# Nitrocellulose Ageing Processes and Their Consequences for Stability Testing

**Beat Vogelsanger and Ruth Sopranetti**

RHEINMETALL NITROCHEMIE

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- Introduction (Cause and Goal of Study)
- Experimental
  - Stability Tests / Heat Tests
  - $NO_x$-Chemiluminescence
  - FTIR-Spectroscopy
  - Electron Paramagnetic Resonance EPR
  - Direct Chemiluminescence
- Interpretation of Results / Conclusions


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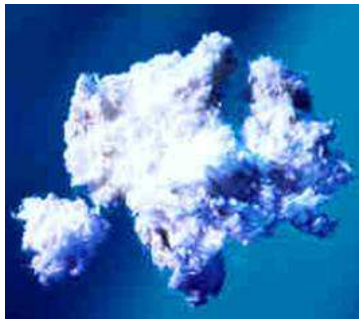
# Cause and Goal of Study // Course of Action



- **Cause:** The commonly used Heat and Stability Tests for Nitrocellulose (NC) often give totally contradictory results
- **Goal:** To obtain better understanding of the ageing process of NC → interpreting the contradictory Heat Test results
- **Course of Action:** Investigating the physical-chemical processes which take place during the ageing of NC using different analytical tools:
  - Conventional Heat / Stability Tests
  - $NO_x$-Chemiluminescence (Detection of traces of gaseous NO and $NO_2$)
  - FTIR-Spectroscopy (Analysis of gas mixtures)
  - Electron Paramagnetic Resonance EPR (Detection of traces of radicals such as NO and $NO_2$ in NC matrix)
  - Direct Chemiluminescence (exclusion of postulated hydroperoxide decomposition pathway)

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# Nitrocellulose Ageing Reactions (according to Literature)

## Radical Reactions

$R–O–NO_2 \rightarrow R–O\cdot + \cdot NO_2$ (1)

Homolytic breaking of the weak CO-$NO_2$ bond

$R–O–NO_2 + R–O\cdot \searrow$ $N_2$, $N_2O$, $\cdot NO$, $\cdot NO_2$, $H_2O$, $H_2$, $CO_2$, CO,
$R–O–NO_2 + \cdot NO_2 \nearrow$ $C_2H_2O_4$, other fragmens (2)

Consecutive reactions of formed radicals with nearby NC molecules – stabilisation of 'backbone alkoxyl radical' R-O· by splitting off into small stable molecules

## Hydrolytic Reaction

$R–O–NO_2 + 2\,H_2O \xrightarrow{H^+} R\text{-}OH + HNO_3$ (3)

Neutral to acid hydrolysis of the nitrate esters of NC

$2\cdot NO + O_2 \rightarrow 2\cdot NO_2 \leftrightarrow N_2O_4$ (4)

$\cdot NO + \cdot NO_2 + H_2O \rightarrow 2\,HNO_2$ (5)

$3\,NO_2 + H_2O \rightarrow 2\,HNO_3 + NO$ (6)

Consecutive reactions of products from (1) – (2) in presence of moisture and oxygen


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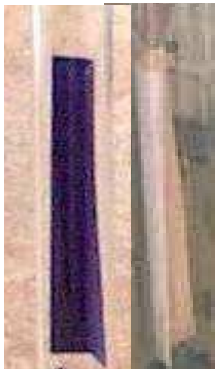
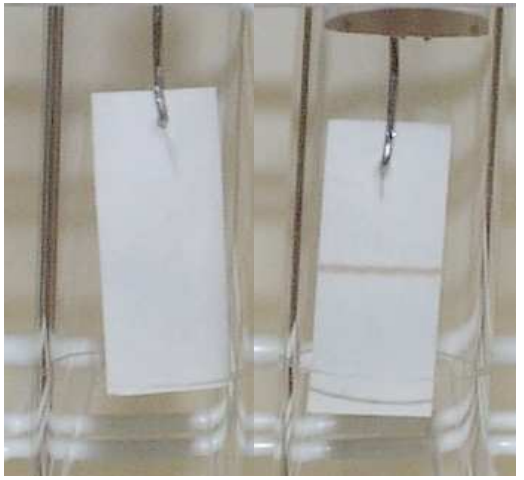
# Stability Testing of Nitrocellulose – Test Methods

**The following standardized NC "Stability Tests" are commonly used:**



- **132°C Stability Test ("Bergmann-Junk Test"):**
  - **STANAG 4178 / UK DEF STD 13-175 / M23**
  - **120' at 132°C**
- **134.5°C Heat Test ("Methyl Violet Test"):**
  - **US MIL-DTL-244B**
  - **30' at 134.5°C**
- **76.6°C Abel Heat Test:**
  - **UK DEF STD 13-189 / 13-175 / M15**
  - **10' at 76.6°C**
- **65.5°C Heat Test ("Abel Heat Test"):**
  - **US MIL-DTL-244B**
  - **35' at 65.5°C**



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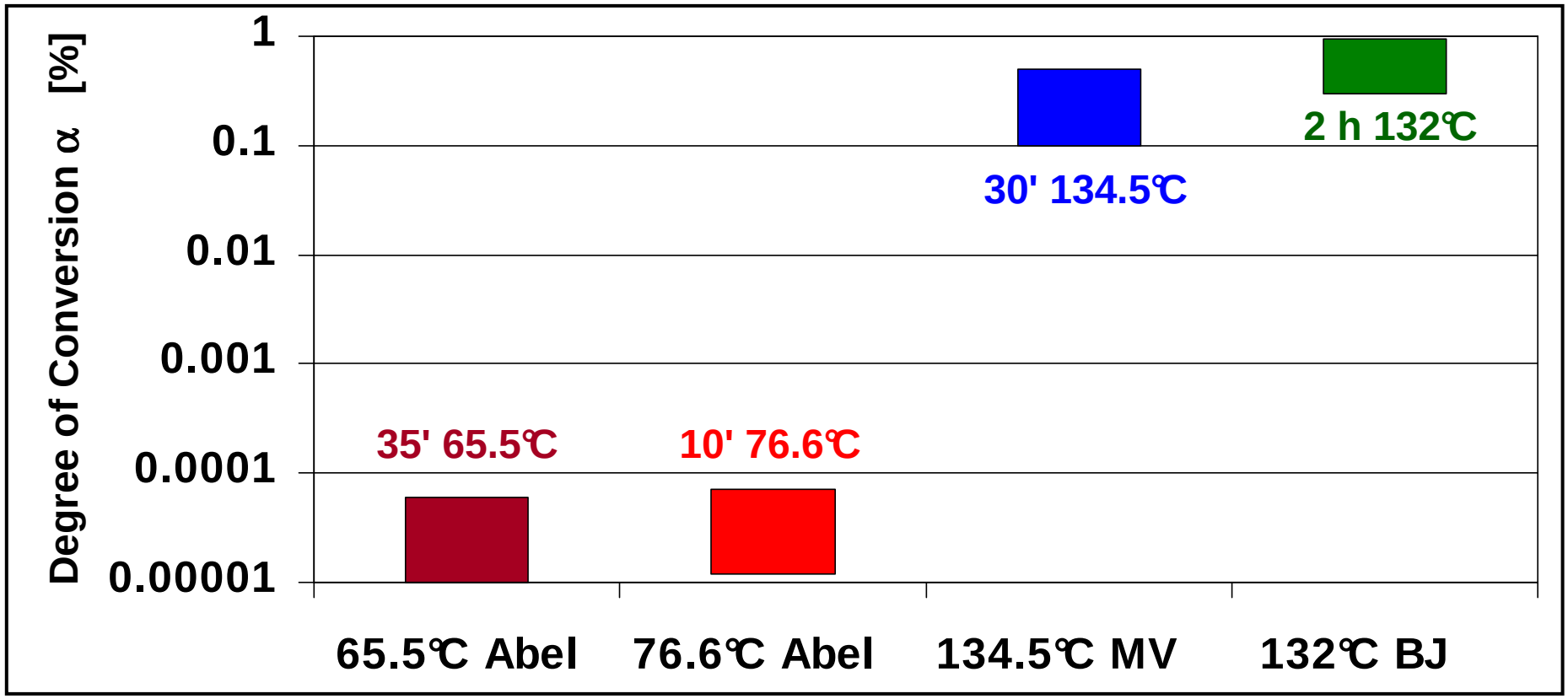
# Degree of Conversion ($NO_x$-Loss) in Different Heat Tests




- **Thermal load / amount of ageing in 65.5°C and 76.6°C Abel Heat Test**
  - **is smaller by factor 10'000 – 30'000 compared to 132°C BJ and 134.5°C MV Tests (based on measured $NO_x$ losses)**
  - **is equivalent to only 1 – 2 days at ambient**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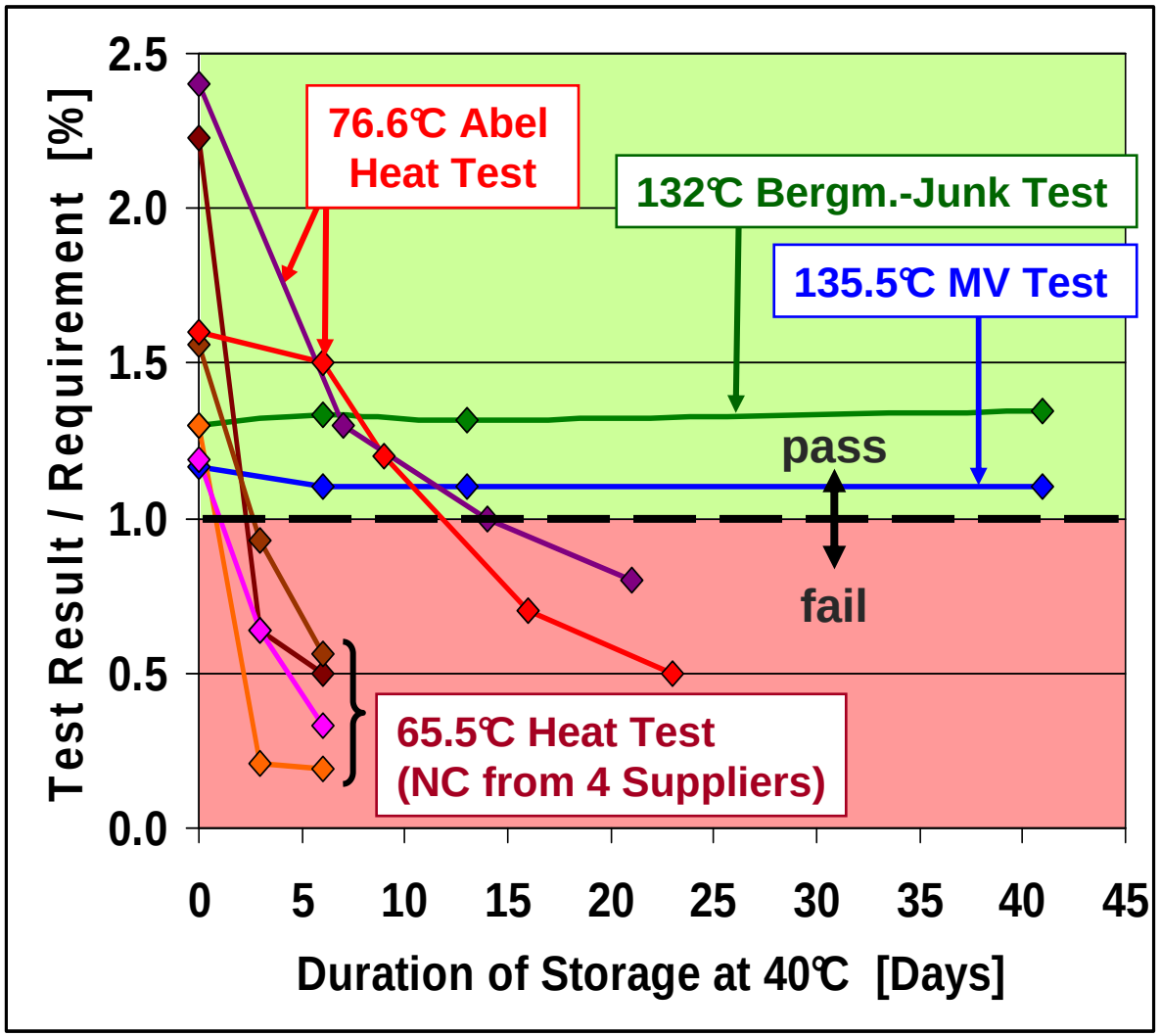
# Influence of Storage Time at 40°C on Different Tests




