three methods
  - All methods have shown the significant improvement in stability due to the stabilization process of guncotton during production
- The **most demanding test is the BJ test**
  - The samples that narrowly failed the 132 °C BJ test (2.5 – 2.7 mL NO / g NC) just passed both the 132 °C BJS and the 134.5 °C MV tests

**Main difference between BJ and BJS:**

**Bergmann-Junk:**

**Beaker filled with 25 ml water**

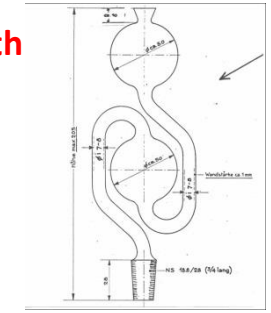
**15 mm immersion depth of the tubes**



**Bergmann-Junk-Siebert:**

**Glass sphere filled with 50 ml $H_2O_2$ 3%**

**20 mm immersion depth of the tubes**



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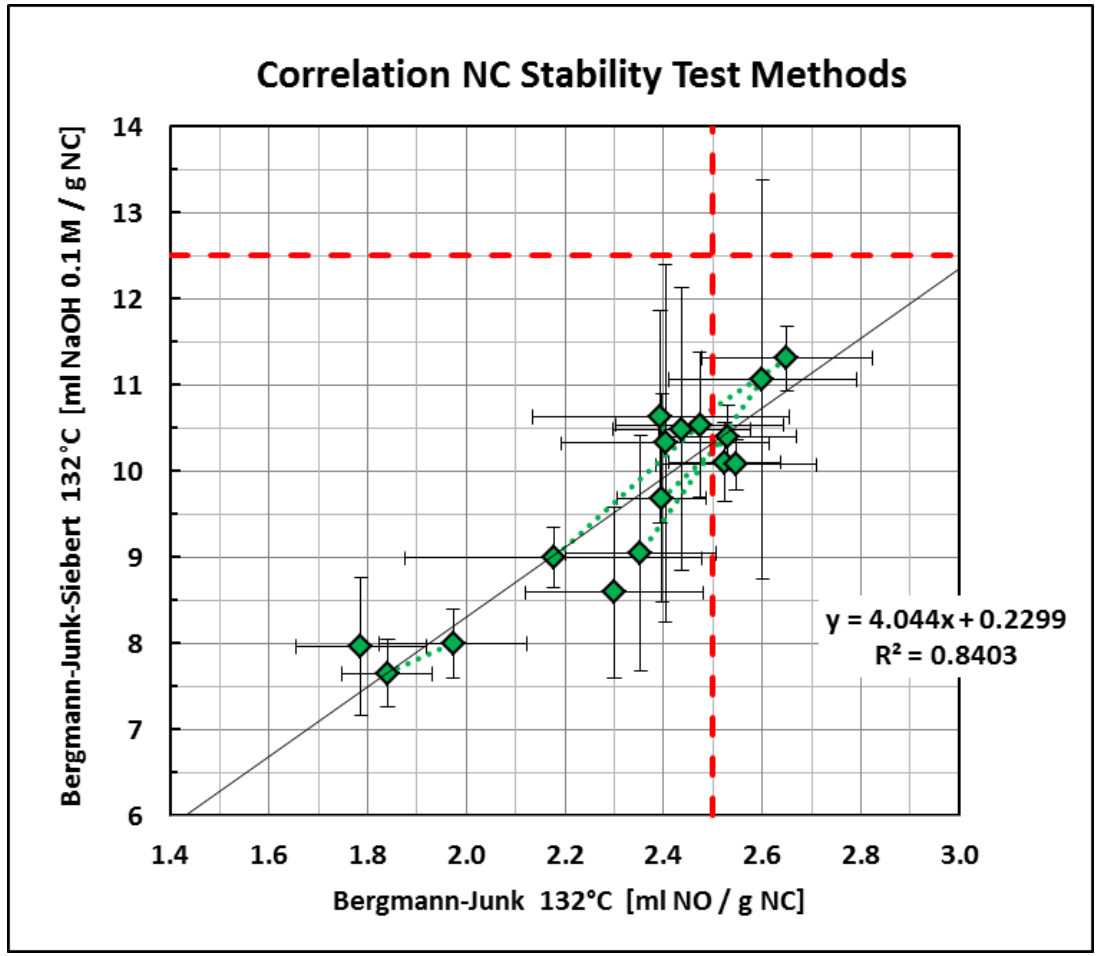
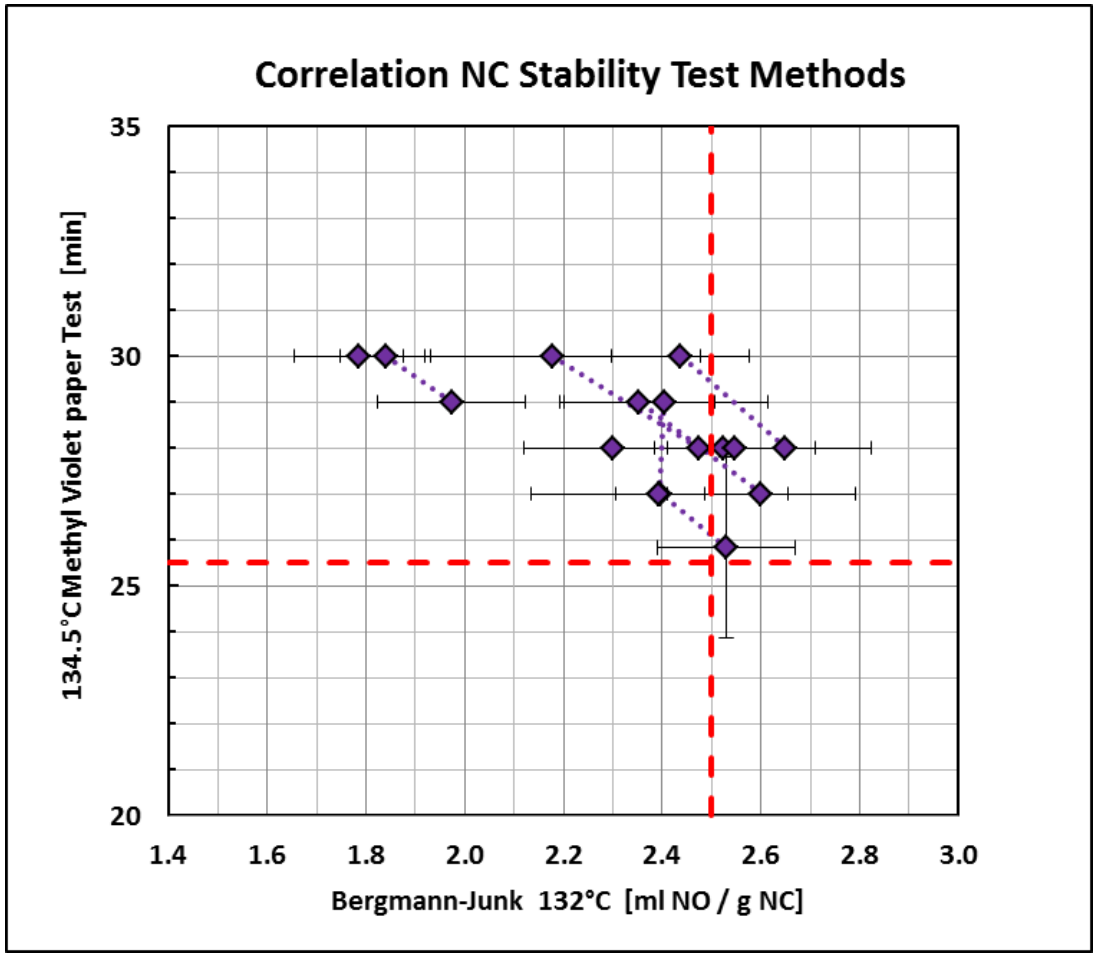
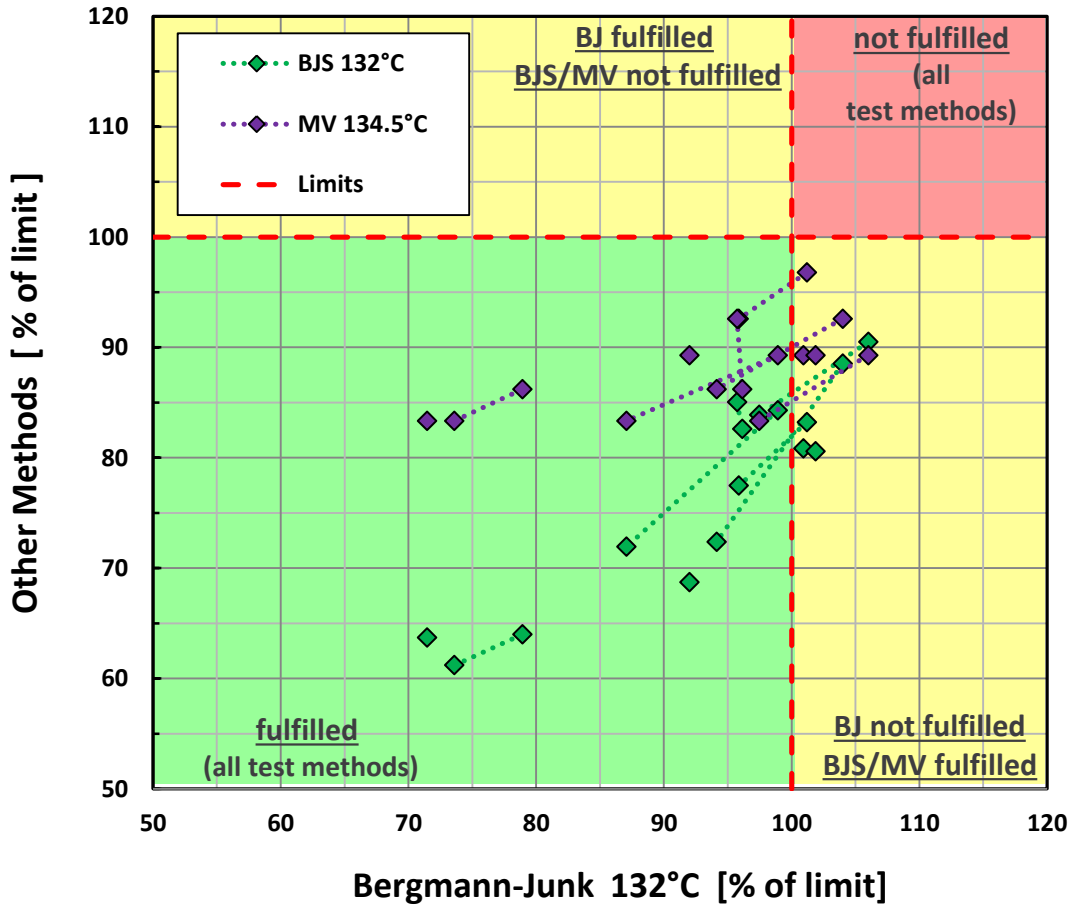


