Practical Issues in Characterizing LNT Materials

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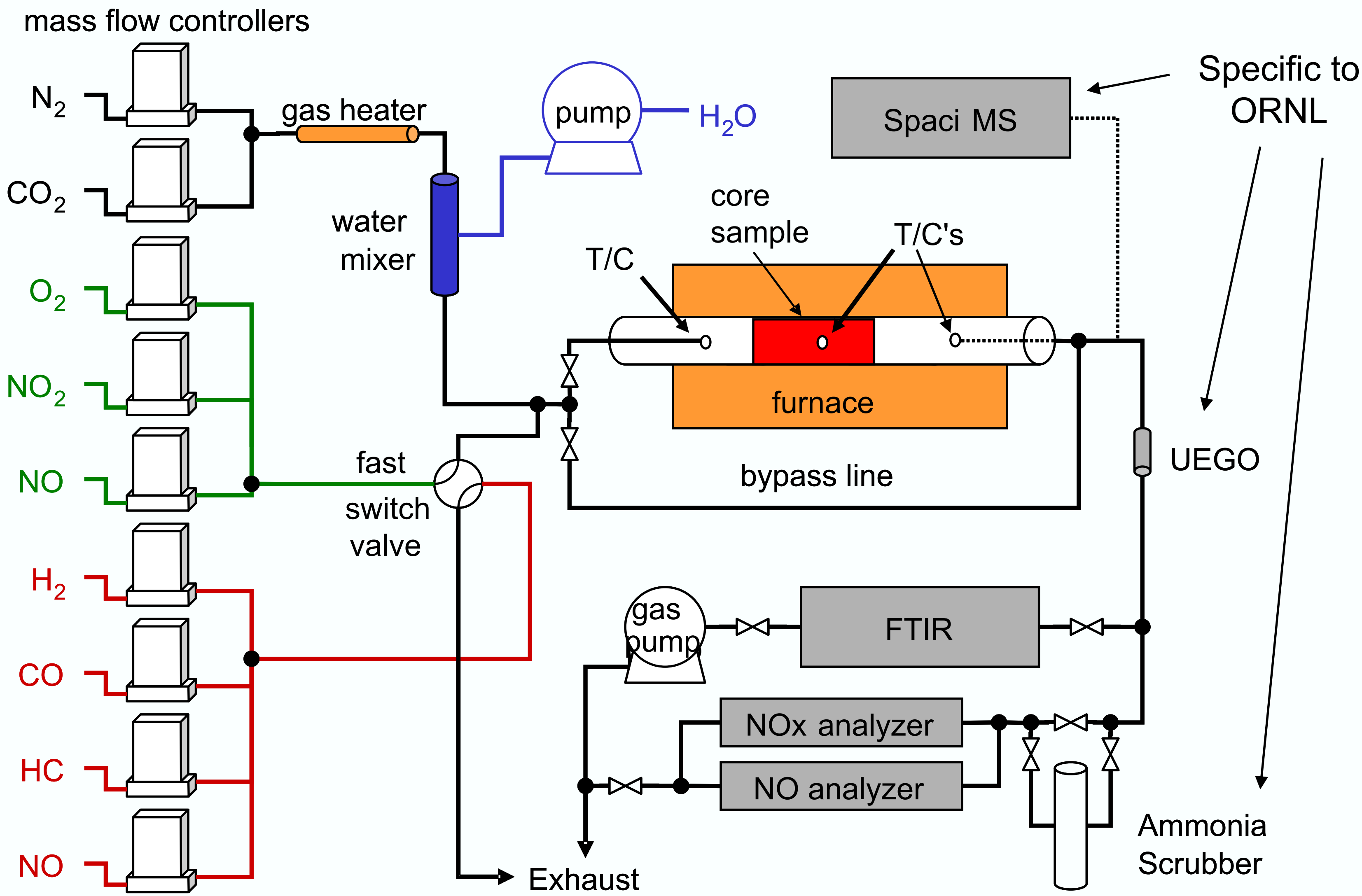
Objectives

