ACTRIS Intercomparison Campaign for Nitrogen Oxides (NO_x) at Forschungszentrum Jülich in 2023

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ACTRIS Intercomparison for Nitrogen Oxides (NO_x)

- **Aim:** (i) To intercompare state-of-the-art instruments for NO_x measurements and investigate potential interferences through experiments under identical conditions, (ii) To train ACTRIS station members on measurement guidelines and calibration procedures
- **Location:** IEK-8 at Forschungszentrum Jülich, Germany, with SAPHIR atmospheric simulation chamber and JULIAC tower part of the setup
- **Measurement techniques:** Chemiluminescence detection (CLD), Cavity-attenuated phase shift (CAPS), Iterative cavity-enhanced differential optical absorption spectroscopy (ICAD), Tunable Diode quantum cascade laser (TDQCL), Long Path Absorption Photometer (LOPAP)
- **Time Period:** set-up 12-16 June 2023; experimental 19-30 June 2023

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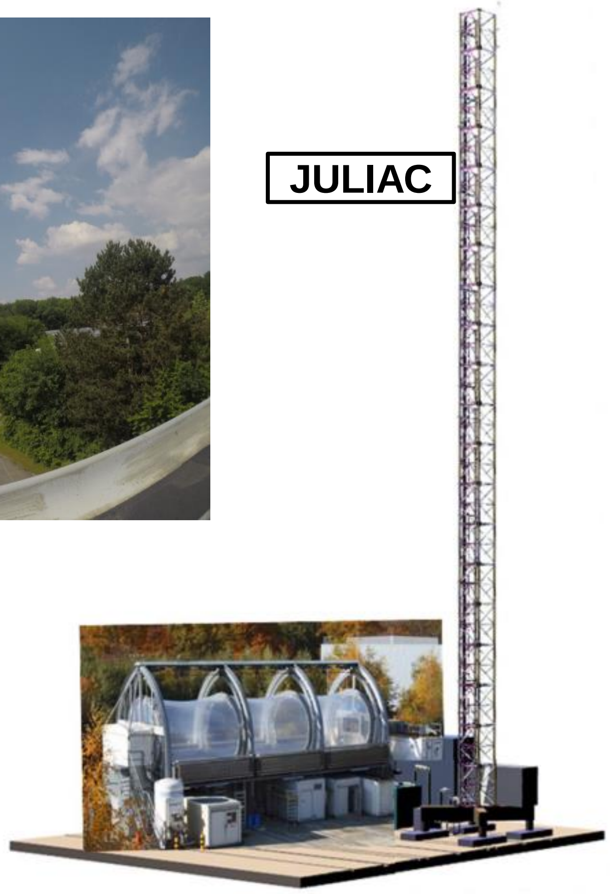
ACTRIS Intercomparison for Nitrogen Oxides (NO_x)

- **Opportunity for participants to:**
  - test their equipment, perform experiments, and discuss experimental data and potential challenges
- **Calibration** → standard reference gases
- **Interference effects** → water vapor, O_3, HONO, glyoxal, HNO_3, N_2O_5
- CLD interferences from
  - reactive nitrogen oxides that release NO_2 during the reduction process
  - quenching of excited NO_2 by water vapor
- CAPS → water vapor bias
- little to no intercomparison and interference data exists for the recent techniques ICAD, TDQCL, CAPS, LOPAP



Overview of groups and instrumentation

	Group	Instruments
1	**HELIOS, France**	Ecophysics CLD 780 TR
		Environnement S.A AS32M CAPS
		Aerodyne CAPS
2	**IMT Nord Douai, France**	Ecophysics CRANOX
		Teledyne T200UP
3	**Mt. Cimone, Italy**	Teledyne T200UP
		Thermo Scientific 42iTL
4	**Univ. of Iasi, Romania**	ECOTECH EC9841
5	**Univ. of Nottingham, UK**	Airyx ICAD 200-UV1-L
6	**Univ. of York, UK**	Airyx ICAD
7	**Univ. of Leicester, UK**	CAPS
8	**Airyx, Germany**	Airyx ICAD-NOx-200D
9	**DWD MOHp, Germany**	Ecophysics CLD 770 AL ppt
		Aerodyne CAPS
		Ecophysics nCLD899
10	**QUAREC, Germany**	LOPAP
		ECO Physics CLD 899 Y
11	**TROPOS, Germany**	Teledyne T200UP
		Aerodyne CAPS
12	**FZJ, Germany**	Ecophysics CLD
		ICAD
		CAPS
		MIRO TDQCL