# Correlation of 132 °C BJ vs. 132 °C BJS and 134.5 °C MV tests



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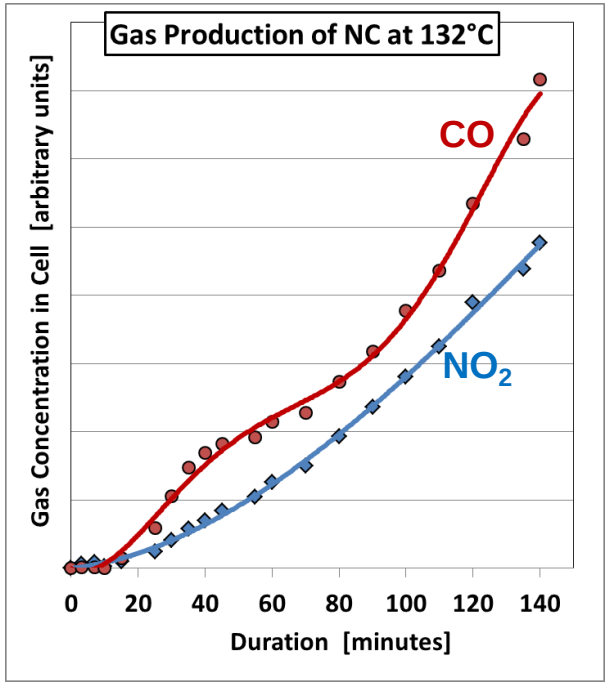
# Stability tests for NC – statements

- **Three** suitable test **methods are available for NC** (BJ, BJS, MV)
  - These conventional tests are **based on gas production** and are performed at relatively high temperatures
- **Modern tests used for propellants** like heat flow calorimetry (HFC) or stabilizer depletion could not be used
  - HFC test criterion would be “time to auto catalysis” which is not reliable, and the testing time would be too long
  - Stabilizer depletion is not possible because NC does not contain any stabilizer
- The formerly used **Abel test** (65.5 °C or 76.6 °C) **is not suited** as stability test
  - Too weak artificial ageing
  - Too sensitive
  - Only suited as purity test

# Stability tests for NC – idea for new stability test

**All three** suitable test **methods are based on gas production**

- Stability test **based on modern gas sensors** would be advantageous
- In an ideal world, they could
  - simplify the test procedure
  - be more precise and reliable (less human interaction, no influence of the test paper)
  - Provide additional information (e.g. gas production rate, gas composition)



# Possible gas sensors / analytic devices for stability tests

- Gas **volume** or **pressure** measurement devices (as for the vacuum stability test)
  - Only measurement of total gas amount
- **Electronic** / semiconductor sensors
  - Too sensitive for this kind of stability test, not selective, cheap
- **Spectroscopic** sensors
  - Ultraviolet spectroscopy (**UV**) – suited for $NO_2$ (basically also for NO), simple, cheap
  - Infrared spectroscopy (**IR**) – miscellaneous gases, FTIR or Laser, very selective, middle and upper price level
  - Near infrared spectroscopy (**NIR**) – miscellaneous gases, relatively expensive, not commonly used for gas measurements
  - Variations of IR/NIR spectroscopy – e.g. photoacoustic spectroscopy (**PAS**) or tunable diode laser spectroscopy (**TDLAS/LAS**)
  - Mass spectroscopy (**MS**) – all gases, only with gas flow, expensive
  - $NO_x$ chemiluminescence (**$NO_x$-CLD**) – $NO_2$ and NO, only with gas flow, intermediate price level