- **Need generic protocol to produce consistent (repeatable & precise) performance information from bench measurements of LNT materials for simulating LNT devices**
- **Specific performance features to be quantified include:**
  - **Rates/capacities for following processes as functions of exhaust temperature, composition:**
    - **NO/NO_2 adsorption during lean condition**
    - **NO/NO_2 release, reduction during rich condition**
    - **Net reductant consumption (by species)**
    - **Byproduct formation (NH_3, N_2O)**
  - **Impact of S poisoning, aging**

Approach

- **CLEERS LNT Group issued draft protocol last June (visit www.cleers.org to download)**
- **Key protocol elements:**
  - **Defined sample (monolith core) size, degreening, T/C's**
  - **Short-cycles (60s/5s) at 5 temps with CO/H_2 reductant**
  - **Short-cycles (60s/5s) at 5 temps with simulated liquid diesel or gasoline reductant**
  - **Long cycles (15/10 min) at 5 temps with H_2 and CO/H_2 reductant**
  - **Exit measurement of NO, NO_2, H_2, CO, O_2, N_2O, NH_3, tHC**
  - **Instrument, switching valve calibrations**
  - **<=2 week completion time (8 hours/day)**

Basic bench-reactor features defined for the protocol



Umicore reference material has been very beneficial for protocol

- **Source: Owen Bailey**
- **Commercial European GDI**
- **Samples**
  - **8 bricks to ORNL, 2 to another CLEERS member**
  - **7 LNT Focus members are testing samples**
- **Dimensions:**
  - **Cylindrical, 4.66"D x 6"L or ~1.7L bricks**
  - **625 cpsi**
- **Composition:**
  - **Alumina washcoated cordierite**
  - **Approximately 110 g/ft3 PGM (Pt/Pd/Rh)**
  - **Ba, Ceria, Zirconia, Lanthanum**

- **Degreening (initial):**
  - **16 hrs at 700°C with 10% H_2O/air**
  - **Desulfation T= 700°C**

No restriction on measurements makes full information integration, site-to-site comparisons possible

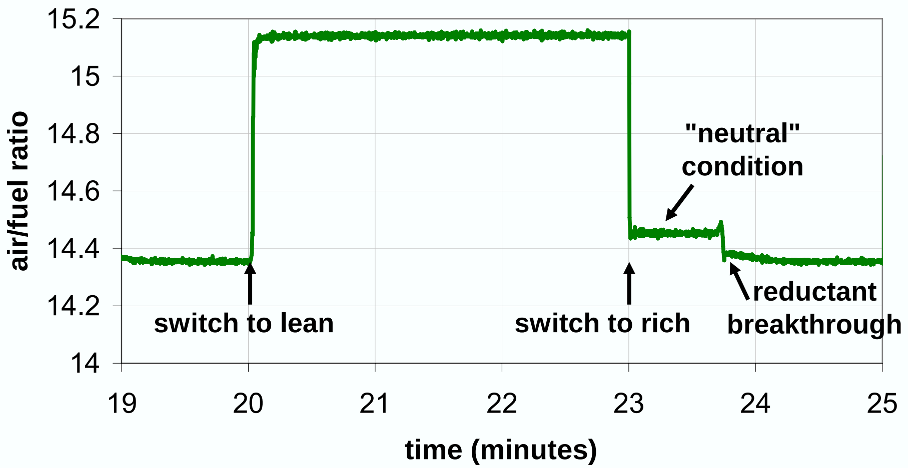
ORNL protocol testing has confirmed some measurement issues to be addressed

- **Corrections for instrument dynamics**
- **O_2 storage measurements**
- **Sample length effects**
- **High NH_3/N_2O levels**
- **Large hysteresis for degreened samples**