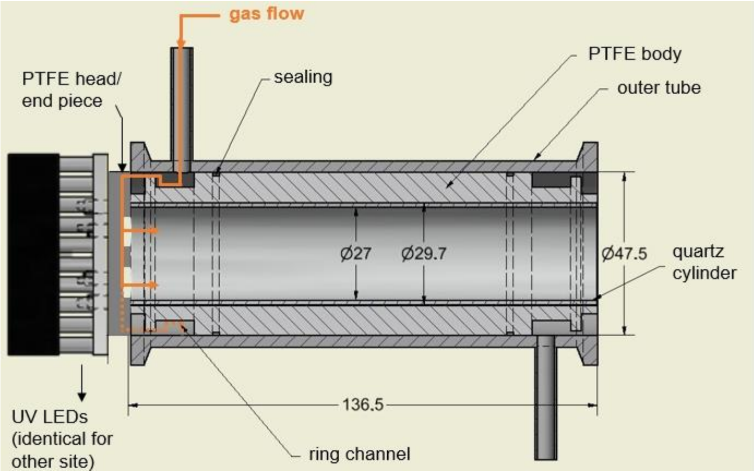
ACTRIS IMP TNA (groups 1–7)

Measurement by chemiluminescence

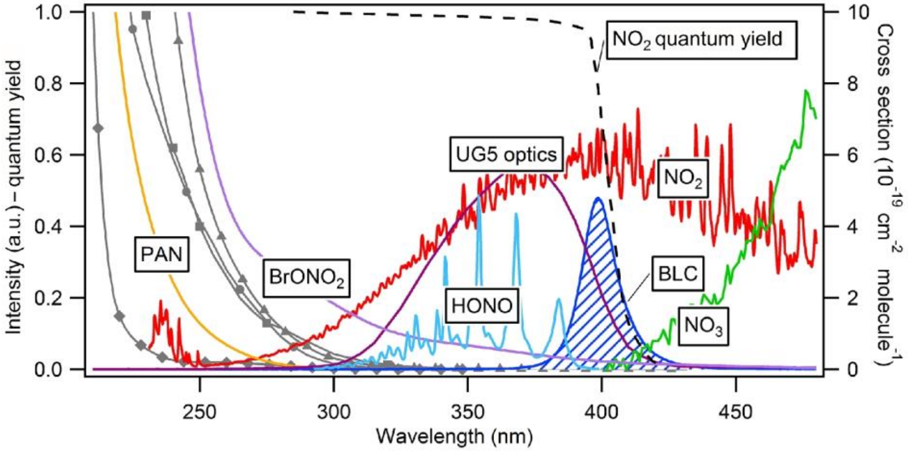
Conversion to NO by Photolysis

$NO_2 + h \cdot \nu \rightarrow NO + O^3(P)$

Xenon lamps or
UV emitting diodes ("blue light converters, BLC")



Nussbaumer, C. M., et al. (2021). "Modification of a conventional photolytic converter for improving aircraft measurements of NO2 via chemiluminescence." Atmos. Meas. Tech. **14**(10): 6759-6776.



Reed, C., et al. (2016). "Interferences in photolytic NO2 measurements: explanation for an apparent missing oxidant?" Atmos. Chem. Phys. **16**(7): 4707-4724.

- Spectral band width should be small
- No overlap with PAN
- But some overlap with HONO and $BrONO_2$

Spectroscopic techniques

Cavity attenuated phase shift spectroscopy (CAPS)

Kebabian et al., 2008. , *Environmental Science & Technology*, 42: 6040-45.

Quantum Cascade Laser (QCL)

Tuzson et al., 2013. *Atmospheric Measurement Techniques*, 6: 927-36.

Iterative cavity-enhanced DOAS (ICAD)

Horbanski et al., 2019. Atmospheric Measurement Techniques, 12: 3365-81.