# UV-spectroscopy

- UV spectroscopy is suited for gas measurements, but it is not as typical as for **IR** or **CLD**
- **$NO_2$** can be **easily measured** (strong absorption between 250 – 650 nm, maximum at 406 nm)
- NO is difficult to measure (3 double peaks at 204, 215 , and 226 nm, superimposed by $NO_2$ signal)
  - Chemometrics is needed for this analysis
- Sufficient sensitivity
- **Simple setup** for gas measurements in gas tube (with fiber-optic)
- UV spectrometers are **relatively cheap** (compared to IR or CLD)

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**Seemed to be a good choice for first experiments !**

# UV-Spectra of $NO_2$ and NO

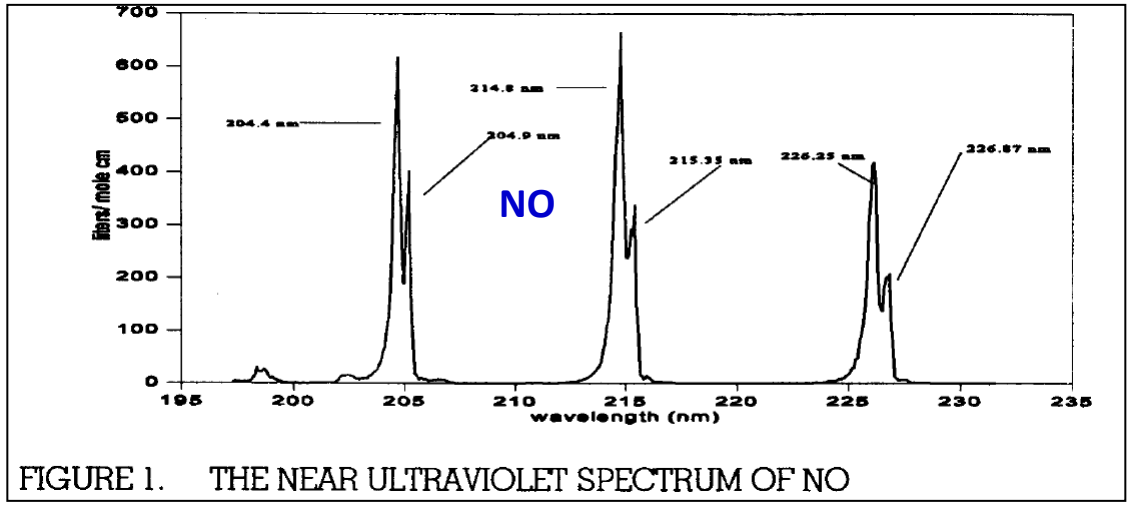
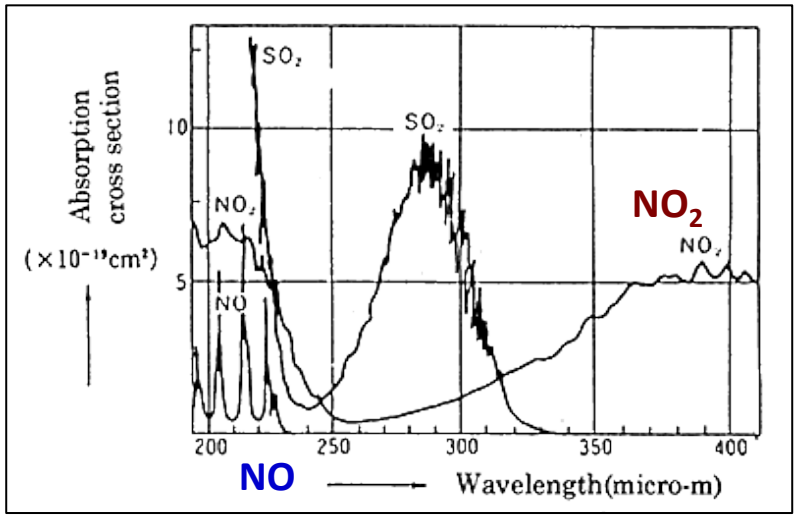



FIGURE 1. THE NEAR ULTRAVIOLET SPECTRUM OF NO




From: P. Harris; *Simultaneous Determination of $SO_2$ and $NO_x$ Concentrations by UV Spectrophotometry*; ISA Analysis Division Spring Symposium, New Orleans, USA, 1997

