
In-Service Aircraft for a Global Observing System

# Measurement of Nitrogen Oxides on IAGOS

## Instrument Characterization, First Observations and Future Developments

# WHY ARE NITROGEN OXIDES IMPORTANT ?

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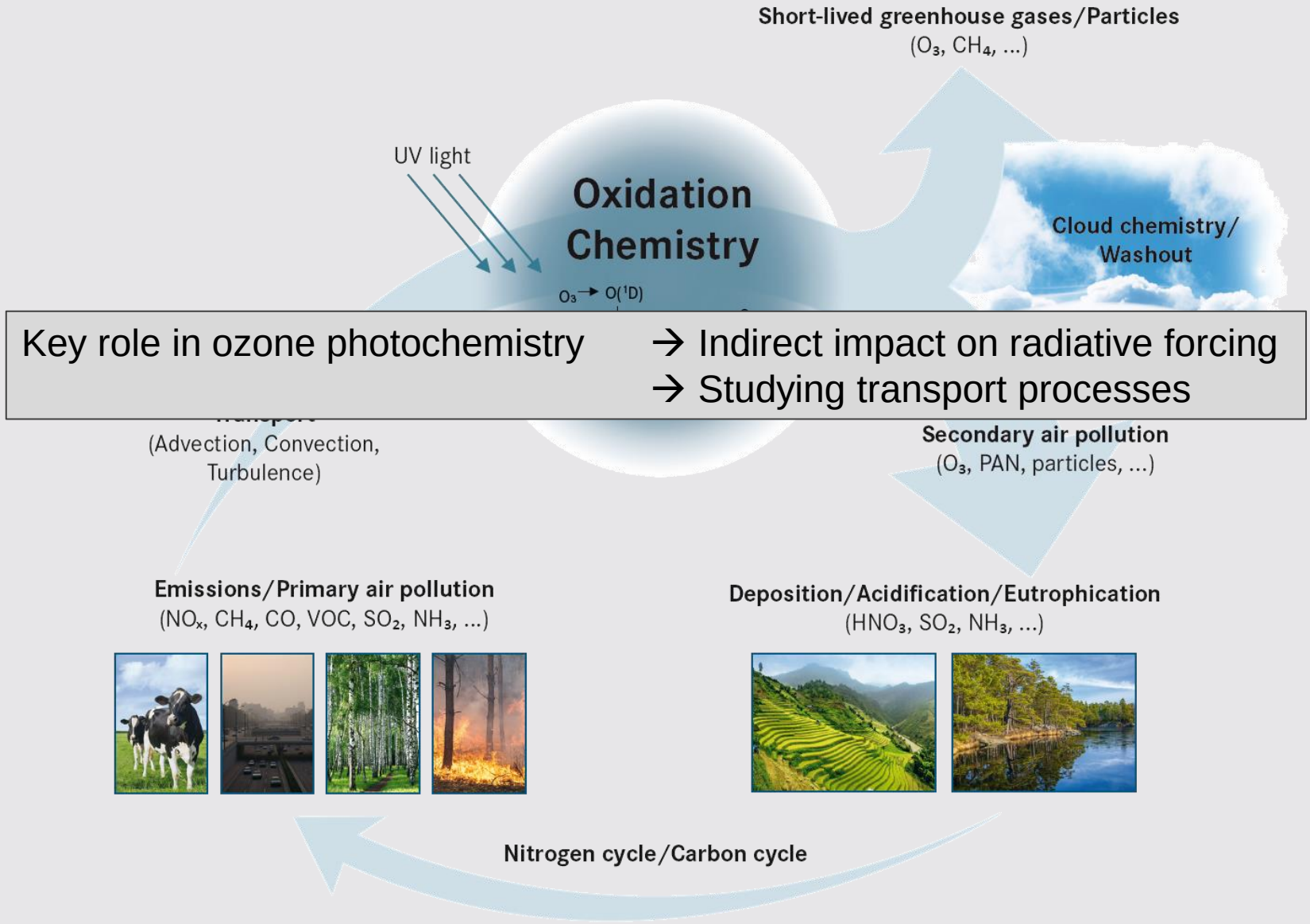


Key role in ozone photochemistry → Indirect impact on radiative forcing
→ Studying transport processes

# How Do We Measure Nitrogen Oxides ?

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**Chemiluminescence** (CL) is the emission of light with limited emission of heat (luminescence), as the result of a chemical reaction.

This definition excludes flames where radiation is emitted as a result of exothermic high-temperature chemical reactions.

Oxidation of NO to $NO_2$ , small part of $NO_2$ goes into the excited state: $NO^*_2$

(1) $NO + O_3 \rightarrow NO_2 + O_2$

(2) $NO + O_3 \rightarrow NO^*_2 + O_2$

Relaxation of $NO^*_2$ into the ground state via

(3) $NO^*_2 \rightarrow NO_2 + h\nu$ emission of radiation ($\lambda$ = 0.59 - 2.8 µm)

(4) $NO^*_2 + M \rightarrow NO_2 + M$ quenching by collision with M ($N_2$, $O_2$)