**Freshly produced NC was aged at 40℃:**

**Results of 65.5℃ / 76.6℃ Abel Heat Tests change rapidly – within 1-2 weeks at 40℃, test requirements are no longer fulfilled**

**132℃ Bergmann-Junk and 134.5℃ Heat Test clearly show that chemical stability remains essentially unchanged even after 40 days of storage at 40℃**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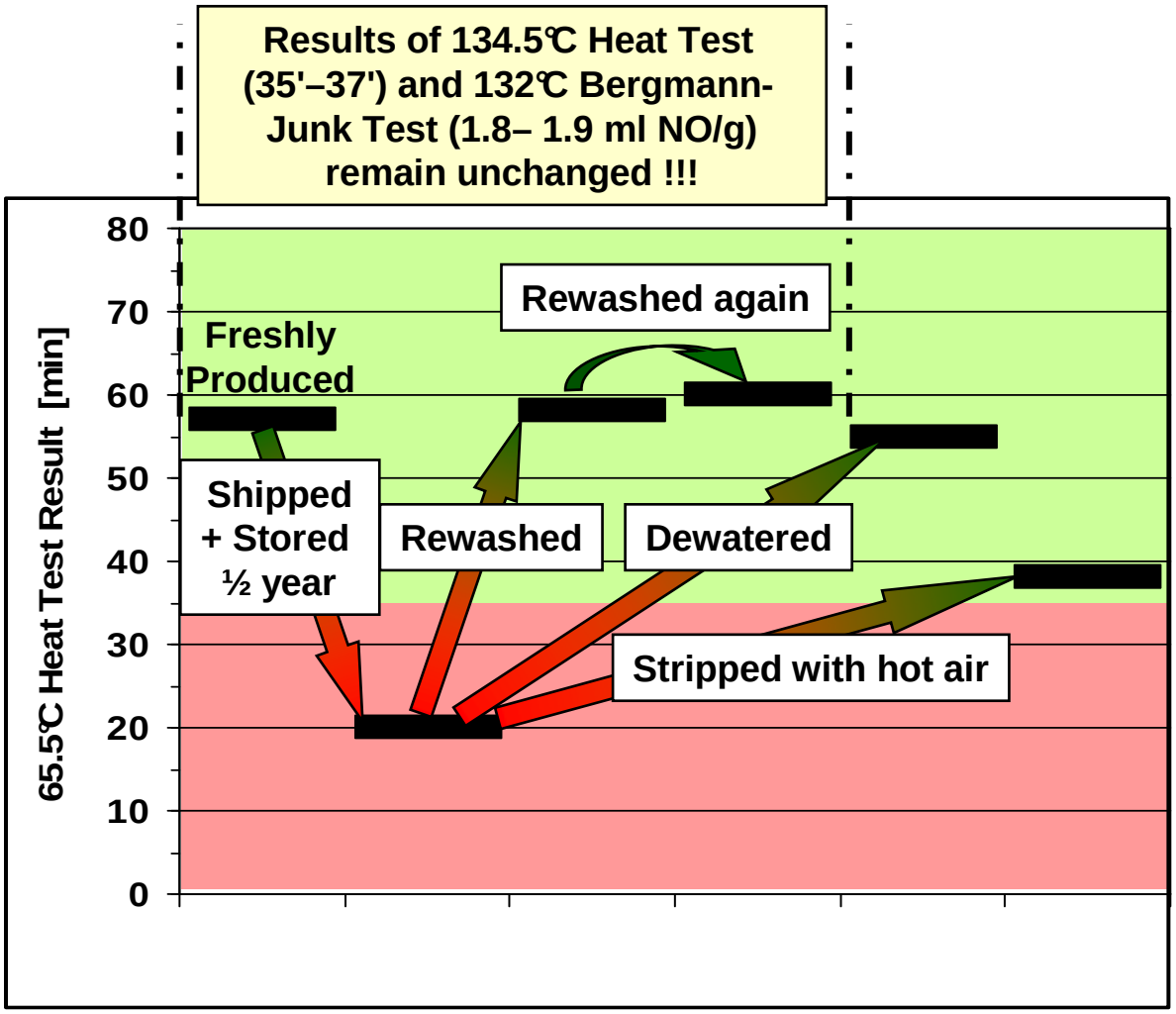
# Processes which Influence 65.5°C Abel Heat Test Results




**The 65.5°C Heat Test result of Nitrocellulose changes:**

- → From 57' of freshly produced NC batch
- → Down to 20' after shipping through hot climate + ½ year storage
- → Rewashing with hot water brings test result back to 58'
- → Similar improvement (to 55') by dewatering with alcohol
- → Improvement from 20' to 38' by 16 h of blowing hot air through sample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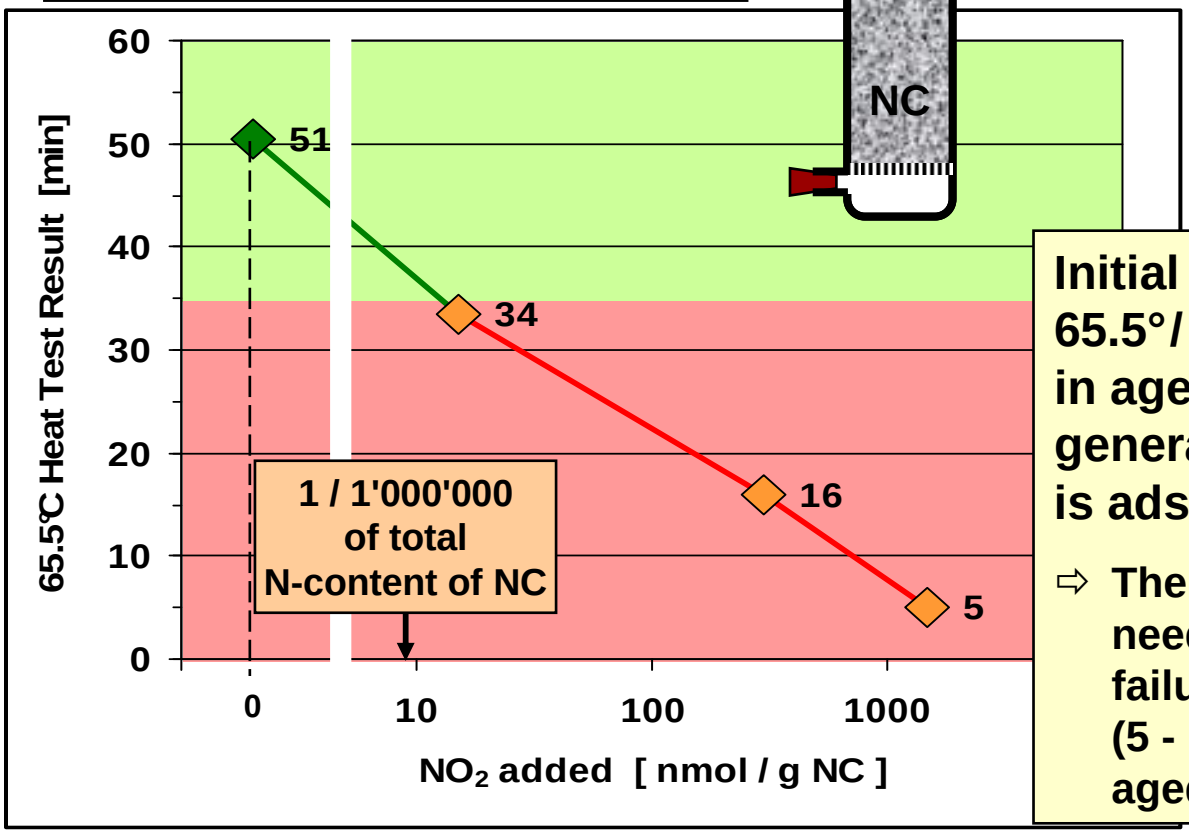
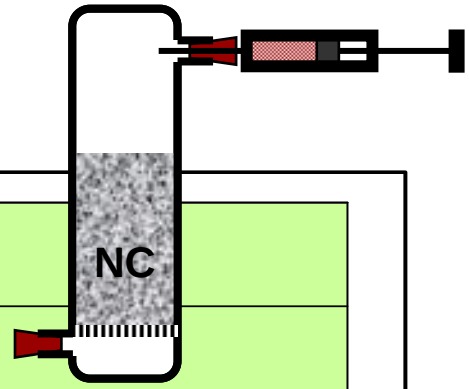
# Artificial Generation of 65.5°C Heat Test Failure

**Result of 132°C Bergmann-Junk Test remains unchanged (1.8 – 2.1 ml NO/g)**




**Experimental:**

- → New NC in bottle
- → Adding $NO_2$ by syringe
- → Shaking, resting for 2 hours
- → Removal of excess $NO_2$ by blowing air through bottle
- → Stability testing of NC

**Initial $NO_x$ peak and thus failure of 65.5°/ 76.6°C Heat Tests (as seen in aged NC) can be artificially generated if a small amount of $NO_2$ is adsorbed on new NC**