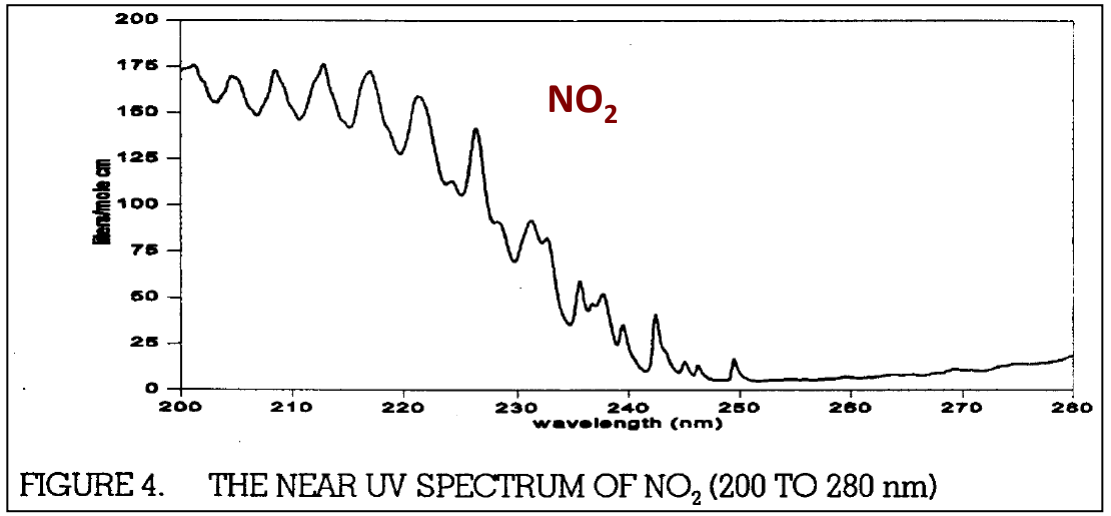



FIGURE 4. THE NEAR UV SPECTRUM OF $NO_2$ (200 TO 280 nm)

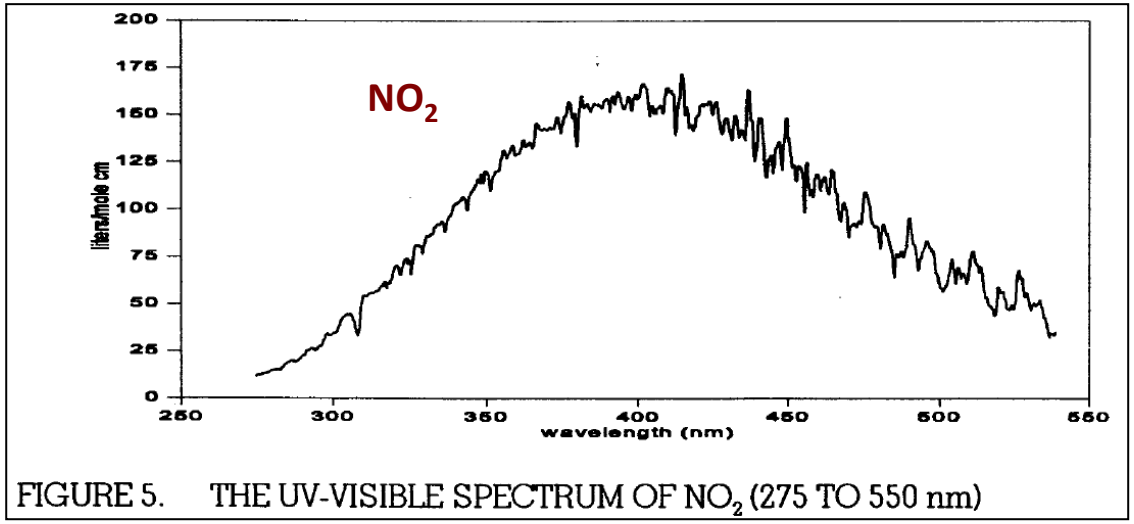
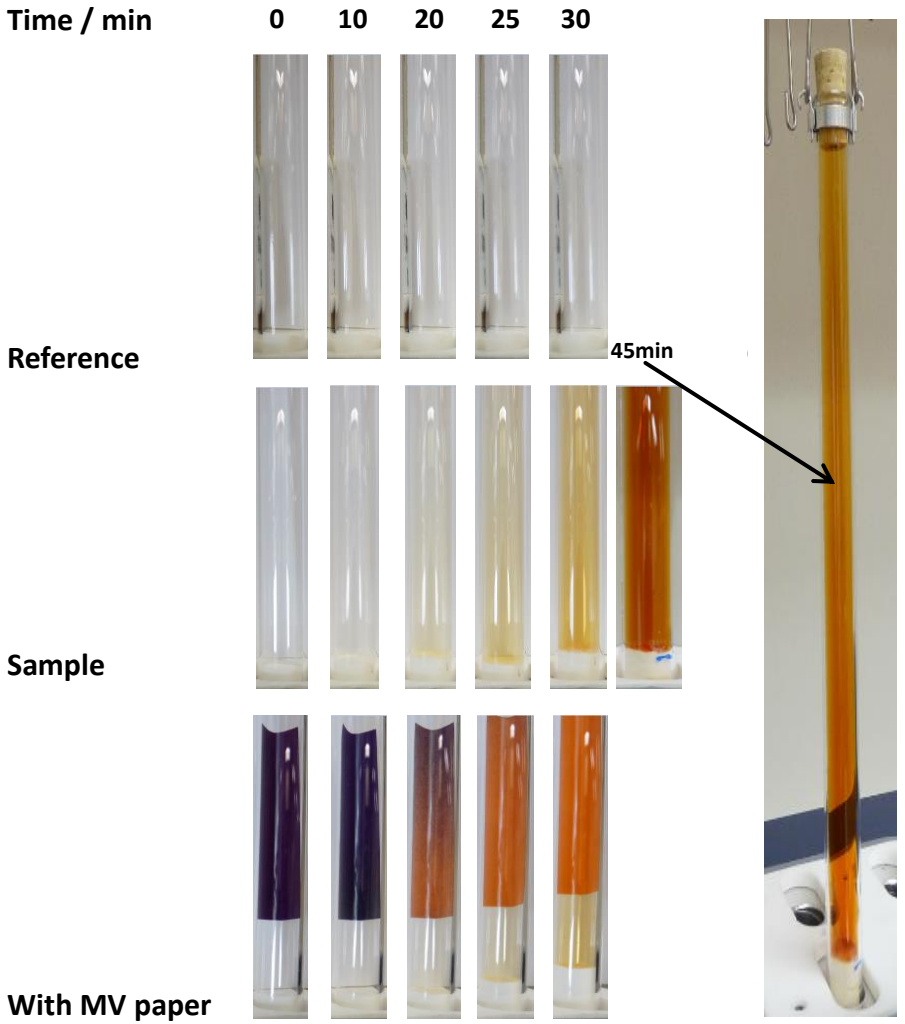