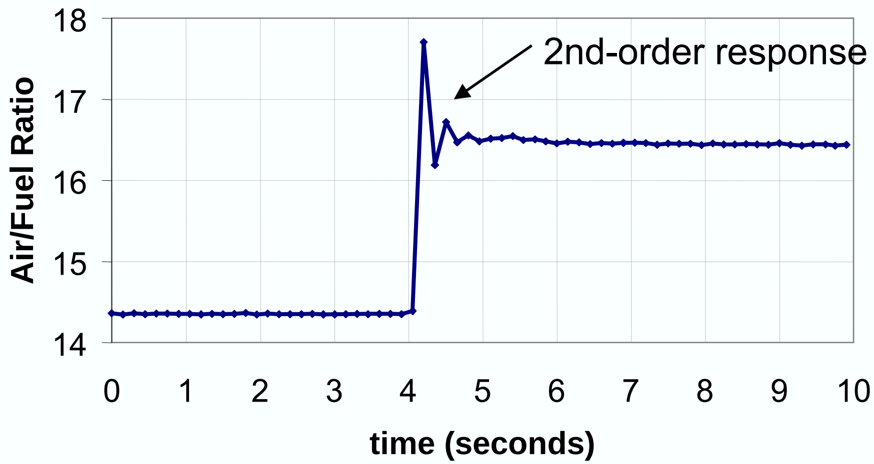
O_2 storage has turned out to be an important feature for LNT's

- **Large O_2 capacity (like 3-way)**
- **Increases reductant consumption**
- **Not explicit in current protocol**
- **Dynamic instrument response important for measurement**

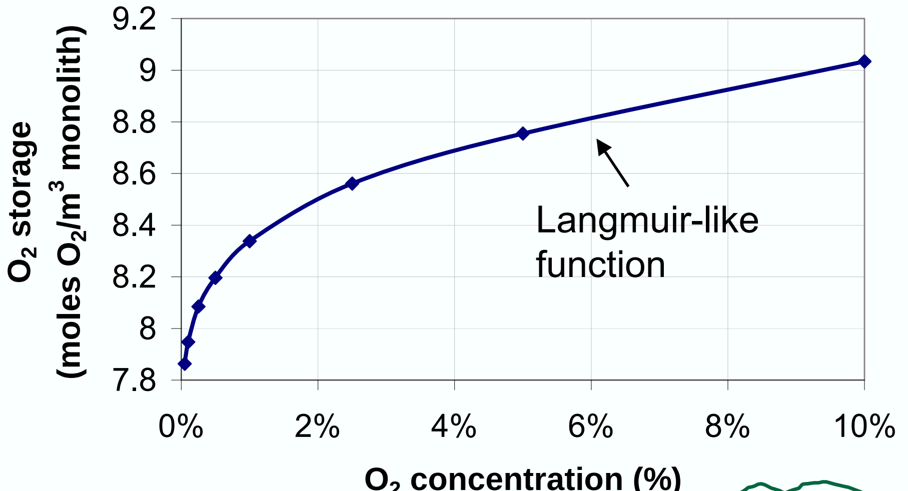
UEGO output for typical O_2 storage run



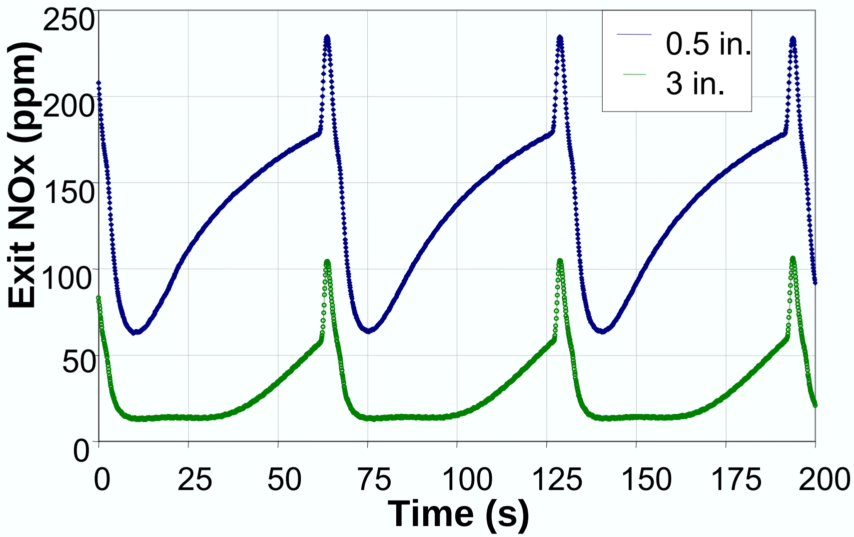
UEGO response confirms 0.2 s rich/lean transition