⇨ **The amount of $NO_2$ (15 nmol/g NC) needed to reach 65.5°C Heat Test failure equals the $NO_2$ amount (5 - 10 nmol/g NC) released from aged samples during initial peak**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  - FTIR-Spectroscopy
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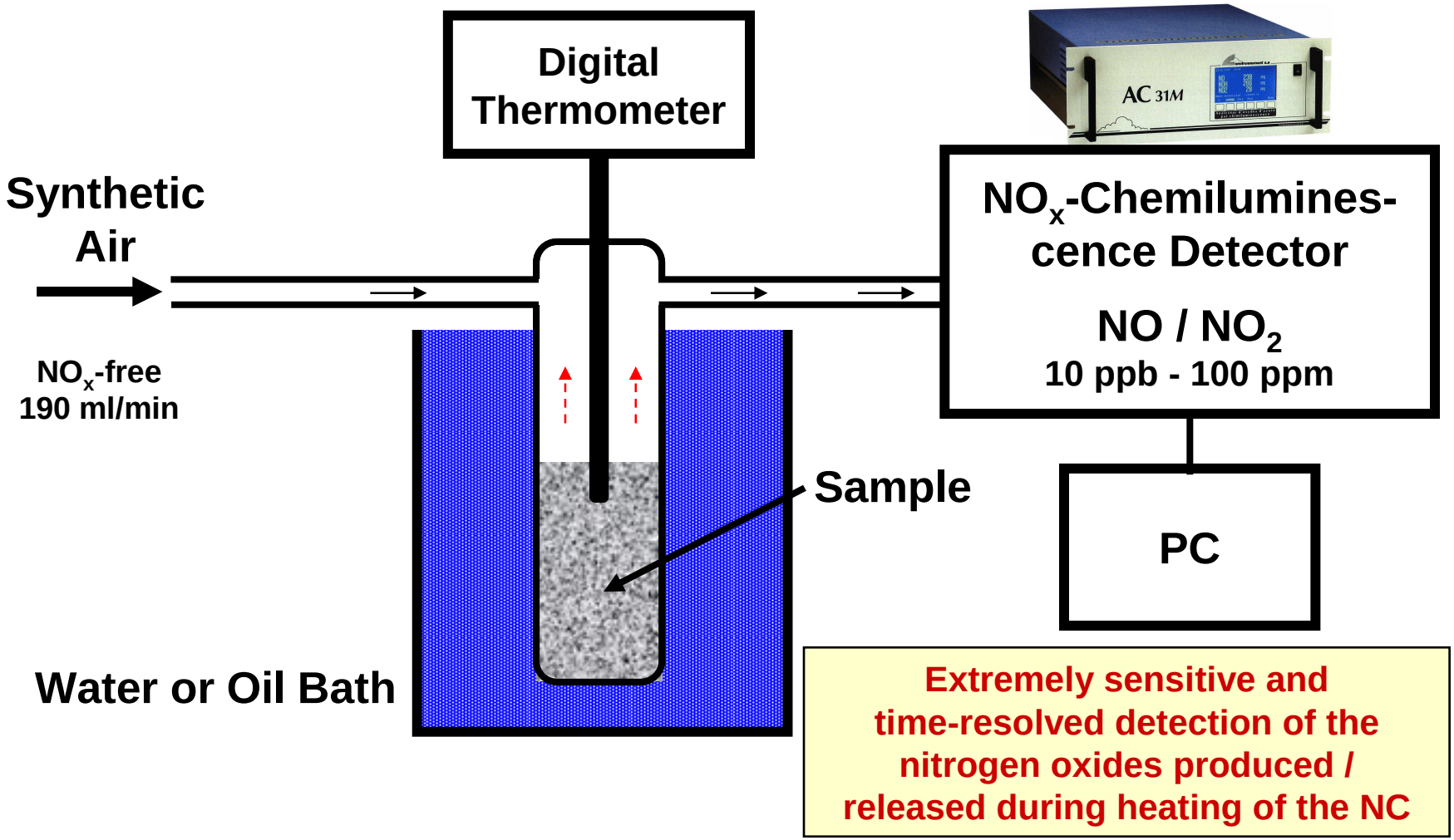
# $NO_x$-Chemiluminescence Test Apparatus




**Extremely sensitive and time-resolved detection of the nitrogen oxides produced / released during heating of the NC**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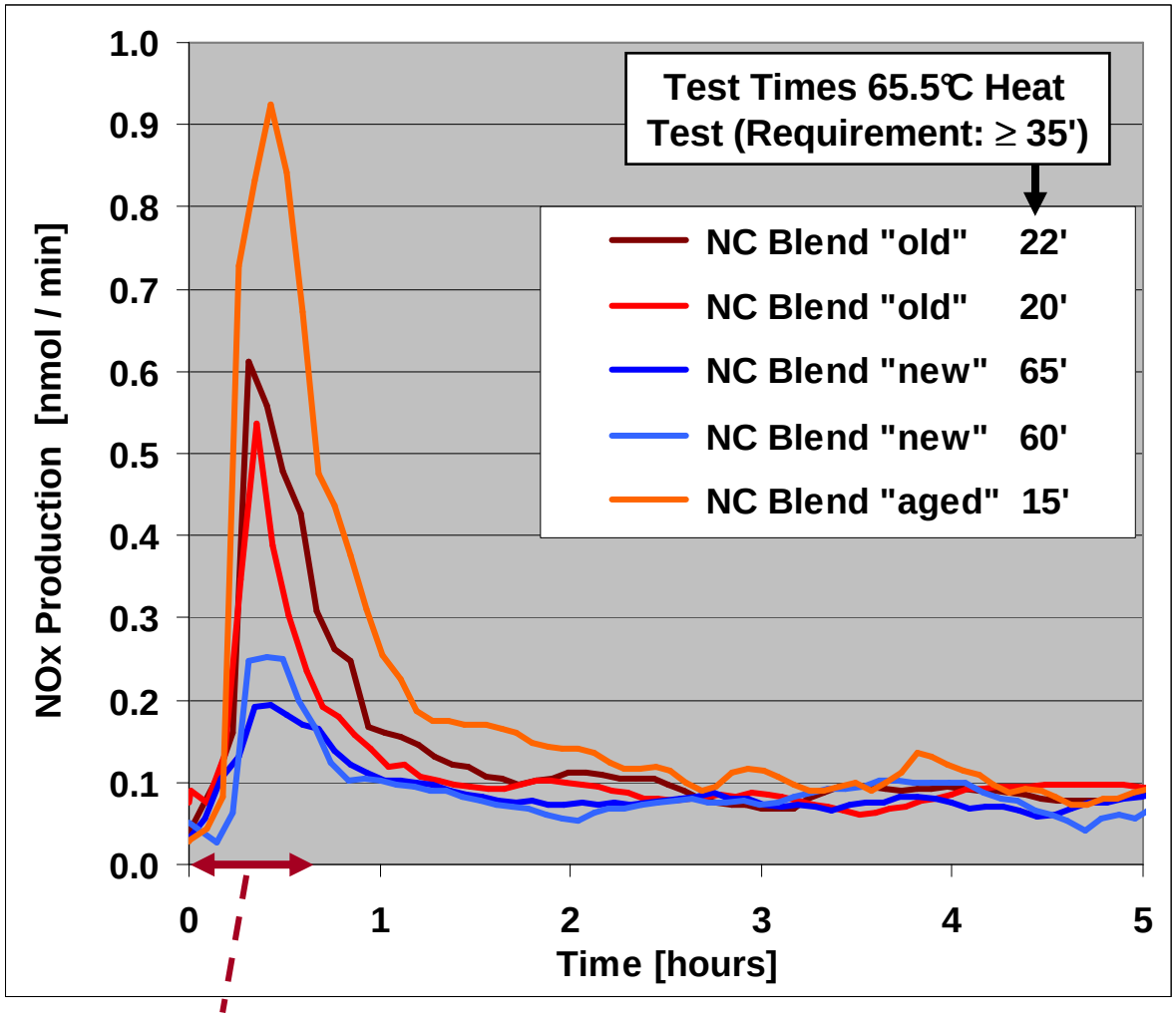
# $NO_x$-Production of NC at Abel Heat Test Temperatures




**Immediately after heating to test temperature (65.5℃), a $NO_x$ peak is produced**

**The $NO_x$ peak height correlates with Heat Test results: NC which "pass" give lower peaks than NC which "fail" the Abel Heat Test**

**This $NO_x$ release is with 0.5 – 2 / 1'000'000 of total N-content of NC extremely small; but obviously determines the result of the Abel Heat Tests**