Long Path Absorption Photometer (LOPAP)

Villena et al., 2011. Atmospheric Measurement Techniques, 4: 1663-76.

- Enable direct NO_2 measurements
- Conversion of NO into NO_2 needed
- Ozone inlet correction still needed
- Also, humidity may cause problems

ACTRIS Intercomparison for Nitrogen Oxides (NO_x)

Atmospheric simulation chamber SAPHIR

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Chamber properties:

Length: 18m

Diameter: 5m

Volume: 270m^3

Ambient pressure / temperature

Minimum wall interaction:

- Double wall made of teflon (FEP)
- Volume : Surface ~ 1
- High purity synthetic air

ACTRIS Intercomparison for Nitrogen Oxides (NO_x)

SAPHIR + JULIAC setup

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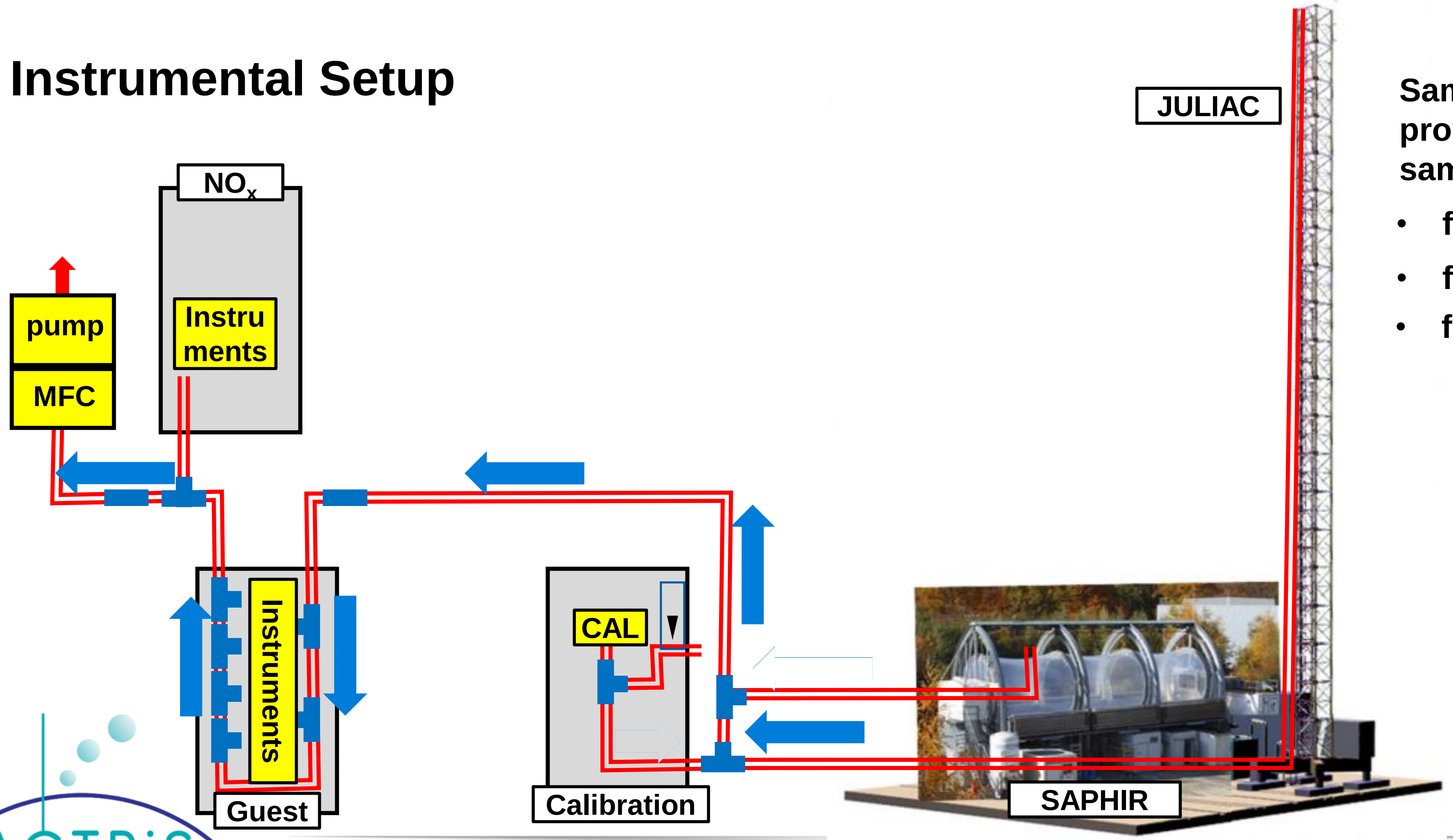
ACTRIS Intercomparison for Nitrogen Oxides (NO_x)

