P13

Influence of water on accuracy and stability of gaseous primary reference materials of nitrogen dioxide

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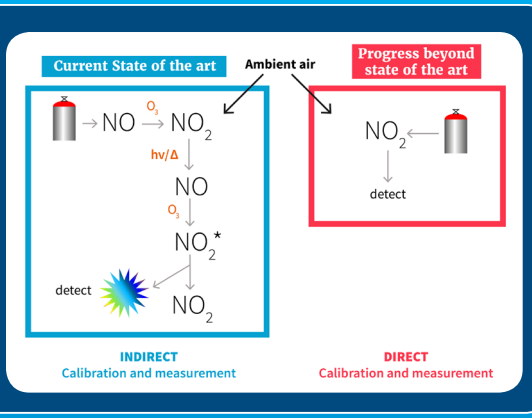
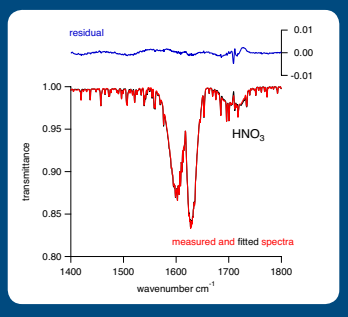
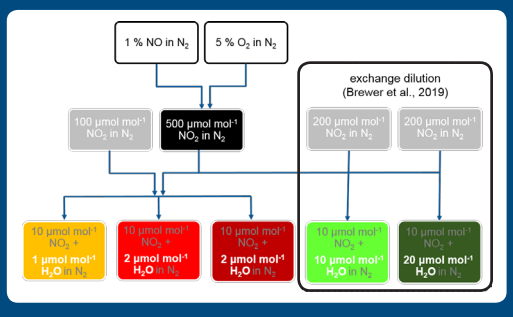
Need

- Nitrogen dioxide (NO_2) is a toxic gas and an essential climate variable
- Urban NO_2 under scrutiny result of vehicle emissions scandal, reported health impacts and continuing widespread breaches of EU legislation (2008/50/EC)
- NO_2 is only regulated air pollutant NOT directly measured ($NO_2 = NO_x - NO$) or calibrated
- Direct measurements now possible due to advancements in spectroscopic methods (e.g., CAPS)
- Widespread uptake requires accurate and stable reference materials
- Accuracy and stability of NO_2 reference materials impacted by NO_2 hydrolysis



Experimental

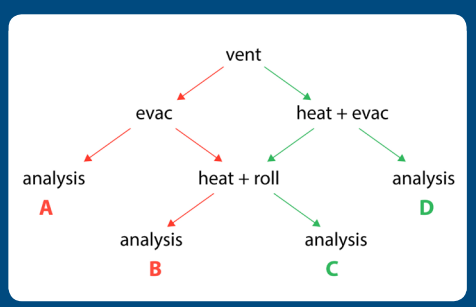


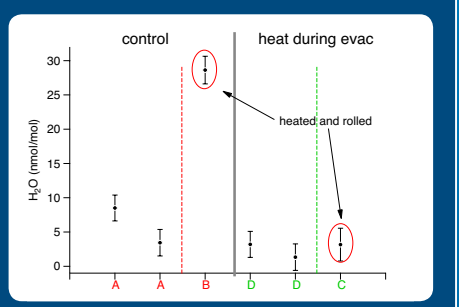


- FTIR measurements using a Nicolet 6700 (Spectral Range: 27,000 – 15 cm-1, Source: Nicolet Ever-glo, Detector: MCT-A, Gas Cell: Specac Cyclone C5, ~8 m OPL)
- Amount fractions assigned via comparison to ref. stds
- No HNO_3 ref. std → quantified against synthetic spectra (HITRAN) (Flores et al., 2013)
- H_2O meas. (nmol/mol) using CRDS (Tiger Optics)

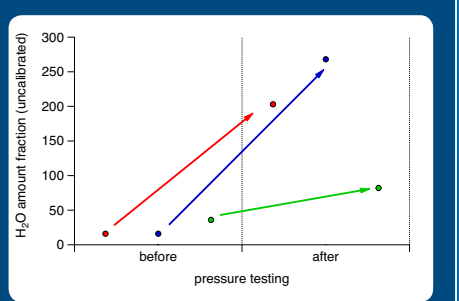
Results II: Cylinder drying/pressure testing