**After initial peak is over, $NO_x$ production goes down to equilibrium level**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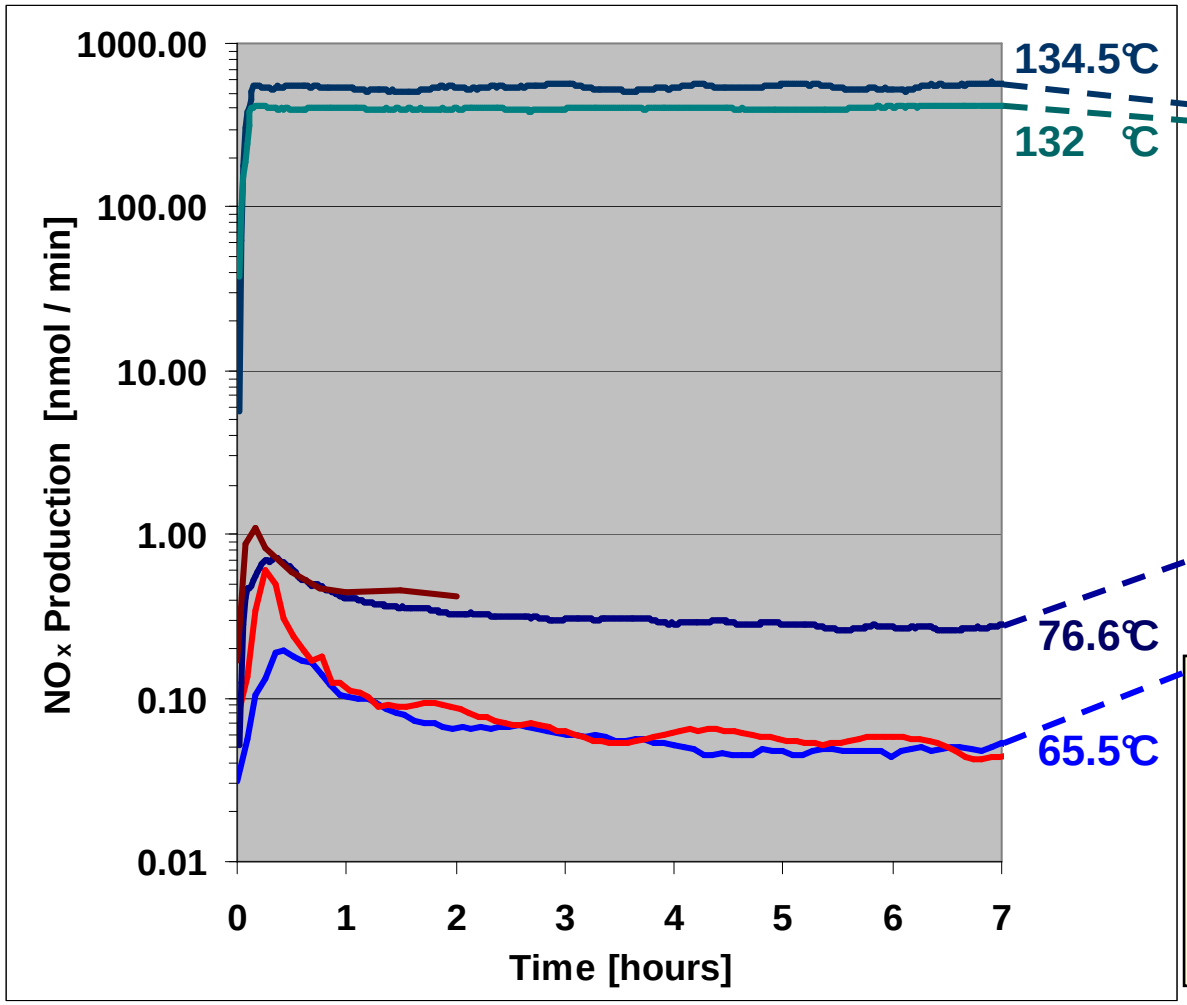
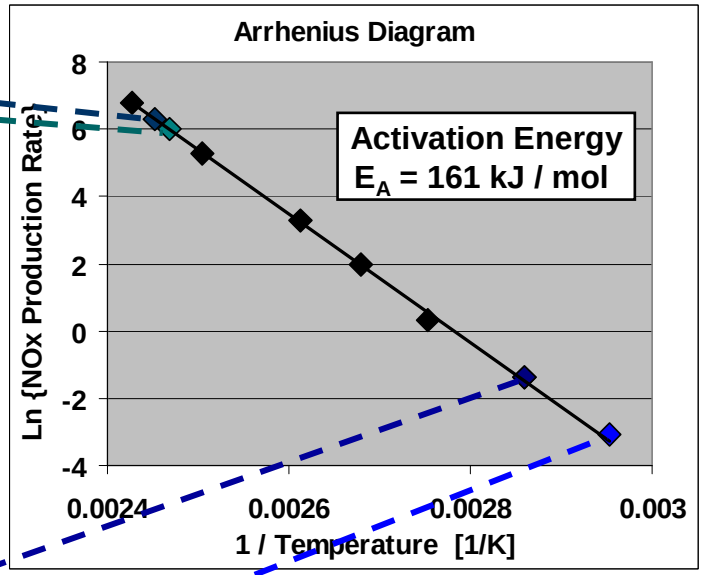
# $NO_x$ Production Rate in the different Stability Tests (I)




**The <u>equilibrium</u> $NO_x$ production rates at all four test temperatures follow the Arrhenius law and thus can be traced back to the same chemical process ("normal NC ageing")**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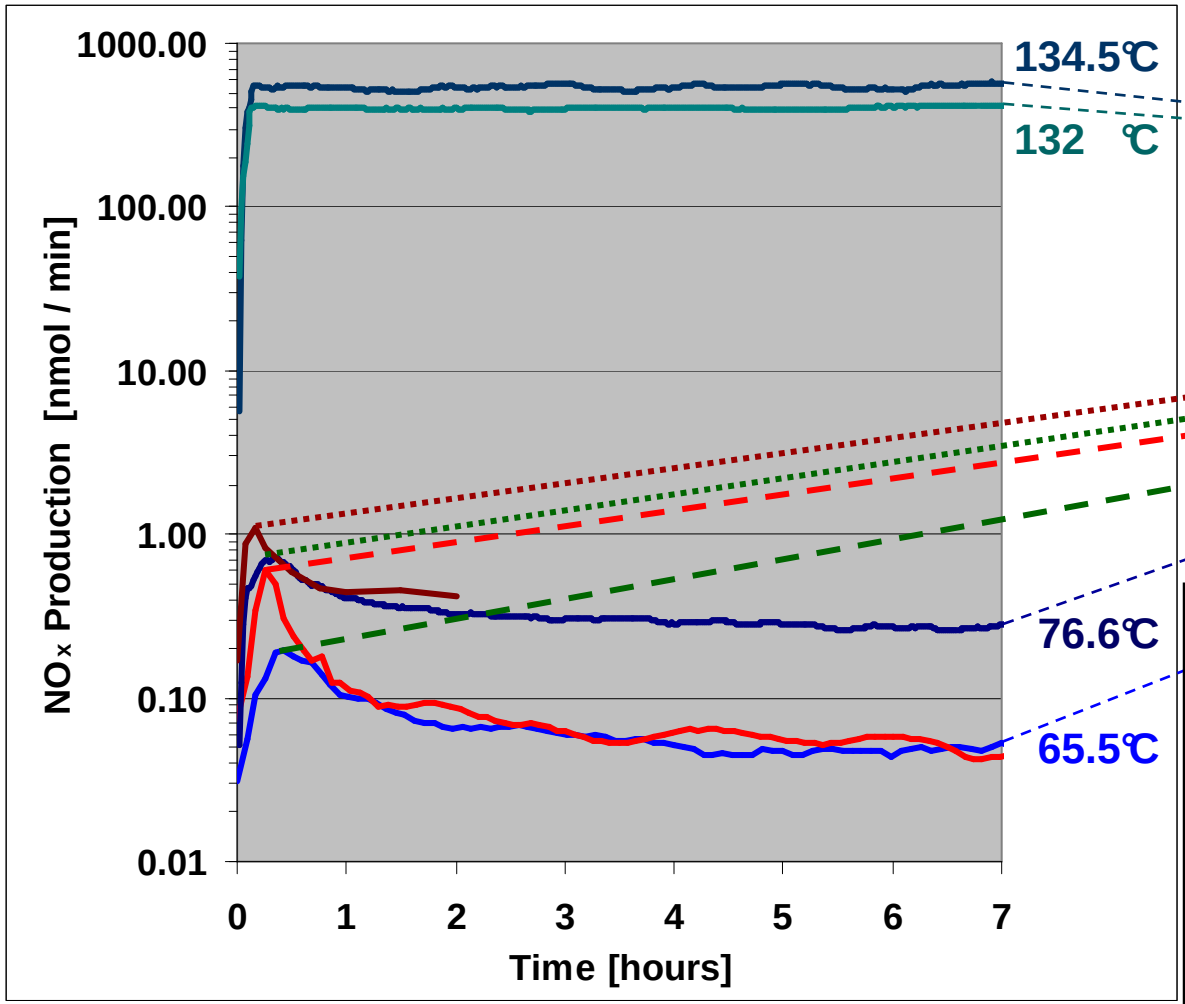
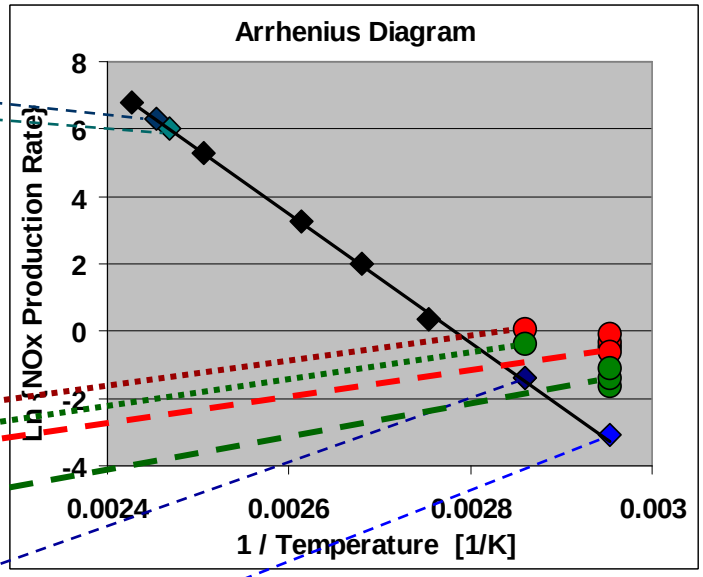
# $NO_x$ Production Rate in the different Stability Tests (II)