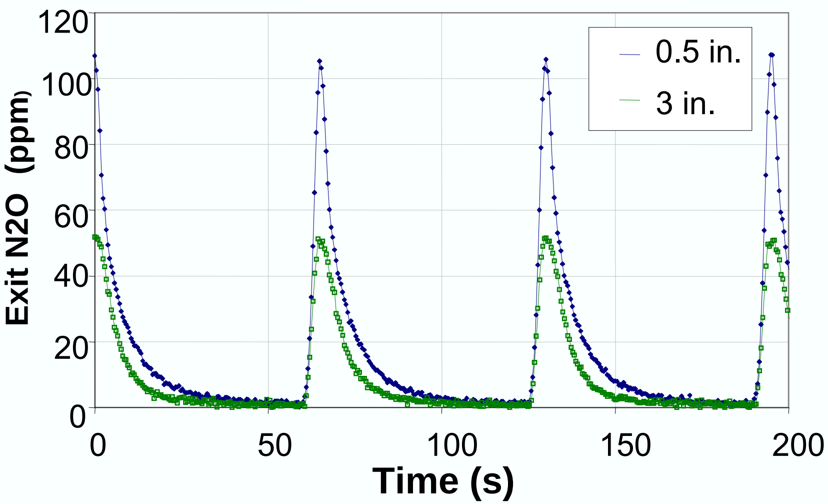


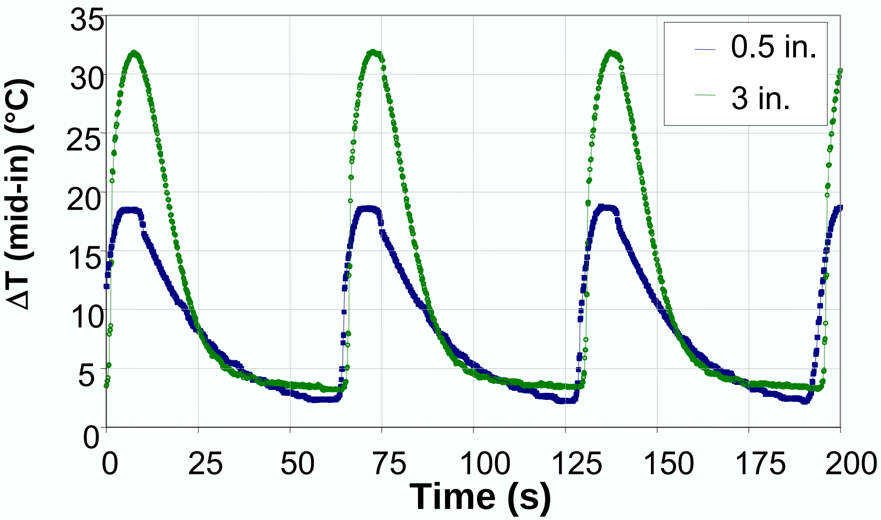
300C O_2 Storage Isotherm for Umicore LNT (from UEGO reductant breakthrough time)