FIGURE 5. THE UV-VISIBLE SPECTRUM OF $NO_2$ (275 TO 550 nm)

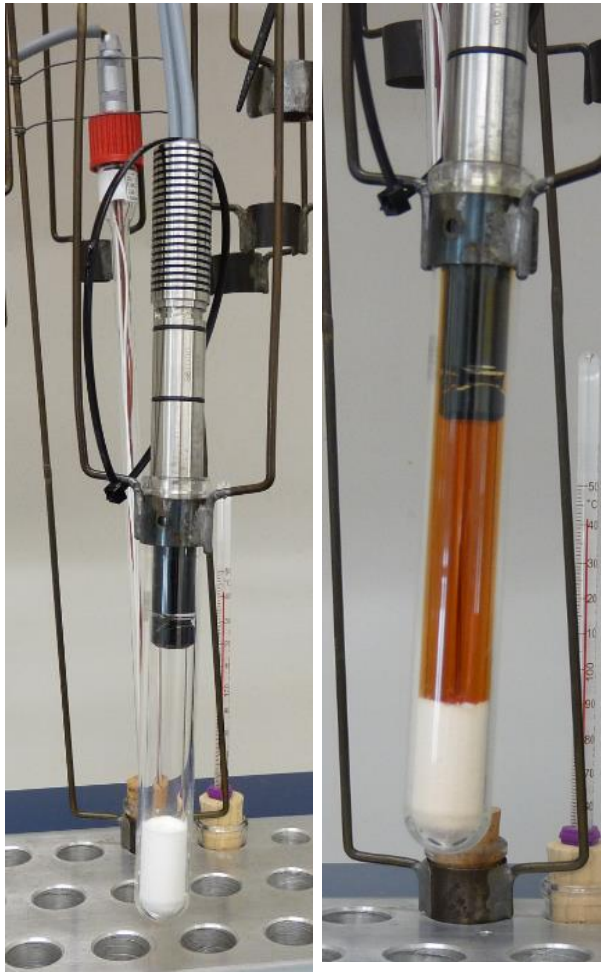
# Preliminary tests

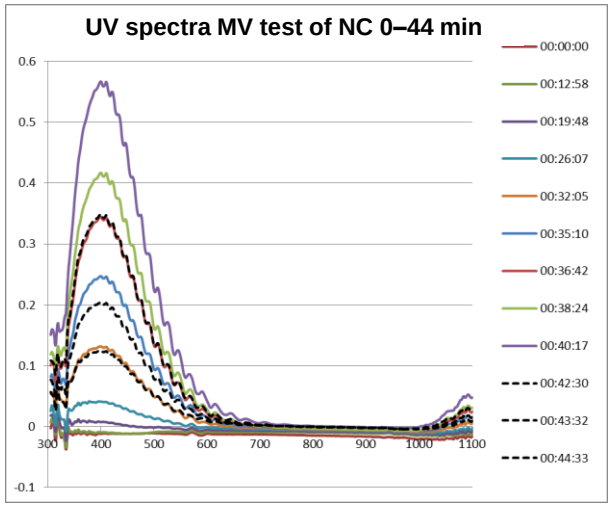
- $NO_2$ was produced in the laboratory from nitric acid and copper
- The spectrum was confirmed by reference spectra from literature
- A suitable pass length for testing probes was obtained
- An MV test was performed and the increase of $NO_2$ was documented with photos over a 45 min period
- The color was more intensive if no MV indicator paper was used
  - The MV test paper adsorbs part of the NOx
- As soon as a weak yellow or brownish color could be seen, UV detection was possible