**NO** direct measurement by CL after reaction with $O_3$.

**$NO_2$** measured by CL after specific conversion to NO via photolytic reaction.

# IAGOS Nitrogen Oxides Instrument

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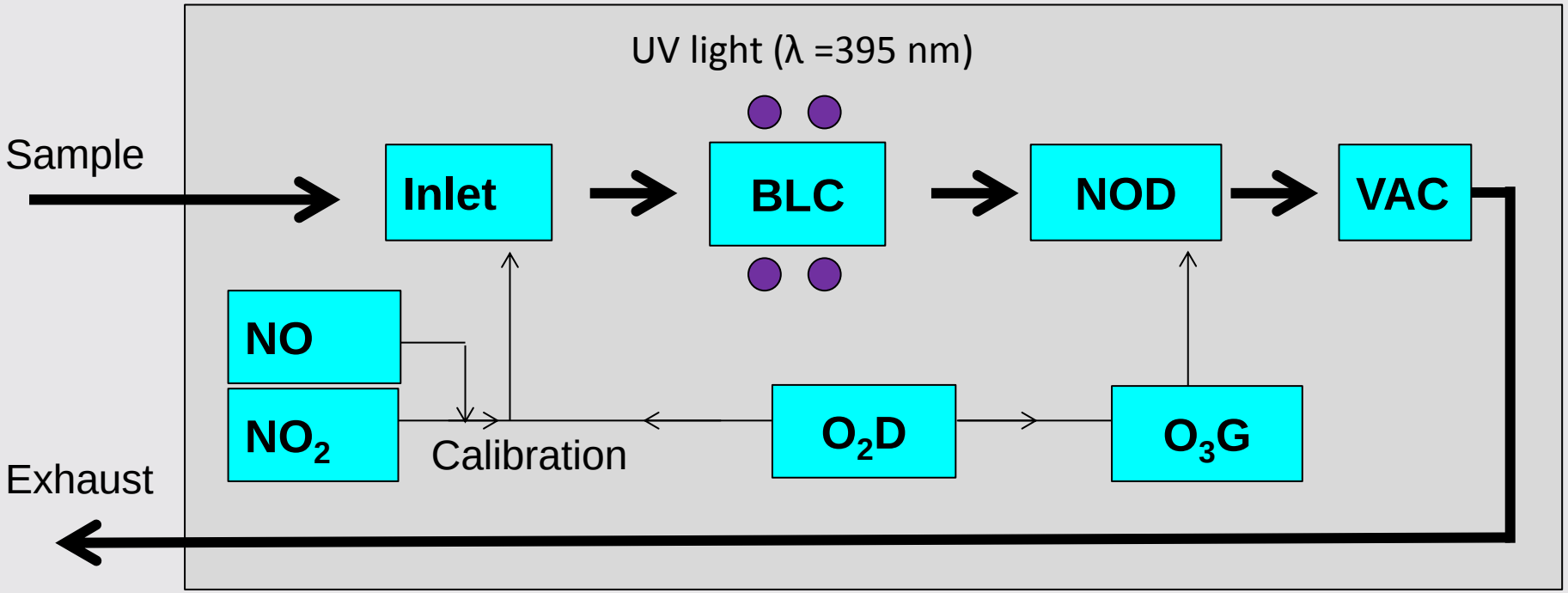


Photolytic conversion in BLC $NO_2 + h\nu \rightarrow NO + O$ (λ =395 nm)

Detection of NO by CL $NO^*_2 \rightarrow NO_2 + h\nu$ (λ = 0.59 - 2.8 µm)

Sequential measurement of NO (BLC UV off) and $NO_x$ (BLC UV on)

# IAGOS Nitrogen Oxides Instrument

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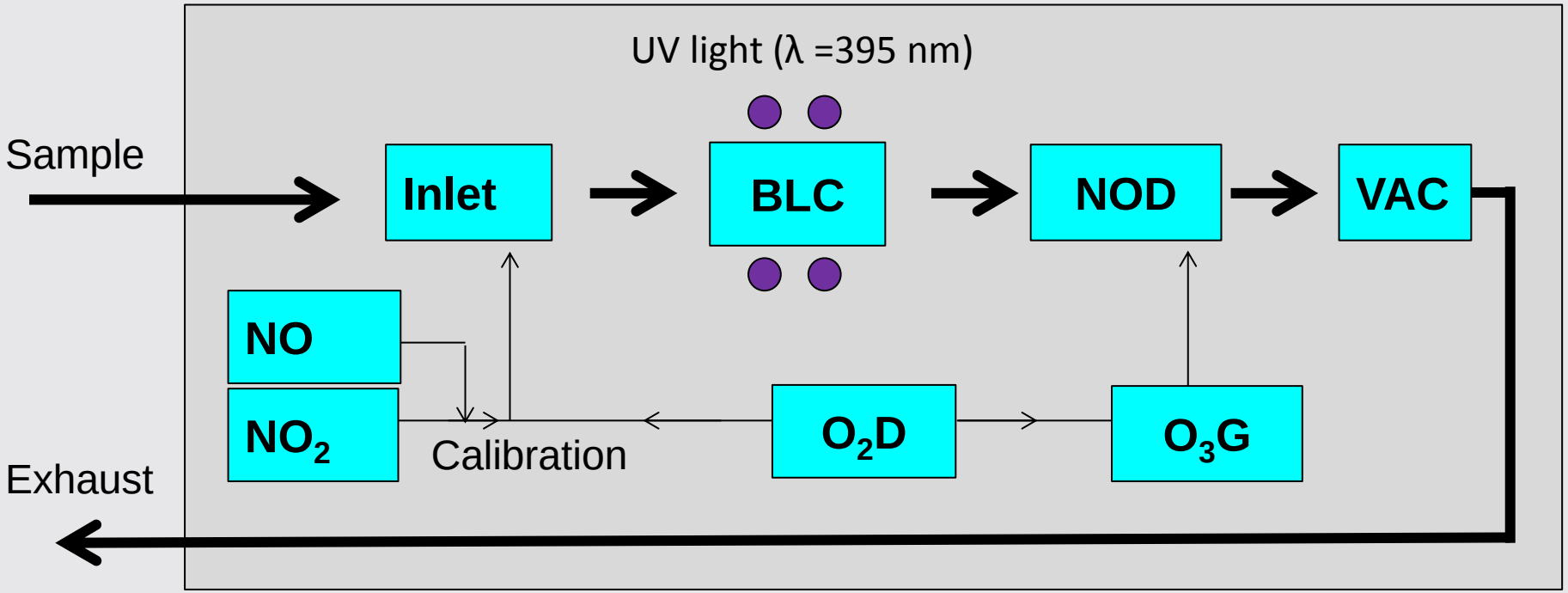