The <u>peak</u> $NO_x$ production which only appears in the 65.5℃ and 76.6℃ Heat Tests is up to 10 times higher than the equi-librium $NO_x$ production and thus must originate from an other chemical process (different to "normal NC ageing")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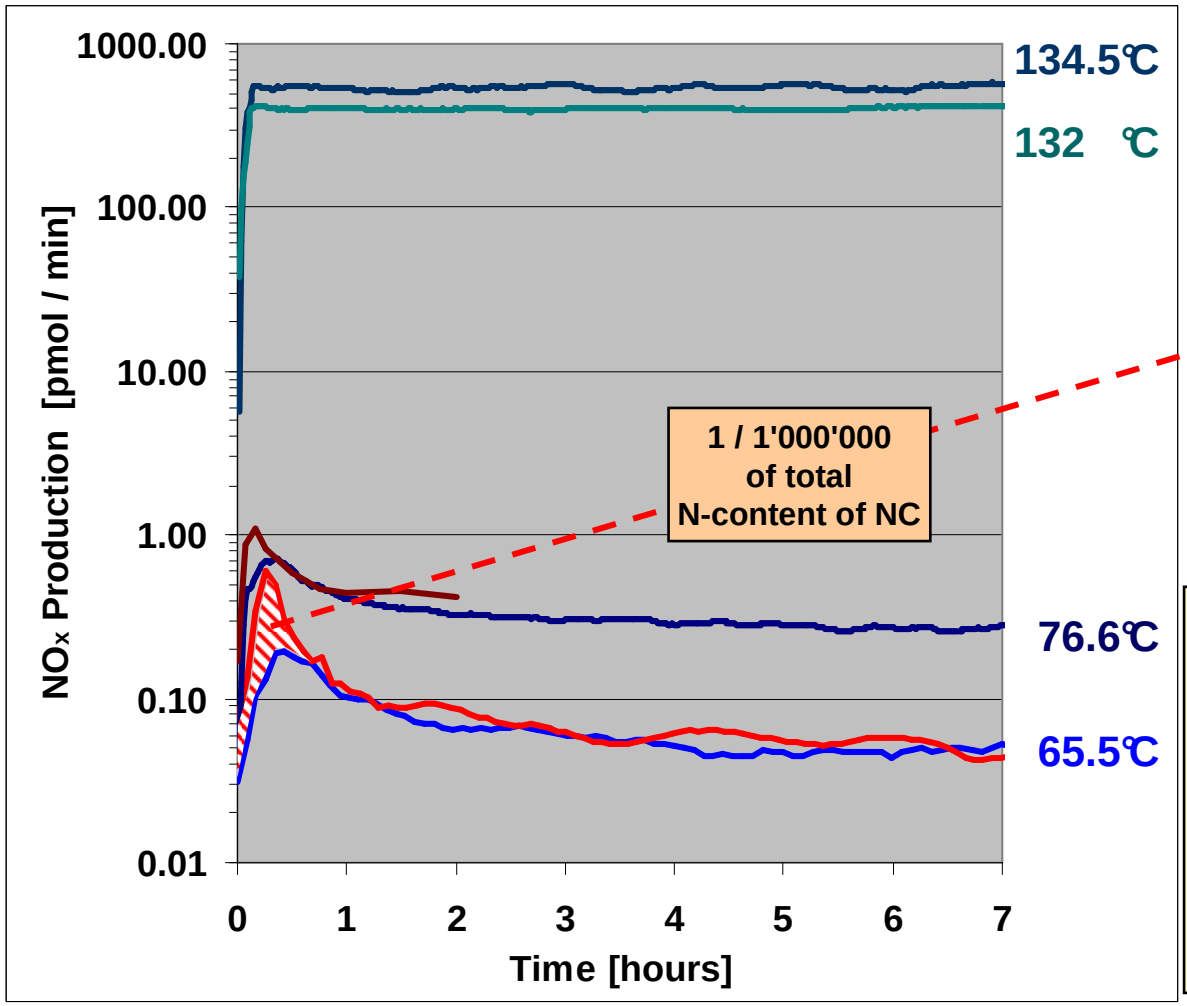
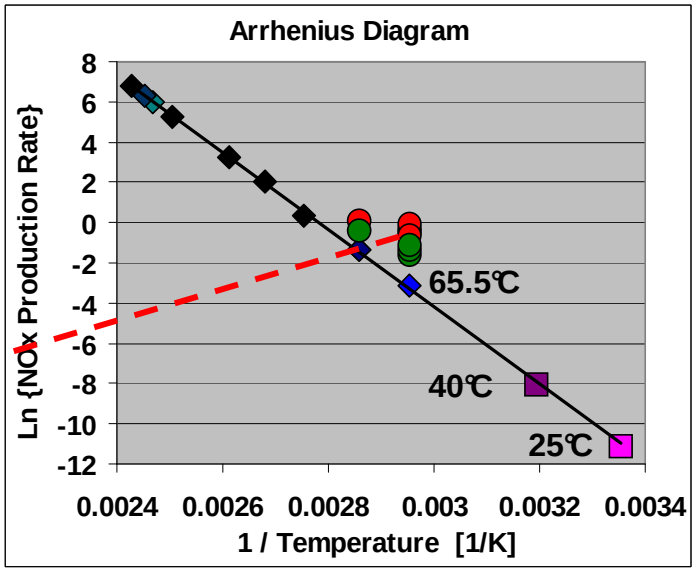
# NOx Production Rate in the different Stability Tests (III)




**The trace amount of $NO_x$ (approx. 5 – 10 nmol / g NC) which makes the NC fail the 65.5℃ Heat Test is calculated to be produced in 1 week at 40℃, or in ½ year at 25℃ ⇨ these are approx. the storage temperatures / times after which the NC fails the 65.5℃ Test**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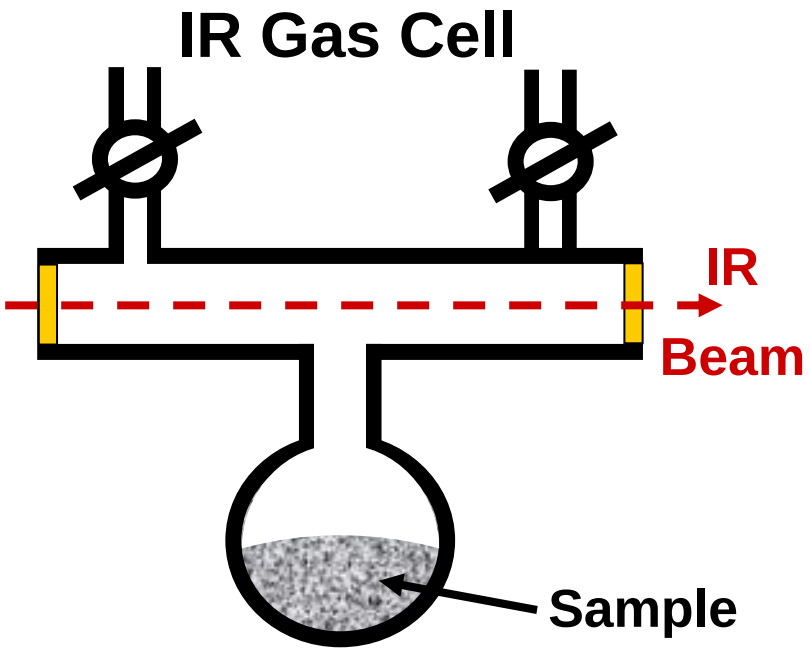
# Fourier Transform Infrared Spectroscopy



**Detection of gases;**
**not limited to NO and $NO_2$**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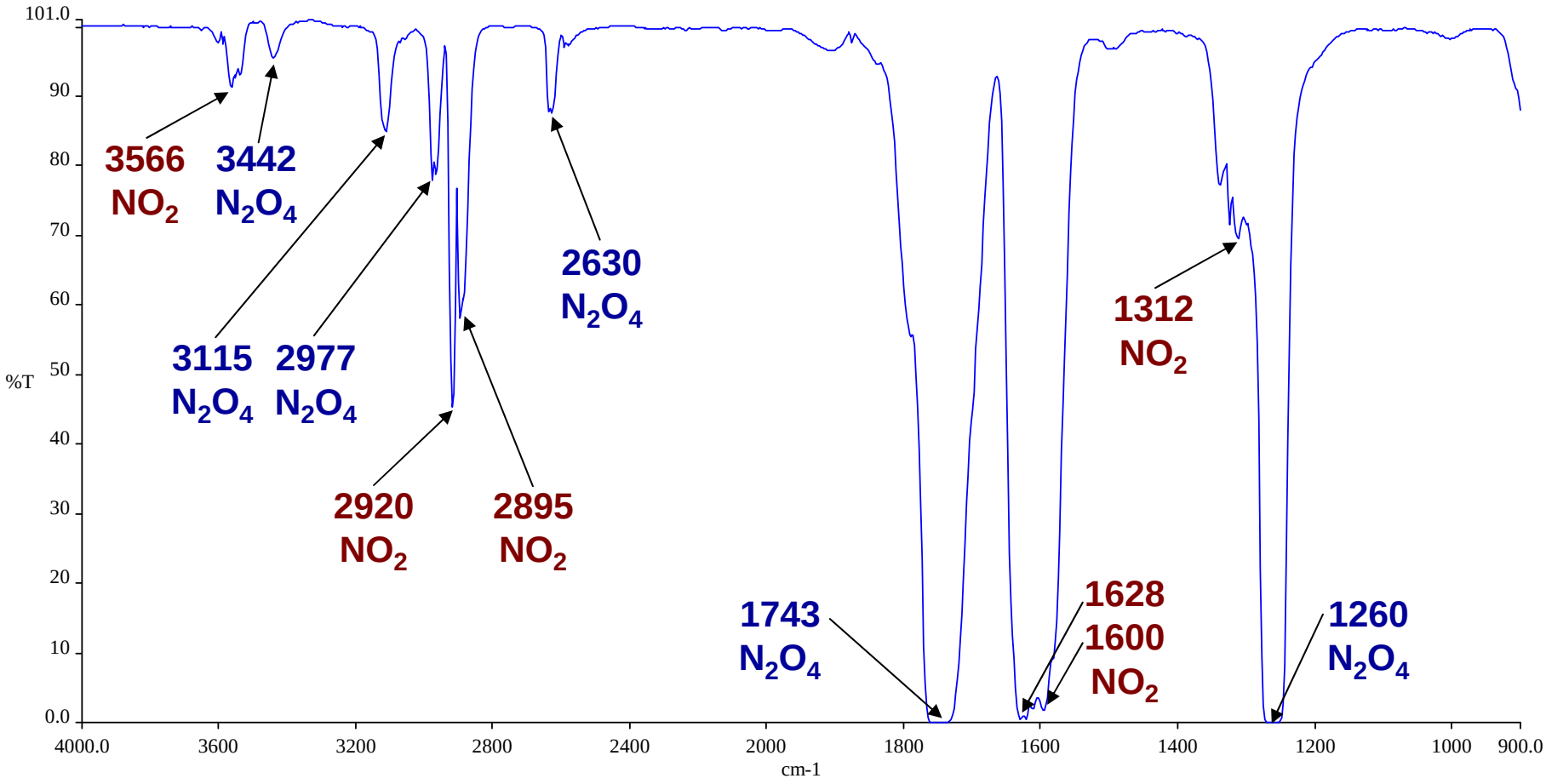
# Infrared Spectrum of 2 $NO_2 \leftrightarrow N_2O_4$