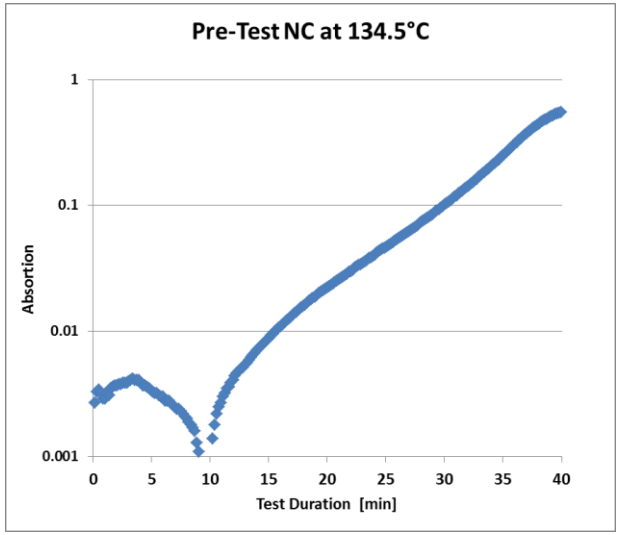


# First UV measurements

- $NO_2$ production during MV test was measured at 134.5 °C with laboratory UV probe with 2 mm path length
- After 10 min a significant amount of $NO_2$ could be detected
- The $NO_2$ concentration doubled all 4.5 min
- A good extinction has been achieved in spite of the short optical path length
- The $NO_2$ formation can be monitored over time