Measuring Mode: Ambient $NO/NO_x$ is measured by reaction with $O_3$

Zero Mode: About 98% of ambient $NO/NO_x$ is oxidized in the pre-volume to determine the background signals from other chemical reactions

Background Mode: Background signal of gas supply is determined

# IAGOS Nitrogen Oxides Instrument

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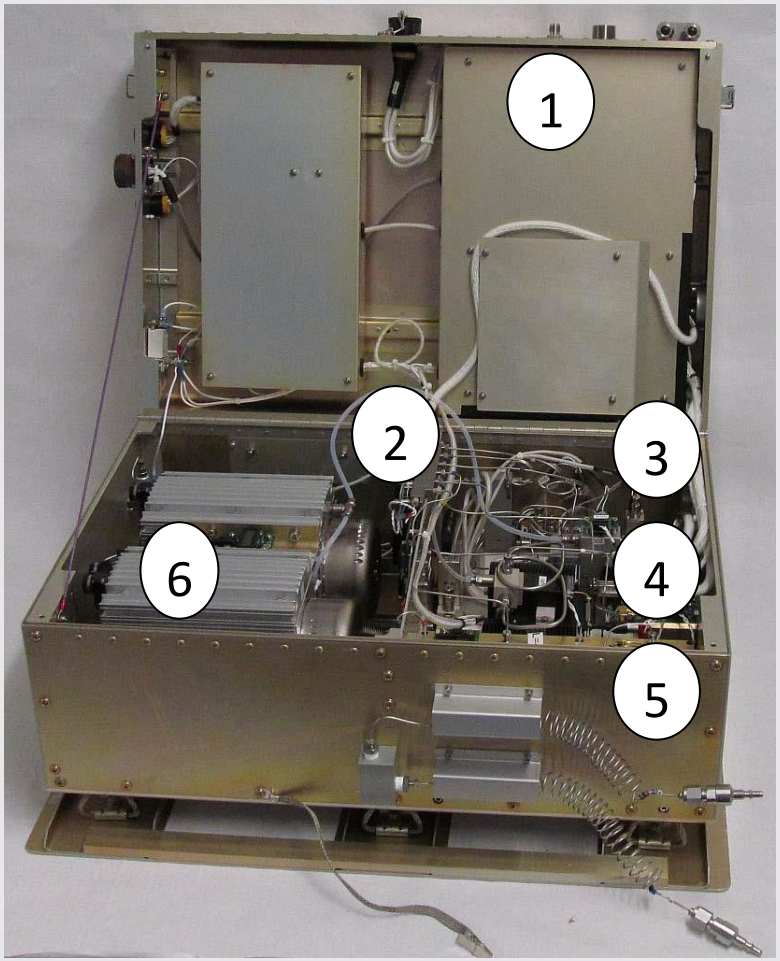


**Functional Units**

1) Data Acquisition System

2) Oxygen Distribution (O2D)

3) Converter and Calibration (ICC)

4) NO Detector (NOD)

5) Ozone Generator (O3G)

6) Vacum Pump (VAC)