**Dimerisation / Dissociation**
**2 $NO_2 \leftrightarrow N_2O_4$ is very fast (< 10 µs)**





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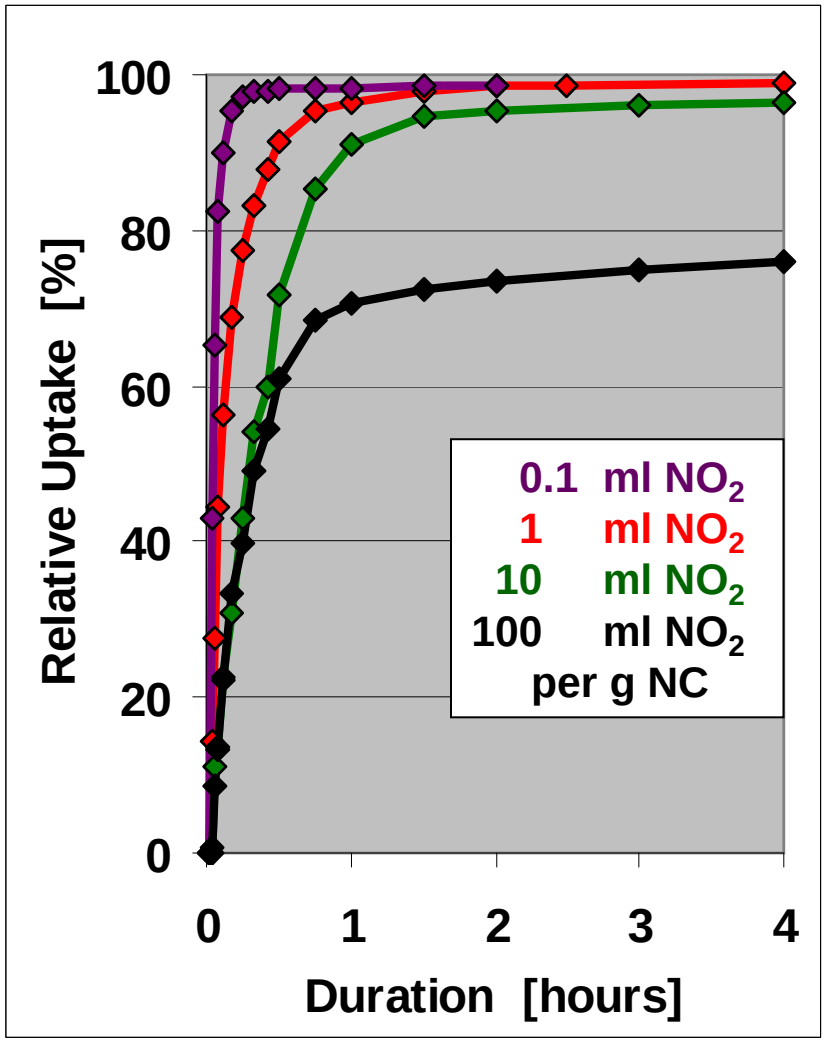
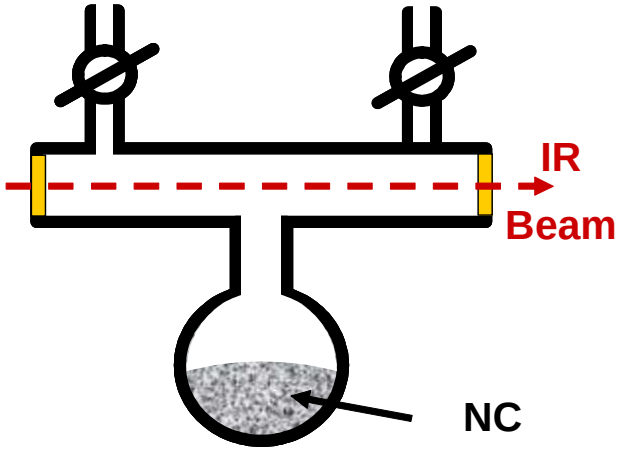
# Nitrogen Oxides Uptake by Nitrocellulose




**Nitrocellulose (as well as cellulose) can take up a considerable amount of nitrogen oxides**

**1 g of nitrocellulose (< 1% water content) can take up more than 50 ml (> 2 mmol) of $NO_2$, which is 200'000 times the amount of nitrogen oxide released from aged NC during the initial peak at Abel Heat Test temperatures**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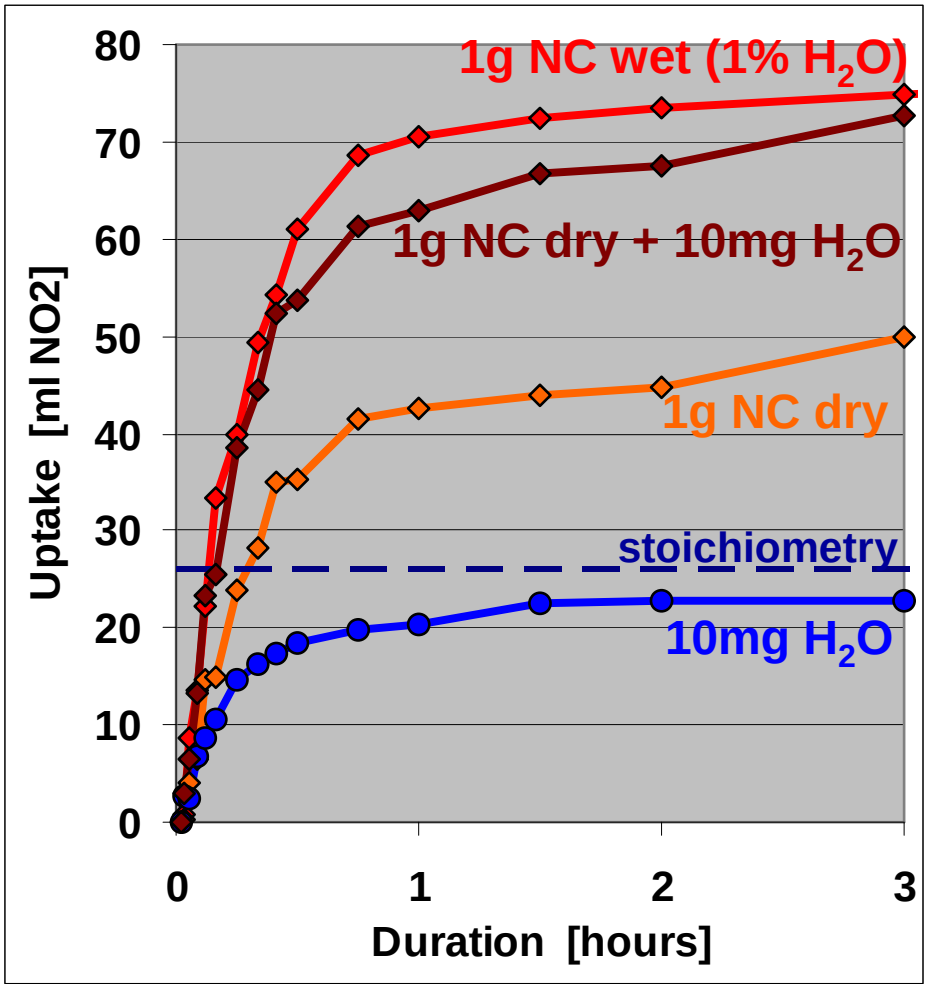
# Influence of Water on Nitrogen Oxides Uptake




**Water** absorbs $NO_2$ (approx 2.2 L/g) → consistent with stoichiometry

$$2\,NO_2 + H_2O \rightarrow HNO_2 + HNO_3$$

1 g of dry NC ($H_2O$ content ≈ 0.2% = 2 mg) takes up ≈ 50 ml (2 mmol) of $NO_2$ – this is much more than the ≈ 4 ml which could be taken up by the remaining water itself which proves that NC really adsorbs a substantial amount of $NO_2$

$NO_2$ uptake of NC with 1% moisture is approximately uptake of (dry NC + water)

Two storage mechanisms found:

⇨ Reaction with moisture present

⇨ Adsorption on NC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# Reported Earlier Results Regarding $NO_x$ Accumulation in NC

**Dry nitrogen dioxide is strongly absorbed by nitrocellulose without any immediate acceleration for decomposition**
**The affinity is specific: Sulphur dioxide is not absorbed**

**But: If nitrogen dioxide is added to wet NC, decomposition occurs rapidly – when a few drops of nitric acid are added, the reaction is even more vigorous**

**F.D. Miles, 'Cellulose Nitrate', Oliver & Boyd, London, 1955; p. 259**

**Pre-formed nitrogen oxides accumulating in the sample during storage will shorten the Abel Heat Test time of nitrocellulose**

**C.G. Bromberger, C.P. Conduit and E.A.A. Hitch,**
**'The Significance of the Abel Heat Test',**
**UK Ministry of Aviation, unclassified Report E.R.D.E. 21/R/62, 1963**


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# Electron Paramagnetic Resonance EPR

**EPR Investigations were performed by Prof. Gunnar Jeschke at the Department of Physical Chemistry of ETH Zurich**

ETH
Eidgenössische Technische Hochschule Zürich
Swiss Federal Institute of Technology Zurich

**Bruker Elexsys E500 CW EPR spectrometer with a super-high Q cavity for highest sensitivity**

**Extremely sensitive detection of paramagnetic species (radicals such as NO and $NO_2$) in solid or liquid matrix**

**Limit of detection for NO / $NO_2$ < 10 nmol / g**


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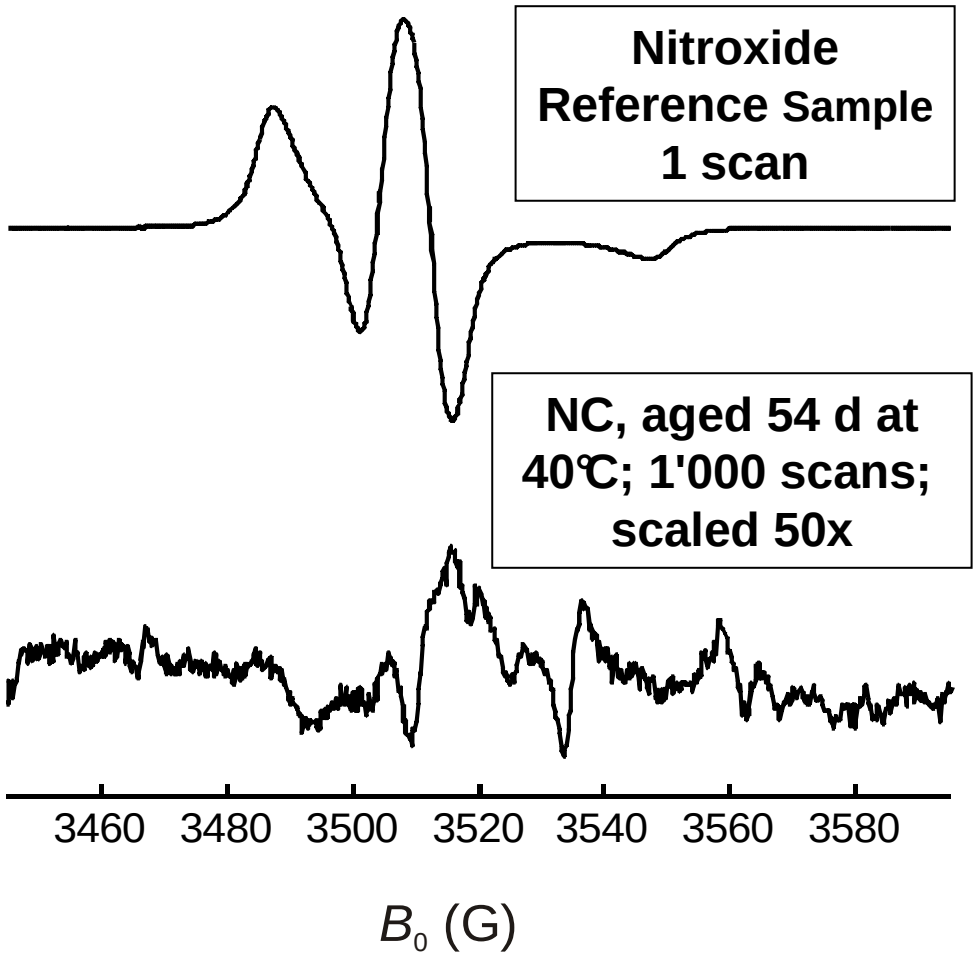
# EPR Spectra of New and Aged NC Samples