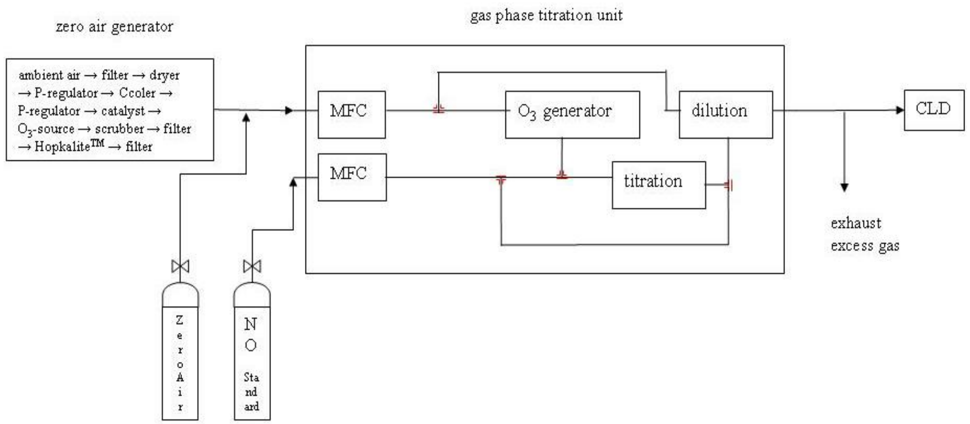
Instrumental Setup

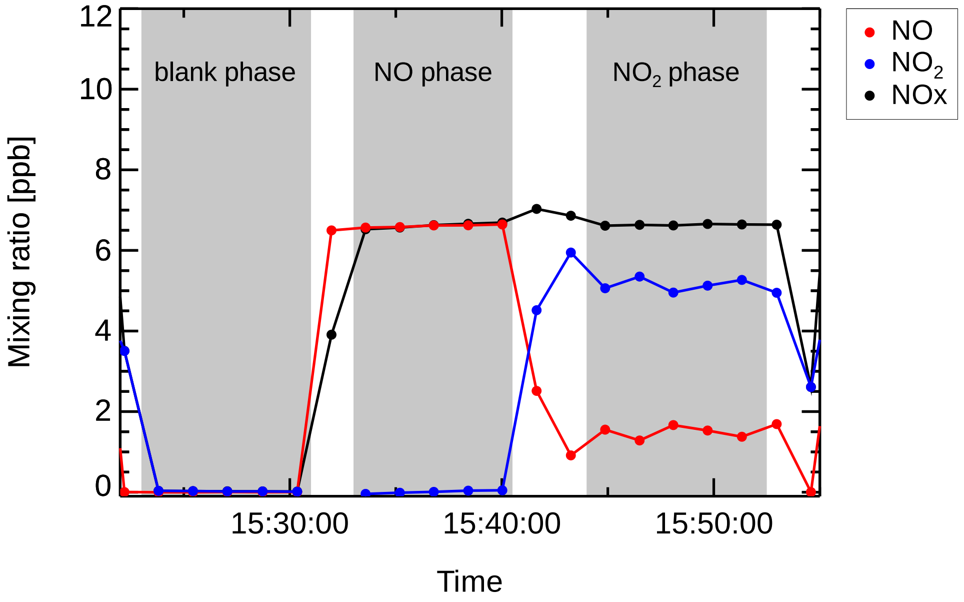


Sample air will be provided via a common sample line either:

- from a calibration unit
- from SAPHIR
- from the JULIAC tower

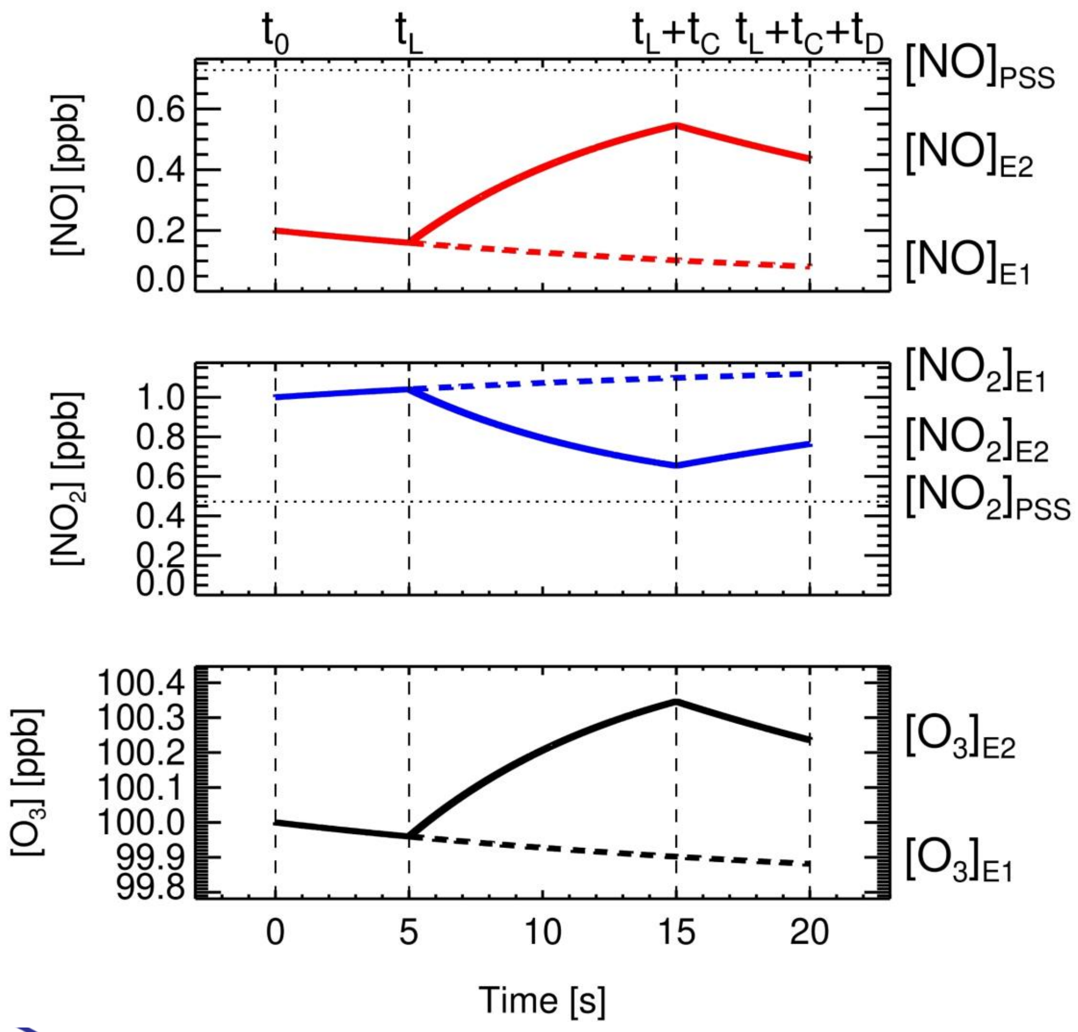
Calibration for NO_x

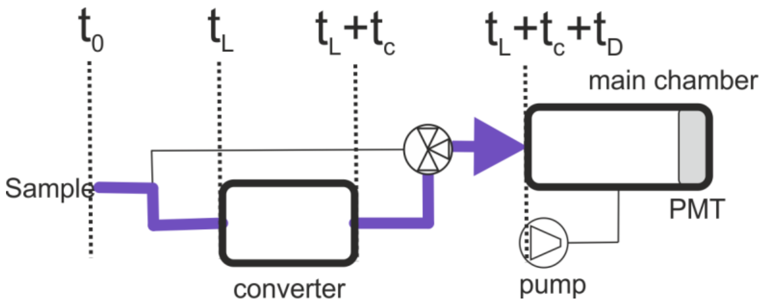




- NO_2 is produced from reaction with Ozone
- The amount of NO_2 is calculated from the loss of NO
- The leftover NO indicates that there are only small amounts of ozone in the system