Source: Berkes et al., in press, AMT 2018

# IAGOS Nitrogen Oxides Instrument

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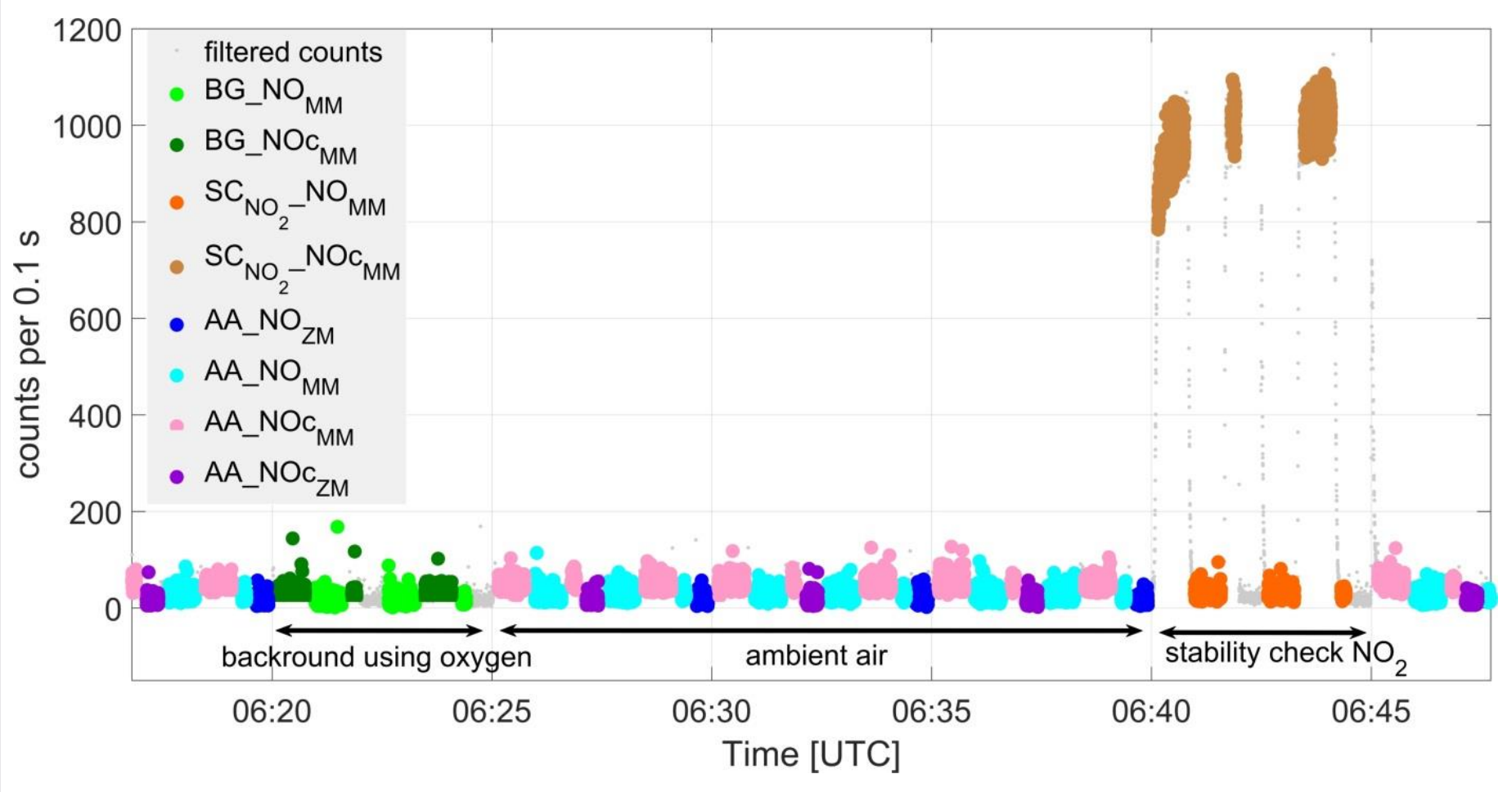


**Different modes of the instrument:**

ambient air: measuring modes (MM) are shown for NO (BLC off) and NOc (BLC on)
zero air modes (ZM) are shown for NO (BLC off) and for NOc (BLC on).

# IAGOS Nitrogen Oxides Instrument

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## Specifications

$$LOD = 2/(S \times CE)\sqrt{\left(\frac{BG_{MM}}{t}\right)^2 + \left(\frac{BG_{NM}}{t}\right)^2}$$

S = sensitivity in cts/ppb
CE = conversion efficiency
BG_MM = background signal measurement mode
BG_NM = background signal zero mode

IAGOS (Berkes et al., 2018)

- NO 24 pptv (2-sigma, 4s)
- $NO_2$ 35 pptv (2-sigma, 4s)

CARIBIC (Stratmann et al., 2016)

- NO 7 pptvl (2-sigma,1s)

NOXAR: (Brunner et al., 2000)

- NO 23 pptv (1-sigma, 2s)
- $NO_2$ 45 pptv (1-sigma, 2s)

## IAGOS CL Instrument

| | |
|---|---|
| Sample flow rate | 150 sccm |
| Inlet flow rate | 1.5 SLM |
| Zero-air flow rate | 250 sccm |
| $O_2$ consumption | ~60L/Flight |
| Weight | 29 kg |
| Size | 560x300x280 mm |
| Detection limit | NO = 21 ppt, $NO_2$ = 27 ppt |

# INSTRUMENT INTERCOMPARISON

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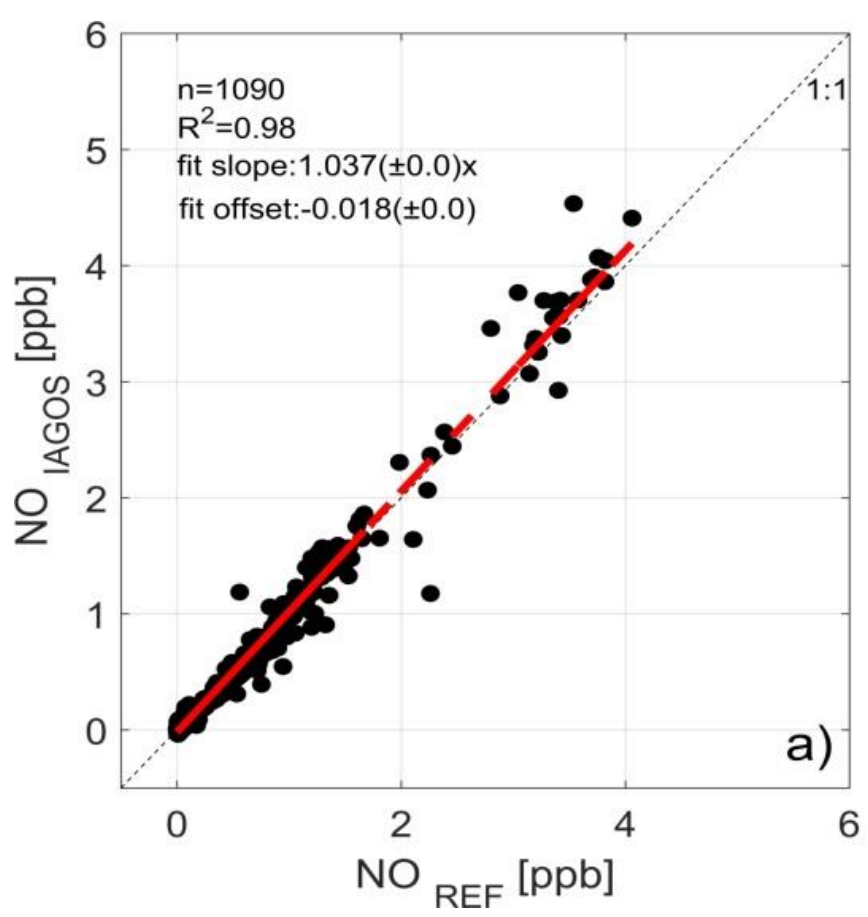