Sample length affects measured response





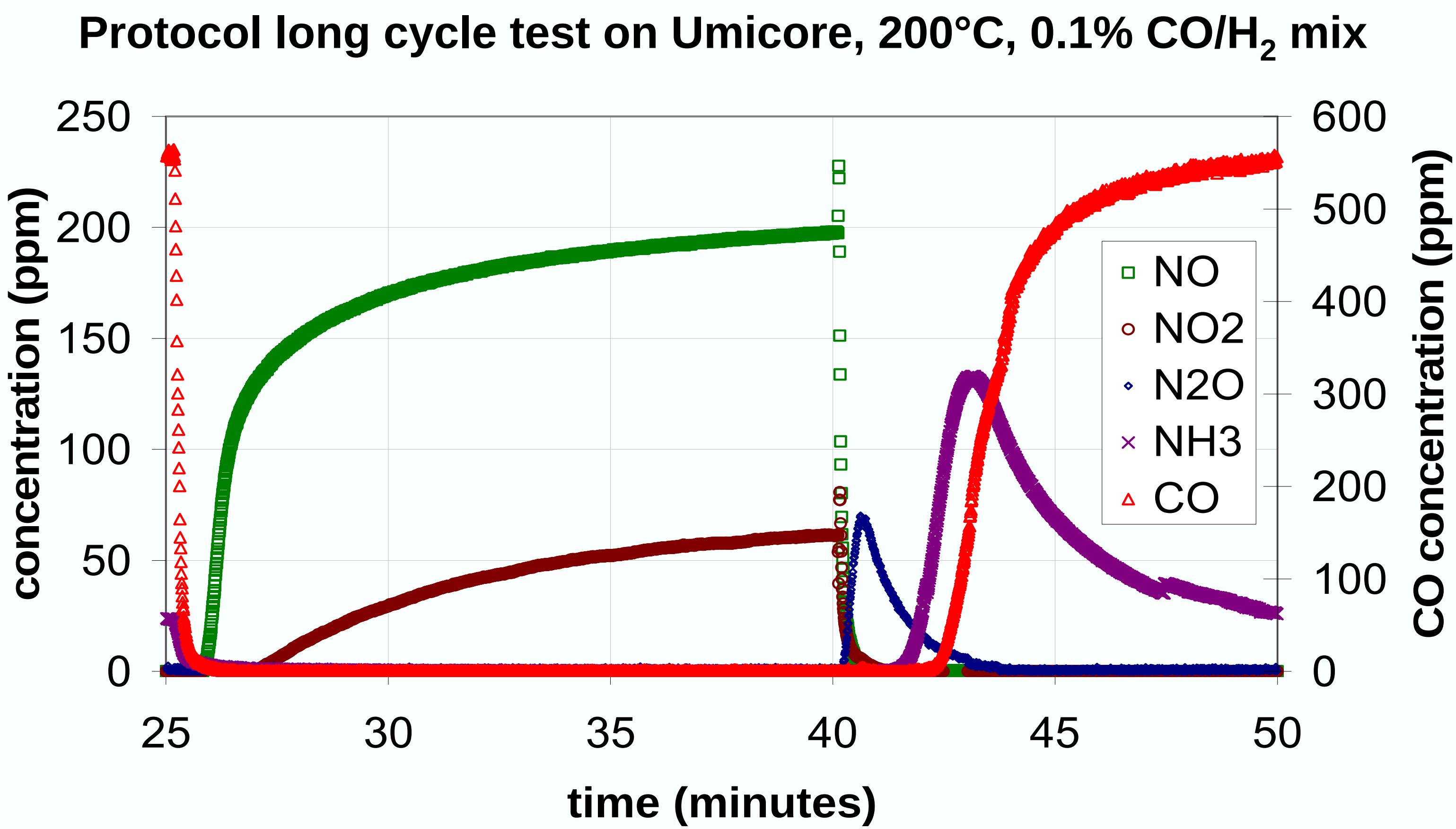


Protocol runs with degreened Umicore samples

- 3-inch and 0.5 inch lengths
- SV = 30,000 1/hr for both
- 60 s lean (300 ppm NO), 5 s rich (9000 ppm C0 / 5400 ppm H_2)
- Examples here at 300°C

NH_3 & N_2O are more plentiful than expected

- **Level depends on T, reductant concentration**
- **Such high levels of NH_3 can cause NOx measurement errors, high reductant consumption**
- **FTIR response is slow, hard to resolve details**