Chemistry in the Inlet





$$[NO]_0 = [NO]_{E1} \times e^{k_{O_3L} \times (t_L + t_B + t_D)}$$

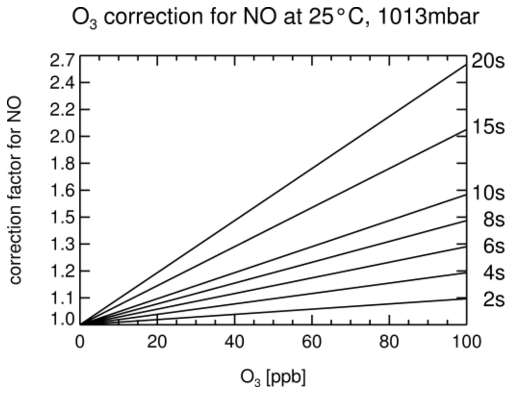
$$NO_2 \rightleftarrows NO + O_3$$

See: https://ebas-submit.nilu.no/SOPs

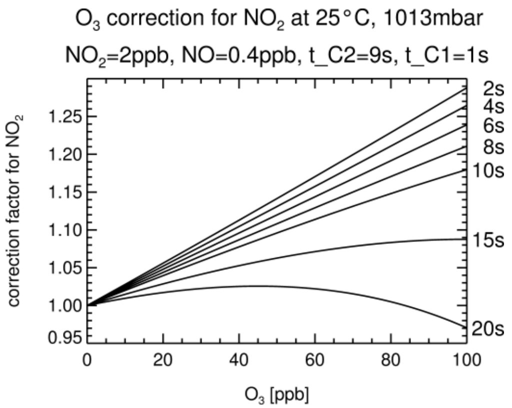
Or:

Andersen, S. T., et al. (2021). "Long-term NOx measurements in the remote marine tropical troposphere." Atmos. Meas. Tech. **14**(4): 3071-3085.

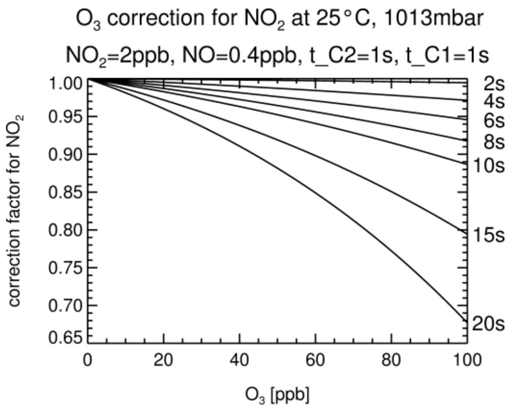
Chemistry in the Inlet



correction factor for NO at different residence times in the sampling line



correction factor for NO_2 at different residence times in the sampling line



correction factor for NO_2 at different residence times in the sampling line

The Humidity Effect

Chemistry in the CLD main chamber

$NO + O_3 \rightarrow NO_2 + O_2$
$NO + O_3 \rightarrow NO_2^* + O_2$
$NO_2^* \rightarrow NO_2 + h\cdot\nu$
$NO_2^* + M \rightarrow NO_2$, $M = N_2, O_2, H_2O, Ar$

Matthews, R. D., Sawyer, R. F., & Schefer, R. W. (1977). Interferences in chemiluminescent measurement of nitric oxide and nitrogen dioxide emissions from combustion systems. *Environmental Science & Technology, 11*(12), 1092-1096. doi:10.1021/es60135a005

		Factor for quenching in ambient air	
$NO_2^* + N_2 \rightarrow NO_2$	$k(NO_2^*+N_2)$		
$NO_2^* + O_2 \rightarrow NO_2$	$k(NO_2^*+N_2)$*1.115	21%	1.034
$NO_2^* + CO_2 \rightarrow NO_2$	$k(NO_2^*+N_2)$*2.05	400ppm	1.000
$NO_2^* + Ar \rightarrow NO_2$	$k(NO_2^*+N_2)$*0.5	1%	0.995
$NO_2^* + H_2O \rightarrow NO_2$	$k(NO_2^*+N_2)$*4.42	1%	1.043