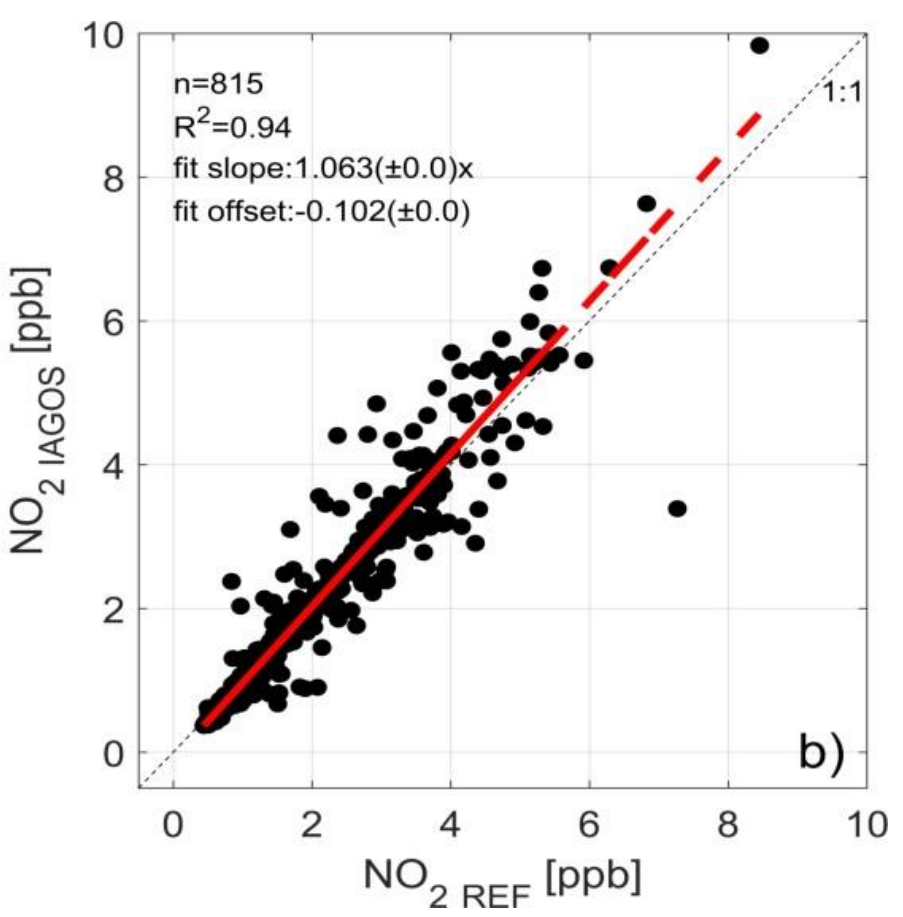


Two days of ambient NO and $NO_2$ measurements at DWD Hohenpeissenberg Observatory in October 2016 during the ACTRIC s-b-s $NO_x$ intercomparison.

The reference instrument (REF) was regularly calibrated during the campaign.