- Heating during evac. removes H_2O from cylinder surface



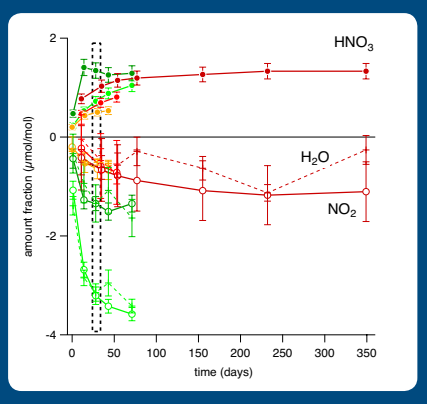


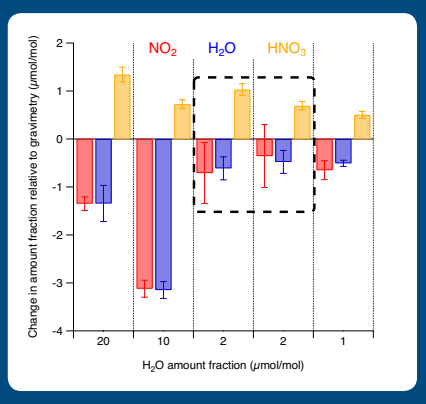
- Cylinder pressure checking (or regulator purging) can undo all this work
- Implications for use of cylinders at monitoring stations



Results I: HNO_3 evolution

- Observe 1:1 NO_2:H_2O loss but variable HNO_3
- Conversion efficiency lower at high H_2O amount fractions: 60 % (1 µmol/mol) to 6 % (20 µmol/mol)



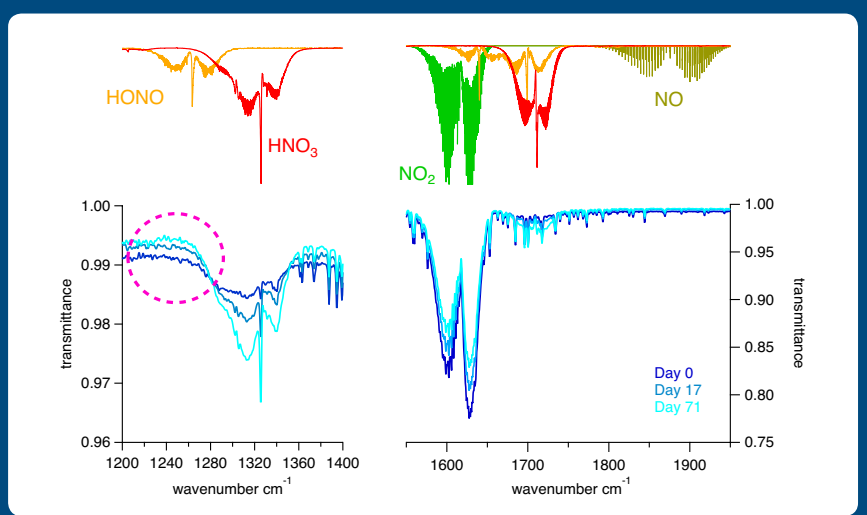


- Mechanism for hydrolysis of NO_2 in atmosphere well known for decades (Ramazan et al., 2006):

$2NO_2 + H_2O + surface \rightarrow HNO_3 + HONO$

- However, HONO not observed in any mixture
- Alternative possibility:

$3NO_2 + H_2O + surface \rightarrow 2HNO_3 + NO$ **$(NO + ½O_2 \rightarrow NO_2)$**



Summary

- Observations of stoichiometric NO_2 + H_2O loss and no HONO formation inconsistent with known mechanism implies NO_2 hydrolysis chemistry within cylinders (high pressure, dark) is different than under atmospheric conditions
- Water needs to be reduced to < 5 – 50 nmol/mol of H_2O in cylinder to enable preparation of 1 – 10 umol/mol NO_2 reference standards with < 0.5 % uncertainty and 2 year stability (achievable but challenging)
- Can in cylinder chemistry be used to make HNO_3 reference mixtures? Current work implies HNO_3 formation limited even at elevated H_2O

P. Brewer et al., (2019) Breakthrough in negating the impact of adsorption in gas reference materials. In press, Analytical Chemistry.

E. Flores et al., (2013) Accurate Fourier Transform Infrared (FT-IR) Spectroscopy Measurements of Nitrogen Dioxide (NO_2) and Nitric Acid (HNO_3) Calibrated with Synthetic Spectra. Applied Spectroscopy, 67(10): 1171-1178. 10.1366/13-07030.

Ramazan et al., (2006) New Experimental and Theoretical Approach to the Heterogeneous Hydrolysis of NO_2: Key Role of Molecular Nitric Acid and Its Complexes. The Journal of Physical Chemistry A, 110, (21), 6886-6897. doi:10.1021/jp056426n.

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