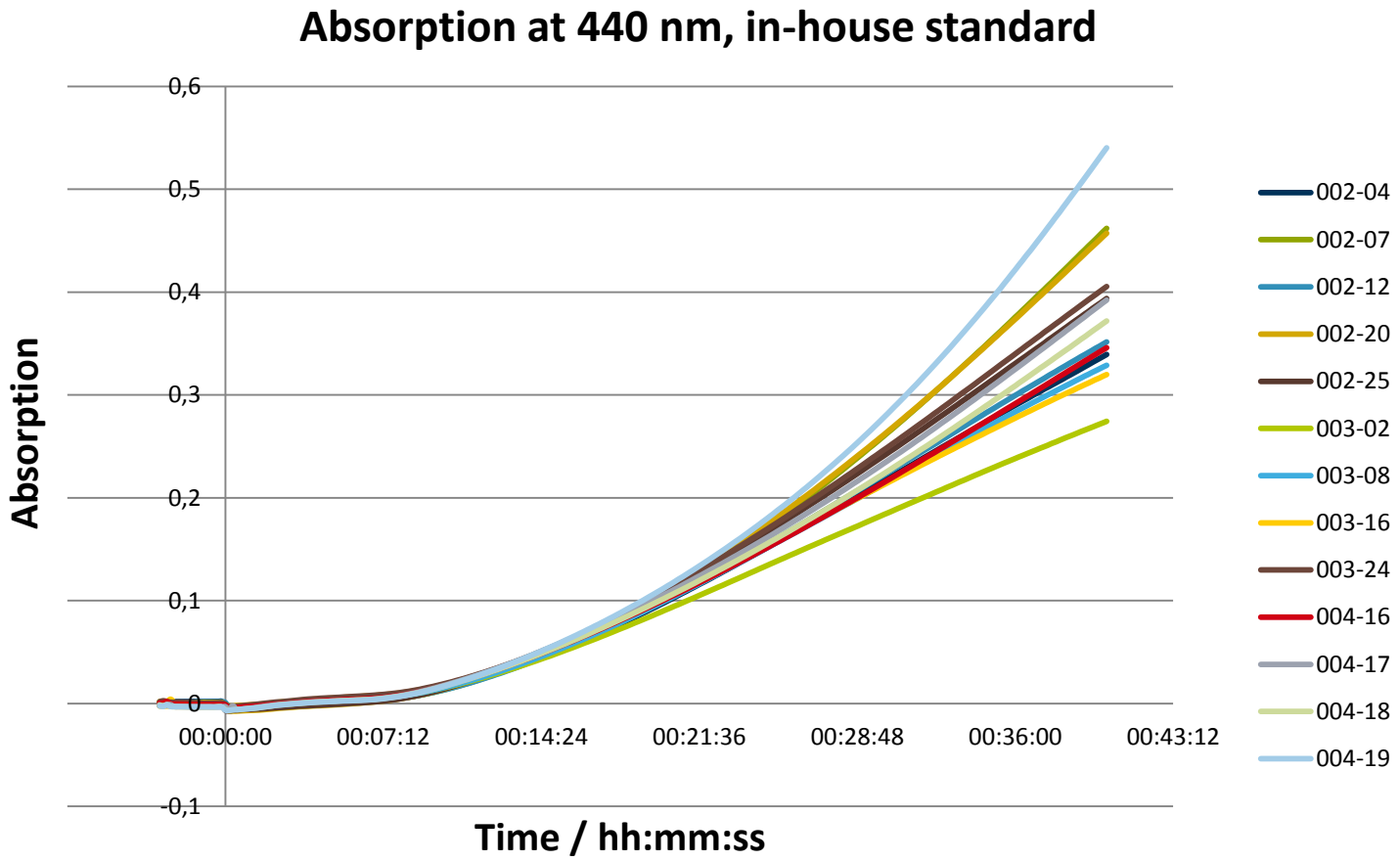


# UV measurements with “optimized” UV testing probe

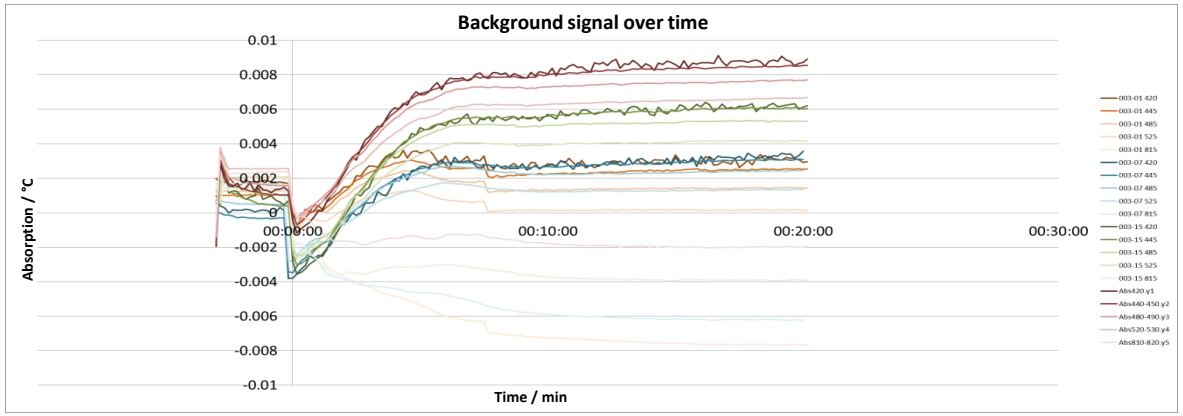
Optimized UV testing probe

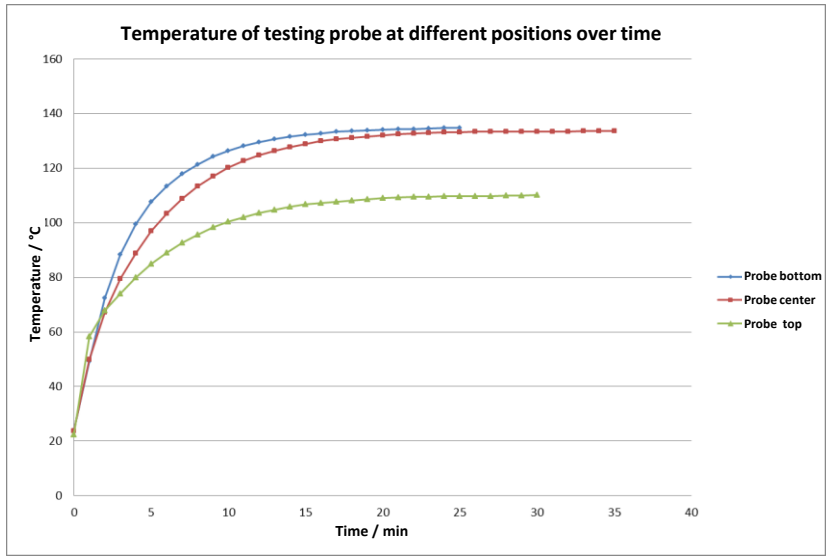
- Measurement at same position as MV paper is located
- Optical path length 10 mm



# First lessons learned

- The UV absorption of the in-house standard showed a too high variance
- The testing probe in the used setup showed a strong temperature depending background
- The temperature depending background is also dependent on the wave length …
- The time to thermal equilibrium of the testing probe is about 20 min
- A very exact blank background correction is needed



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# Summary

- **Three** suitable test **methods are available for NC** (BJ, BJS, MV)
  - **Good correlation** of all three methods
  - The **most demanding test was the BJ test**

- However, either a **subjective color reaction** and **test paper** or a more **complex analysis** is involved

- Stability test **based on modern gas sensors** would be advantageous
  - simpler test procedure, more precise and reliable, additional information

- A **simple test setup** for stability measurements by **UV spectroscopy failed** due to a too strong temperature depending blank value of the testing probe resulting in poor precision and reproducibility of test results

- Further tests are planed with more sophisticated, but even more expensive equipment

# THANK YOU FOR YOUR ATTENTION !

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