# NO AND $NO_2$ MIXING RATIOS AT NIGHT

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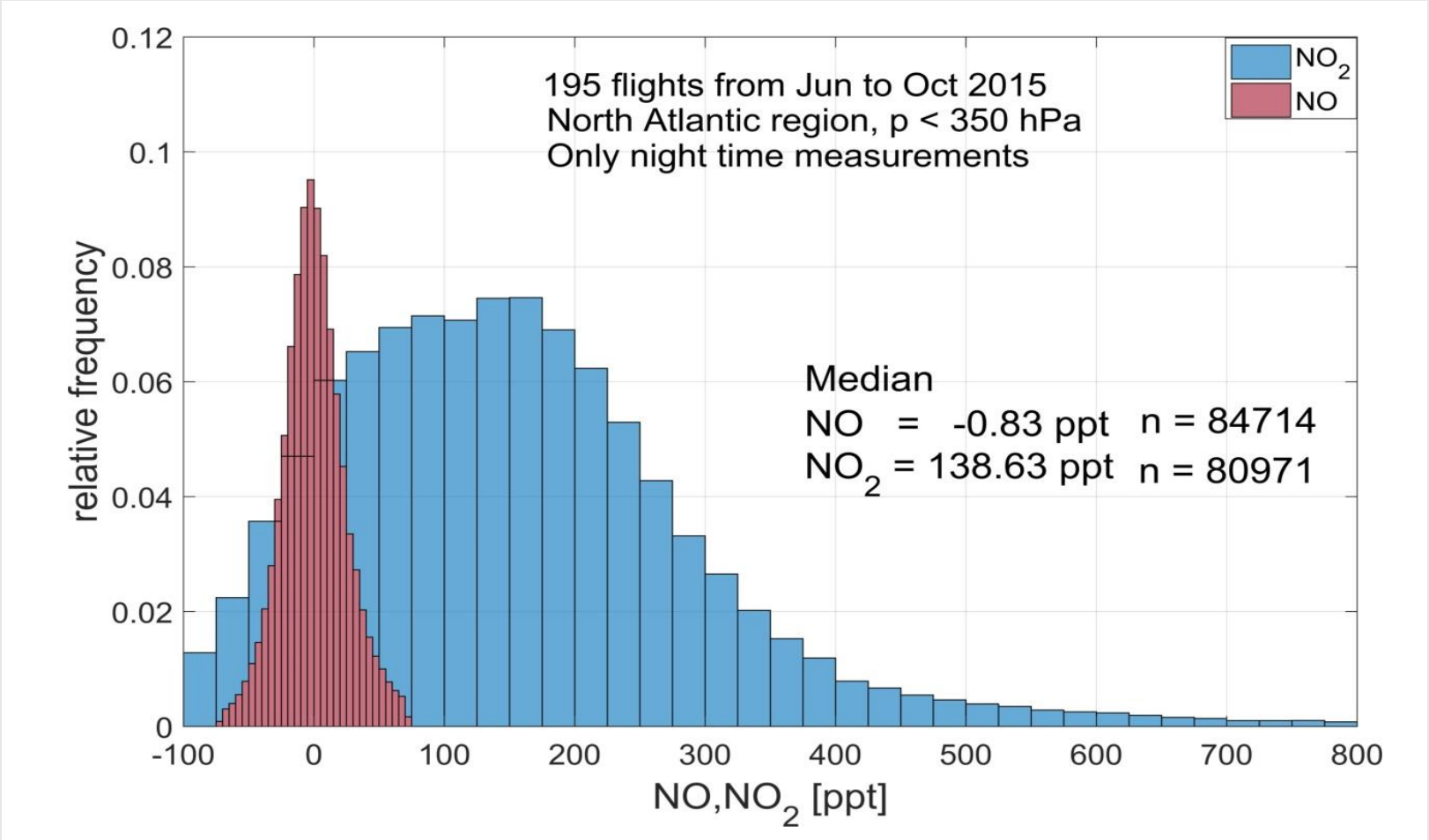


Night: $NO + VOC, HO_2 \rightarrow NO_2 + products$

Day: $NO_2 + sunlight \rightarrow NO + O$

# NO AND $NO_2$ VERTICAL PROFILES

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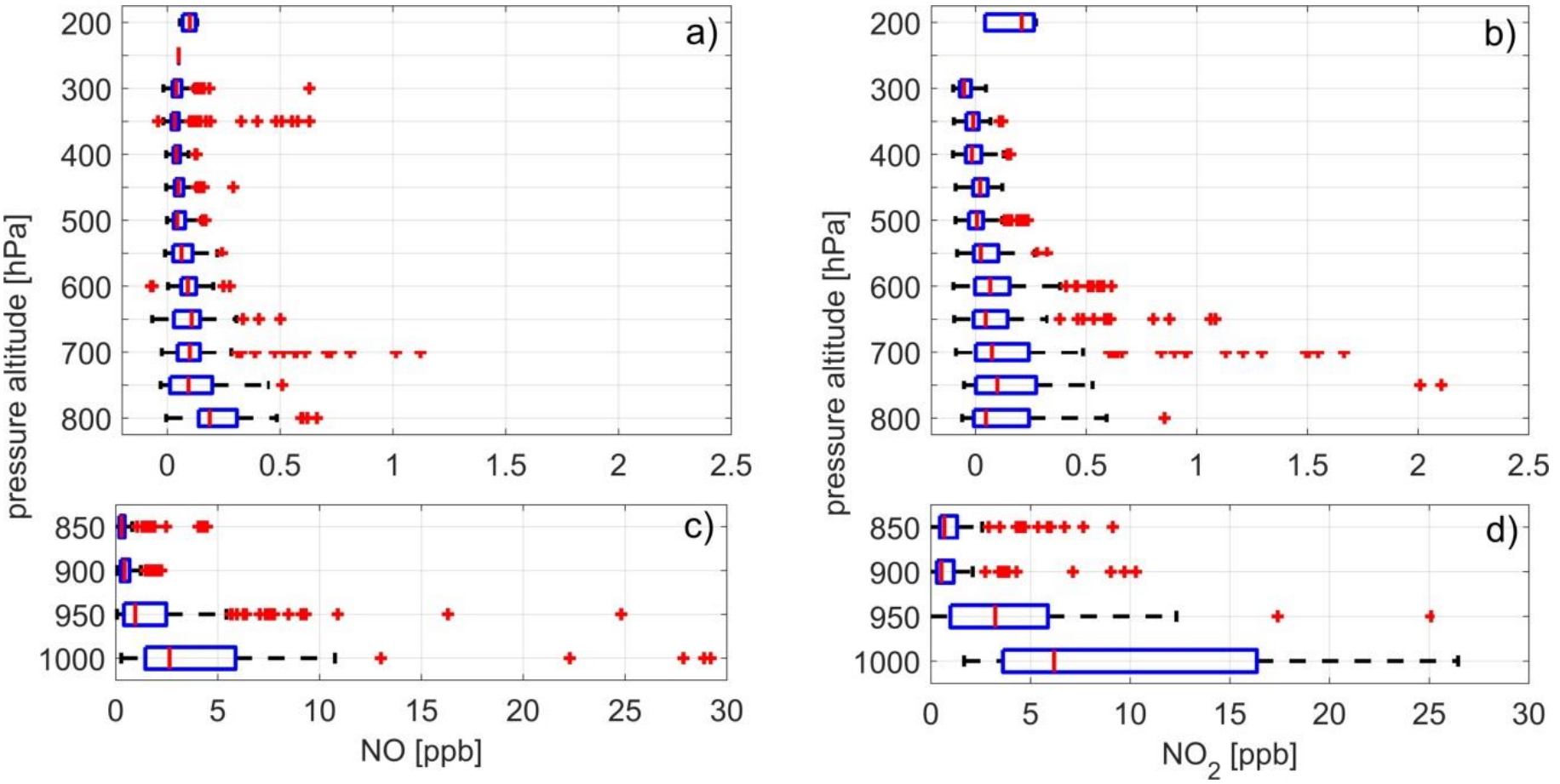