**<u>No signals</u> in EPR spectra of new & aged NC and of NC with added $NO_2$ (up to 0.1 mmol/g):**

**→ No free radicals present**

**→ No ongoing chain reactions**

**→ Nitrogen oxides are stored in NC as diamagnetic molecules (presumably as $HNO_2$ / $HNO_3$ or, less likely, as $N_2O_4$, $N_2O_3$, etc.)**

~~·NO~~

~~·$NO_2$~~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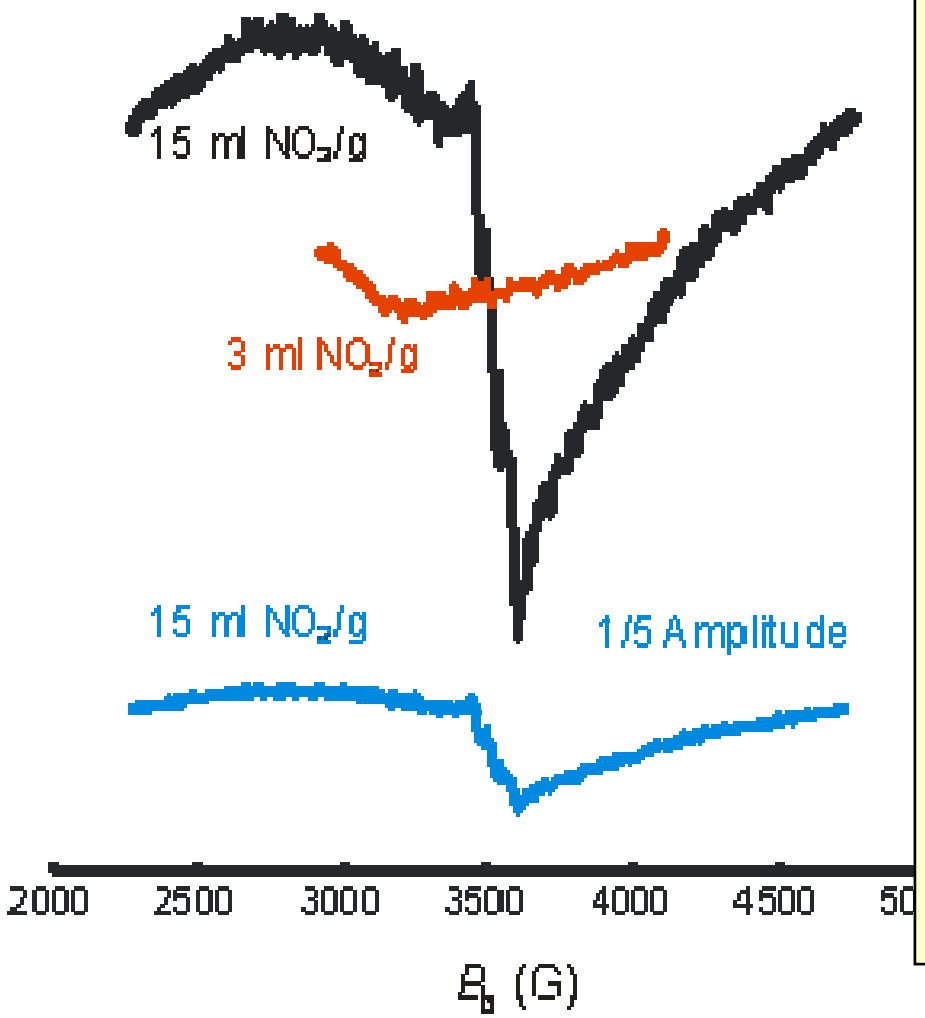
# EPR Spectra of NC Samples with Added $NO_2$




**<u>No signals</u> in EPR spectra of NC with added $NO_2$ up to 0.1 mmol/g (this amount of $NO_2$ is produced by ageing of the NC at 132℃ for > 2 hours)**

**Weak EPR signal appears in NC with even higher amounts of added $NO_2$ (above approx. 0.5 mmol/g)**

**→ Increase in peak intensity is disproportionately high; much higher than the increase of $NO_2$ content (which is factor 5)**

**→ Signal is still weaker by orders of magnitude than expected from the high $NO_2$ content of the sample**

**→ Signal shows $NO_2$ or similar radical in condensed phase (not gaseous $NO_2$ !)**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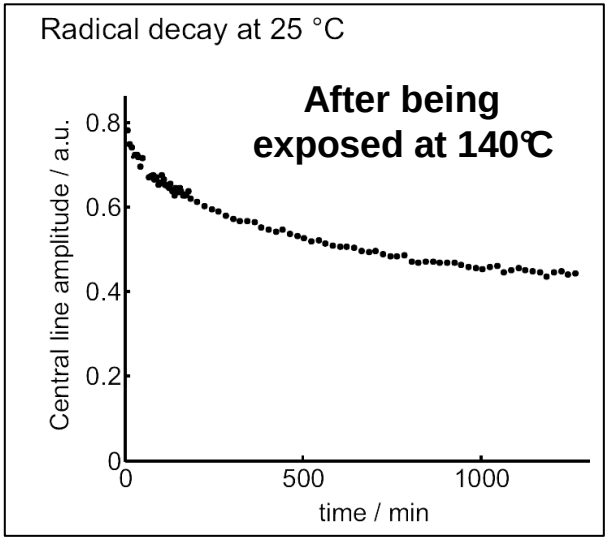
# EPR Spectra of NC at different Temperatures

**If NC is heated to above ≈ 60℃, an EPR signal typical for nitrogen oxide radicals appears**

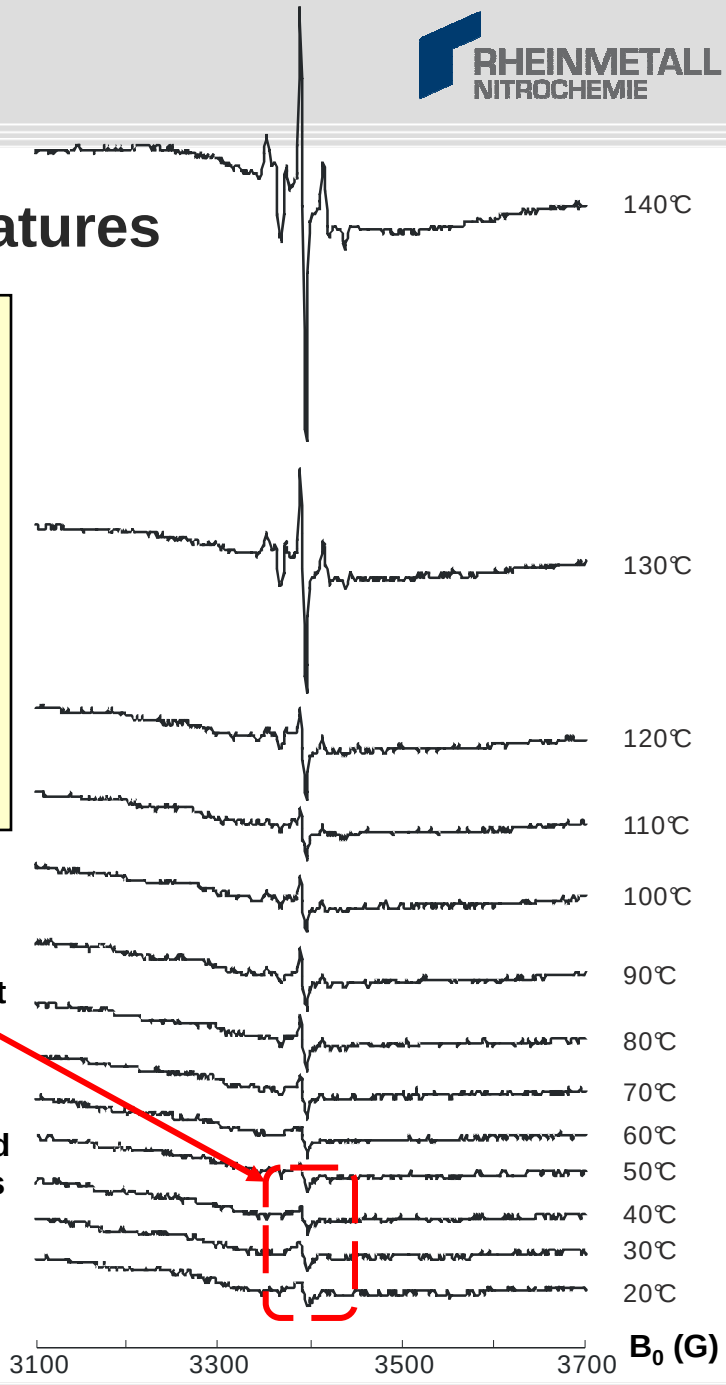
**Signal intensity strongly increases with temperature → this clearly proves that radical reactions become predominant at high T**

**After cooling the sample to 25℃, the ESR signal falls slowly (exponentially) → radicals are still present for several days / weeks**




**This sample was measured 2 days after vacuum-drying at 60℃ → EPR signal visible also at lower temperatures**

**(all other samples were stored after drying for several weeks before testing → these samples show no trace of an EPR signal)**