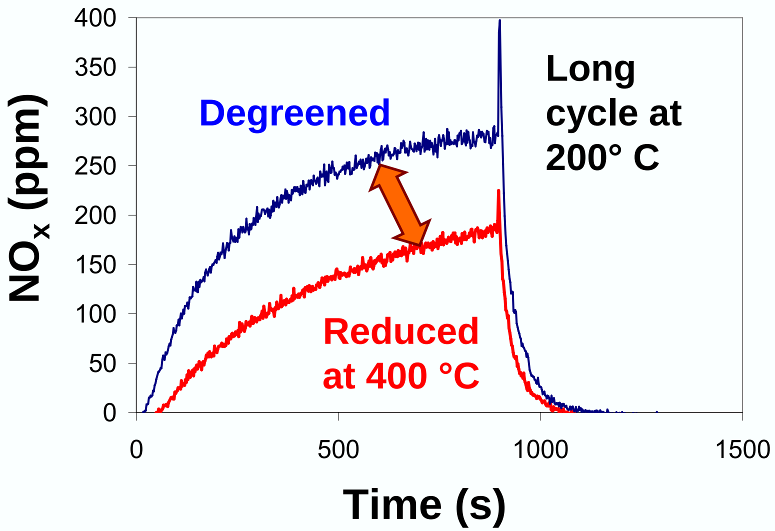


Hysteresis has also been greater than expected for degreened LNT samples

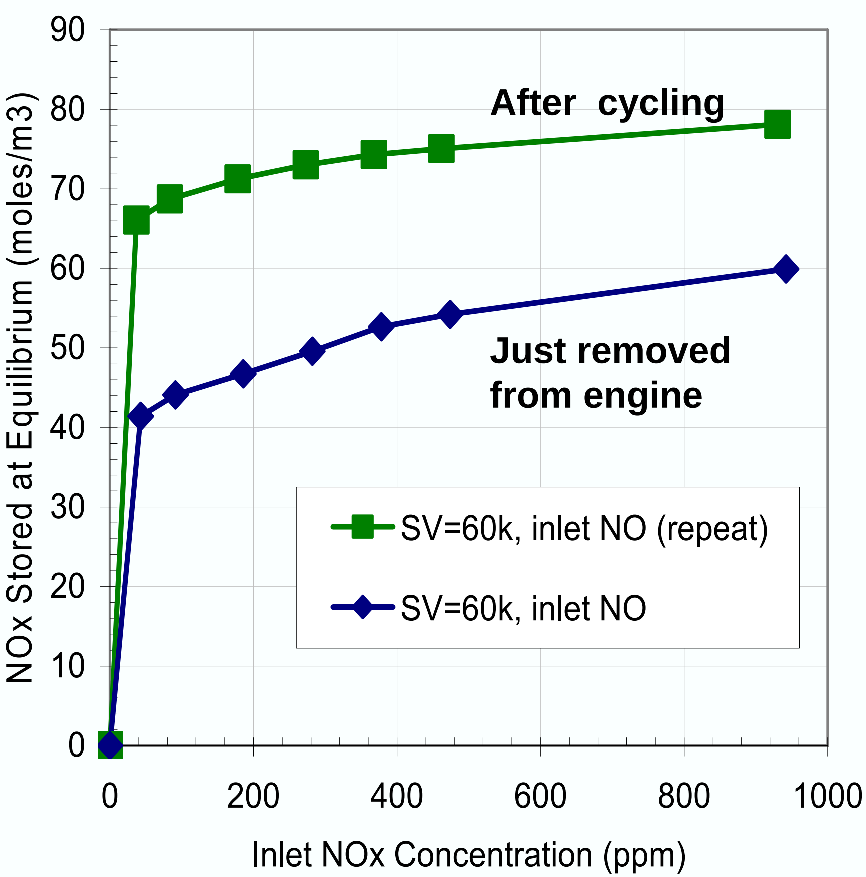
Analysis of original Umicore sample

Sample	Total BET area (m^2/g)
Original	29.1
Degreened[1]	20.6
Reduced Degreened[2]	27.1

[1] Aged 16 h in 10% H_2O/air
[2] Reduced in 1% H_2/Ar over night at 450°C



Bench test of engine-aged MECA sample



Summary of LNT Bench Observations

- **LNT protocol has remaining issues to be resolved:**
  - **O_2 storage measurement**
  - **Accounting for length effects, instrumentation response, NH_3**
  - **Consistent reduction of degreened samples (sample stability, handling)**
  - **Integration with aging assessment**
- **Consistency among labs greatest near 300°C, worst <=200°C, >=500°C**
- **Consistency problems imply greater care, more standardization needed**
- **Current LNT published data probably do not meet the required consistency standard**