Vertical distribution of NO and $NO_2$ at day time for NO (left) and $NO_2$ (right) over Düsseldorf airport in summer (JJA) 2015. Note the different x-axis-scale.

# $NO_2$ Detection by Optical Means

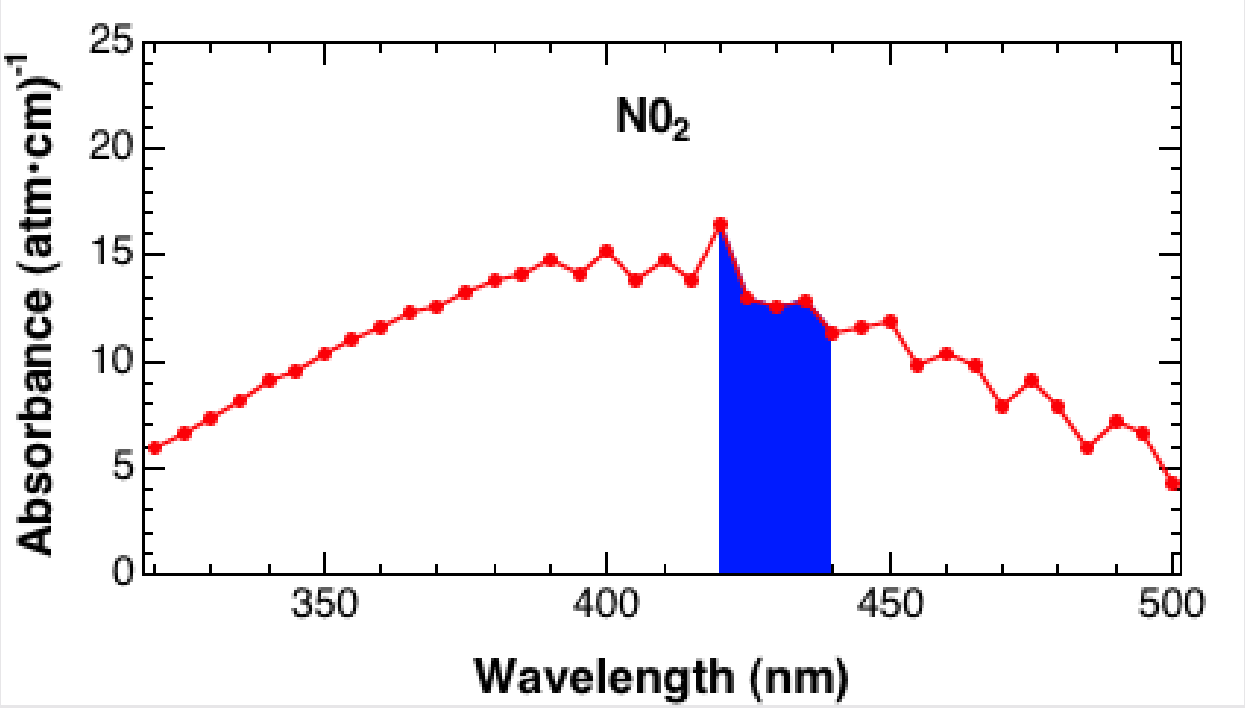
$NO_2$ is a Brown Gas...