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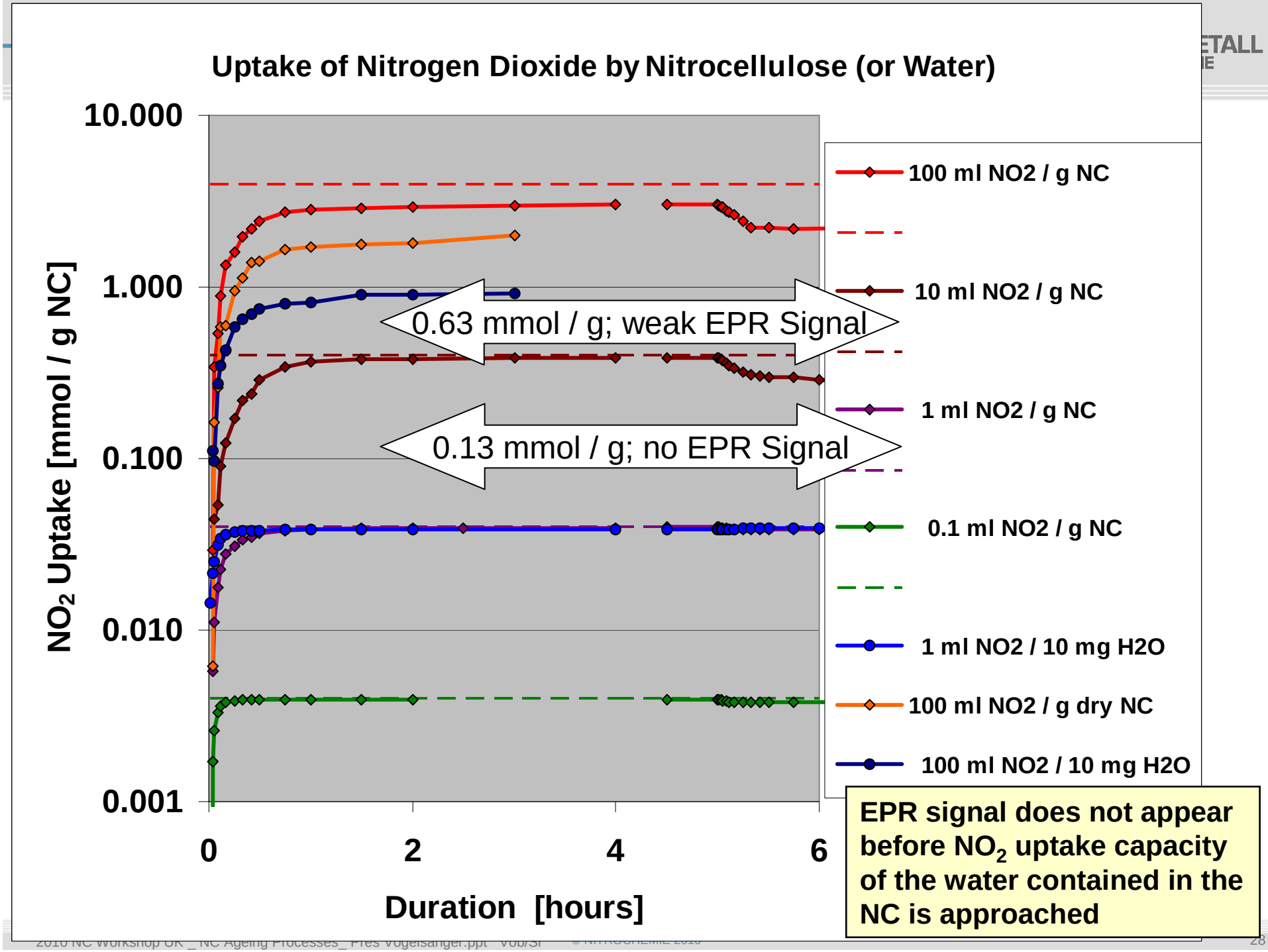



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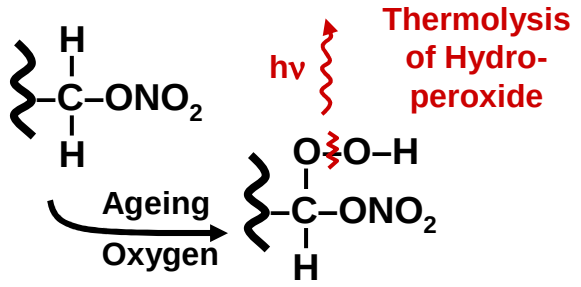
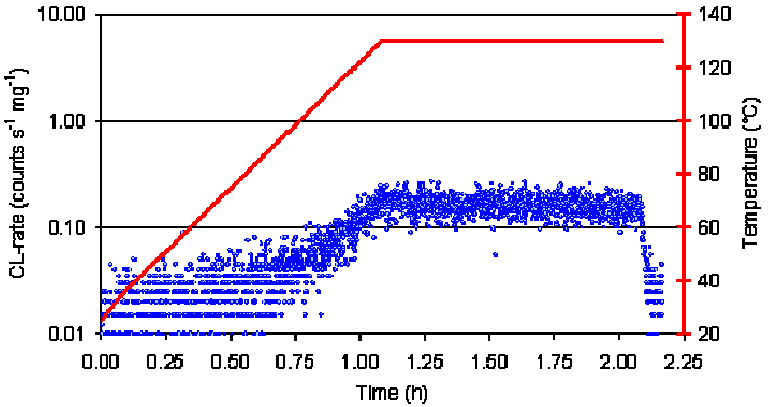
# Exclusion of Hydroperoxide Decomposition

- **J. Kimura (Japan Defence Agency) has shown that nitrate esters such as NC can form hydroperoxides during ageing under presence of oxygen (autoxidation) – these hydroxyperoxides decompose if the nitrate ester is heated to 80℃-110℃ under emi ssion of chemi-luminescence light – intensity of chemiluminescence correlates with age of nitric ester (and thus hydroperoxide content)**




- **The ageing related deterioration of 65.5℃ / 76.6℃ Heat Test results was found to be <u>not</u> connected with this autoxidation / thermolysis of hydroperoxides:**
  - **NC was aged at 40℃ under air, oxygen and nitrogen → deterioration of 65.5℃ Heat Test results of air and nitrogen samples was comparable, and that of oxygen sample even slower (if autoxidation would be involved, deterioration of Heat Test results would have to be fastest in the oxygen sample and lowest in the nitrogen sample)**
  - **New and aged NC was investigated by direct chemiluminescence at the Technical University Bern – both samples showed similar chemi-luminescence signals which presumably arise from excited $NO_x$ states (will be confirmed later) – no signals which could arise from hydro-peroxide decomposition were found**
    **(Diagram shows CL-results of "old" NC which fails 65.5℃ Heat Test; Heat Test time = 20 min)**




Chemiluminescence Mesearuements performed by Fabian Käser, ACL Instruments AG, Kerzers, Switzerland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  - Direct Chemiluminescence
- **Interpretation of Results / Conclusions**


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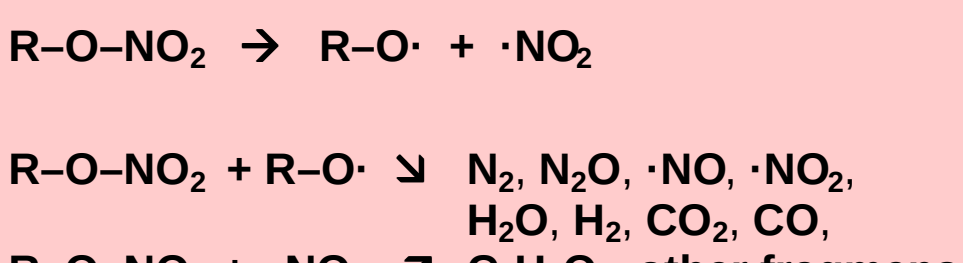
# Interpretation of Results 1 – NC-Ageing at High Temperatures

- **Hypothesis 1: In the higher temp. range, homolytic primary and consecutive radical reactions are predominant – these radical reactions determine the outcome of 132°C Bergmann-Junk and 134.5°C Methyl Violet Stability Tests**

- **Hypothesis 1 is supported by the following experimental evidence:**
  - **$NO_x$-CLD shows Arrhenius-type equilibrium $NO_x$ production rates**
  - **EPR confirms presence of radicals / ongoing radical reactions in the NC matrix at temperatures >60°C**
  - **Results of 132°C BJ and 134.5°C MV Tests are not influenced by the accumulation of small amounts of nitrogen oxides / acids in the NC**

## Radical Reactions




(1) Homolytic breaking of the weak CO-$NO_2$ bond

(2) Consecutive reactions of formed radicals with nearby NC molecules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# Interpretation of Results 2 – $NO_x$ Accumulation in NC

- **Hypothesis 2: The nitrogen oxides produced by NC during storage at ambient and slightly elevated temperatures are easily absorbed by the NC matrix – there they react with the moisture present to nitrous + nitric acids**

- **Hypothesis 2 is supported by the following experimental evidence:**
  - **FTIR experiments show that high amounts of $NO_x$ accumulate in dry NC and water; uptake is much higher in wet NC (capacity of dry NC + water)**
  - **EPR shows that absorbed $NO_x$ are <u>not</u> present as free radicals and thus must have been converted to diamagnetic molecules; most plausible by reaction with the moisture present in the NC matrix (other possibility, selective adsorption of dimer $N_2O_4$, is much less plausible)**
  - **EPR signal when $NO_2$ uptake capacity of water in NC is approached**
  - **$NO_x$-CLD and Abel-type Heat Tests show release of previously accumulated nitrogen oxides**
    - **Amount of accumulated $NO_x$ correlates with ageing time**
    - **Effect can be artificially reproduced by adsorbing $NO_x$ on new NC**
    - **Washing of NC removes this acccumulated $NO_x$**


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# Interpretation of Results 3 – NC-Ageing at Low Temperatures

- **Hypothesis 3: At ambient and slightly elevated storage temperatures, ageing of NC is dominated by hydrolytic rather than by radical reactions**

- **Hypothesis 3 is supported by the following experimental evidence:**
  - **Accumulation of $NO_x$ in the NC matrix and their likely reaction with moisture to acids (acids catalyze hydrolysis of NC) – see Hypothesis2**
  - **EPR finds no radicals in the low temperature range → no ongoing radical reactions (or at least only negligible amount of radical reactions)**

**Hydrolytic Reaction**

$$R\text{–}O\text{–}NO_2 + 2\,H_2O \xrightarrow{H^+} R\text{-}OH + HNO_3$$

**(3)** **Neutral to acid hydrolysis of the nitrate esters of NC**


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# Conclusions

- This investigations yielded a much better understanding of the chemical and physical-chemical ageing processes taking part in NC
- The findings of this study as well as the hypotheses drawn from these results need to be confirmed by further experiments
- None of the actually used stability tests and heat tests for NC investigate the hydrolytic ageing process which is dominant at storage temperatures!
  - 132°C Bergmann-Junk and 134.5°C Heat (Methyl Violet) Test assess the extend of homolytic primary and consecutive radical reactions
  - Many different processes contribute to the results of 65.5°C and 76.6°C Abel Heat Tests: Homolytic and other radical ageing reactions + release of nitrogen oxides accumulated in the NC matrix (from radical and/or hydrolytic reactions + other reactions) – there is always the question which of these processes has produced/dominated the test result
- New stability tests capable of assessing the extent of chemical ageing of NC at typical storage temperatures should be developed


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# Acknowledgement


- **Audience:** For your Attention
- **Co-author:** Ruth Sopranetti
- **Stability Tests:** Analytics Team Nitrochemie Wimmis
- **FTIR:** Bruno Ossola
- **$NO_x$-CLD:** Jürg Kislig
- **EPR:** Prof. Gunnar Jeschke; ETH Zurich
- **Direct CL** Fabian Käser; ACL Instruments AG

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