Consequences (for CLD instruments)

- no correction needed when frequent spiking of ambient air is performed
- 0-10% correction needed for calibrations using NO/N_2 diluted by synth. air
- no water correction needed if the ambient air is dry or dried
- 3.4% additional correction needed for calibrations using NO/N_2

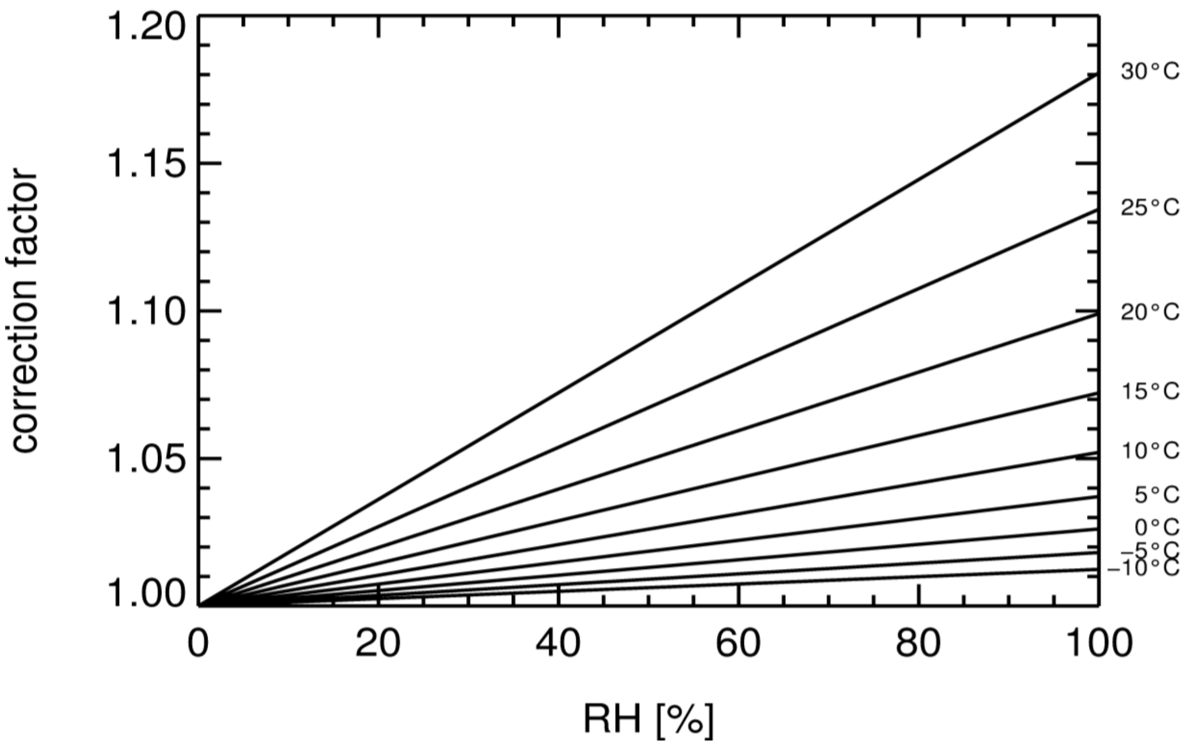
Humidity effect and correction

$$[NO]_{H_2Ocorr} = [NO] \cdot (1 + \alpha \cdot [H_2O])$$

$$\alpha = (4.3 \pm 0.3) \cdot 10^{-3} \cdot \frac{flow_{sampleair}}{flow_{ozone} + flow_{sampleair}}$$

(α taken from Ridley et al., 1992; $[H_2O]$ given in parts per thousand)

Ridley, B. A., et al. (1992). "A Small, High-Sensitivity, Medium-Response Ozone Detector Suitable for Measurements from Light Aircraft." Journal of Atmospheric and Oceanic Technology **9**(2): 142-148.



Thank you!

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