weak absorber,

peaks at 400-450 nm

use blue LED to detect
1 $Mm^{-1}$ ~ 1 ppb $NO_2$

air Rayleigh scattering
~ 29 $Mm^{-1}$ at STP




Kebabian et al., Environ. Sci. Technol., 42:6040-6045. 2008

# $NO_2$ Detection by Optical Means

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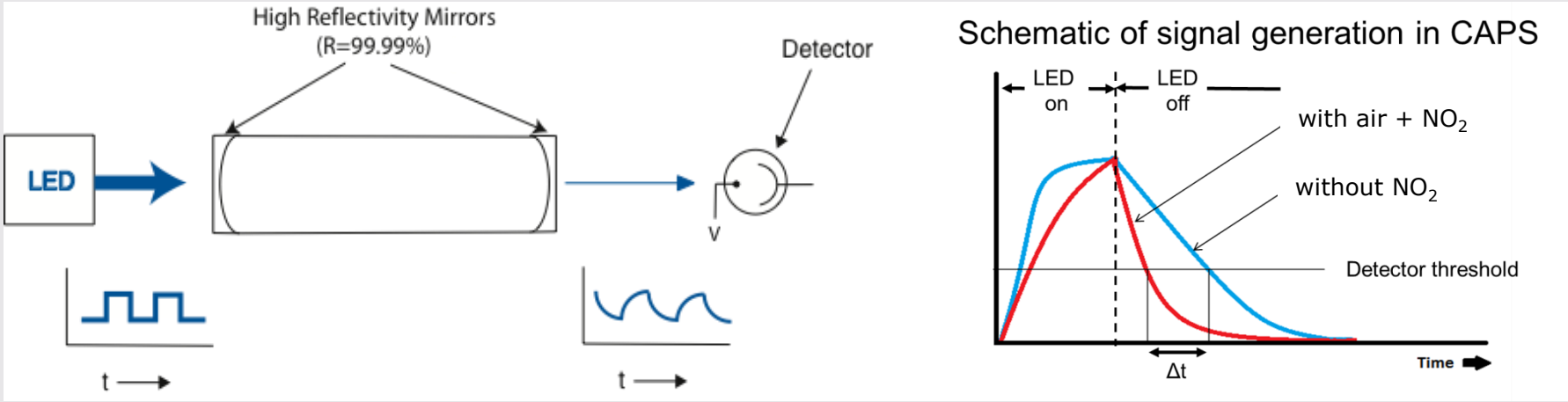
## Cavity-Attenuated Phase Shift (CAPS) Technique

Method similar to cavity ring-down spectroscopy




- Light Source — LED (blue)
- High Reflectivity Optical Cell — Pathlength: ~2 km
- Detector — Vacuum Photodiode

Kebabian et al., Rev. Sci. Instrum., 78, 063102 (2007)

# $NO_2$ Detection by Optical Means

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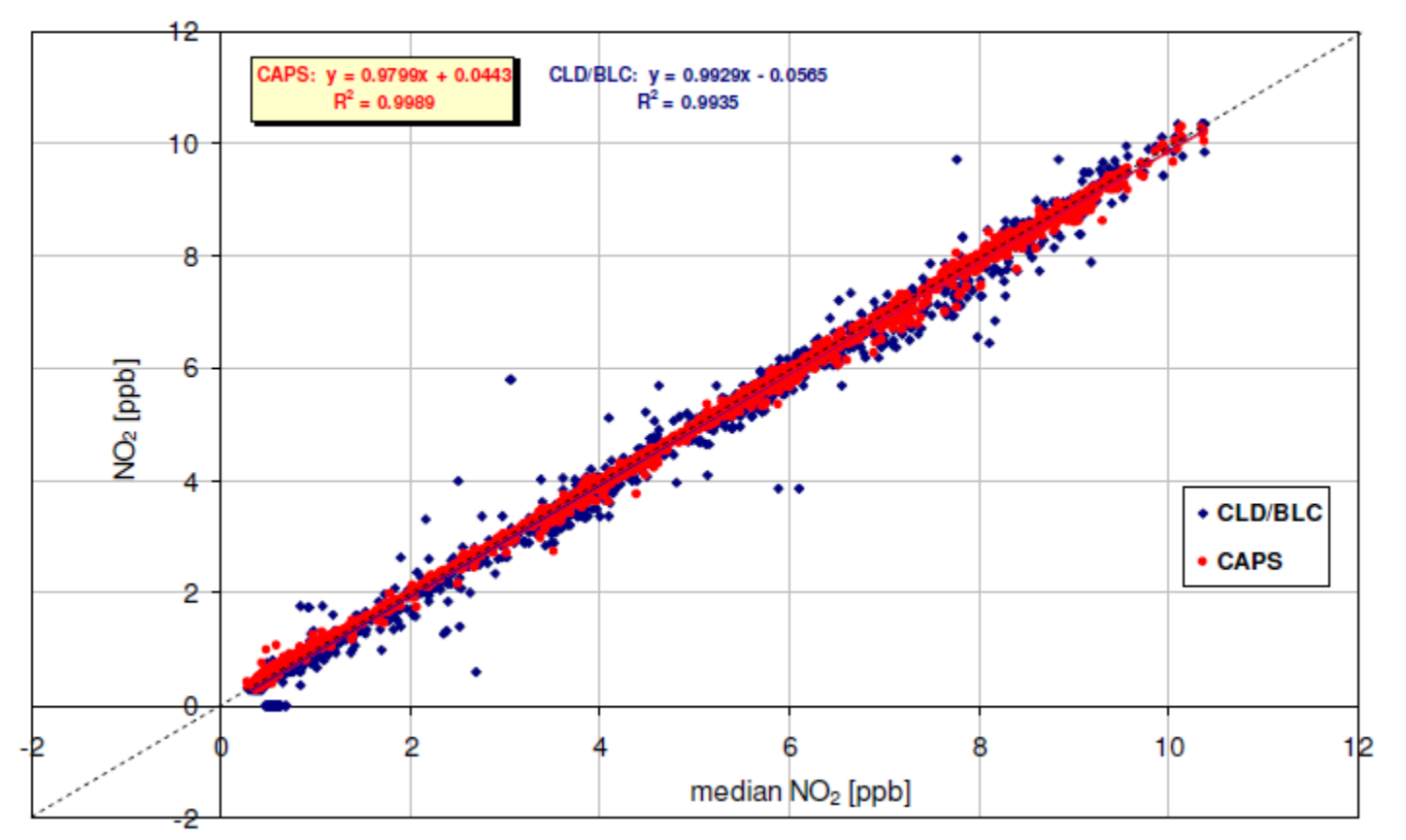
## Cavity-Attenuated Phase Shift (CAPS) Technique




$NO_2$ data from CAPS and CLD/BLC in ambient air at DWD Observatory Hohenpeissenberg, Nov. 2012 (gaw_brief_059)

# IAGOS Air Quality Package

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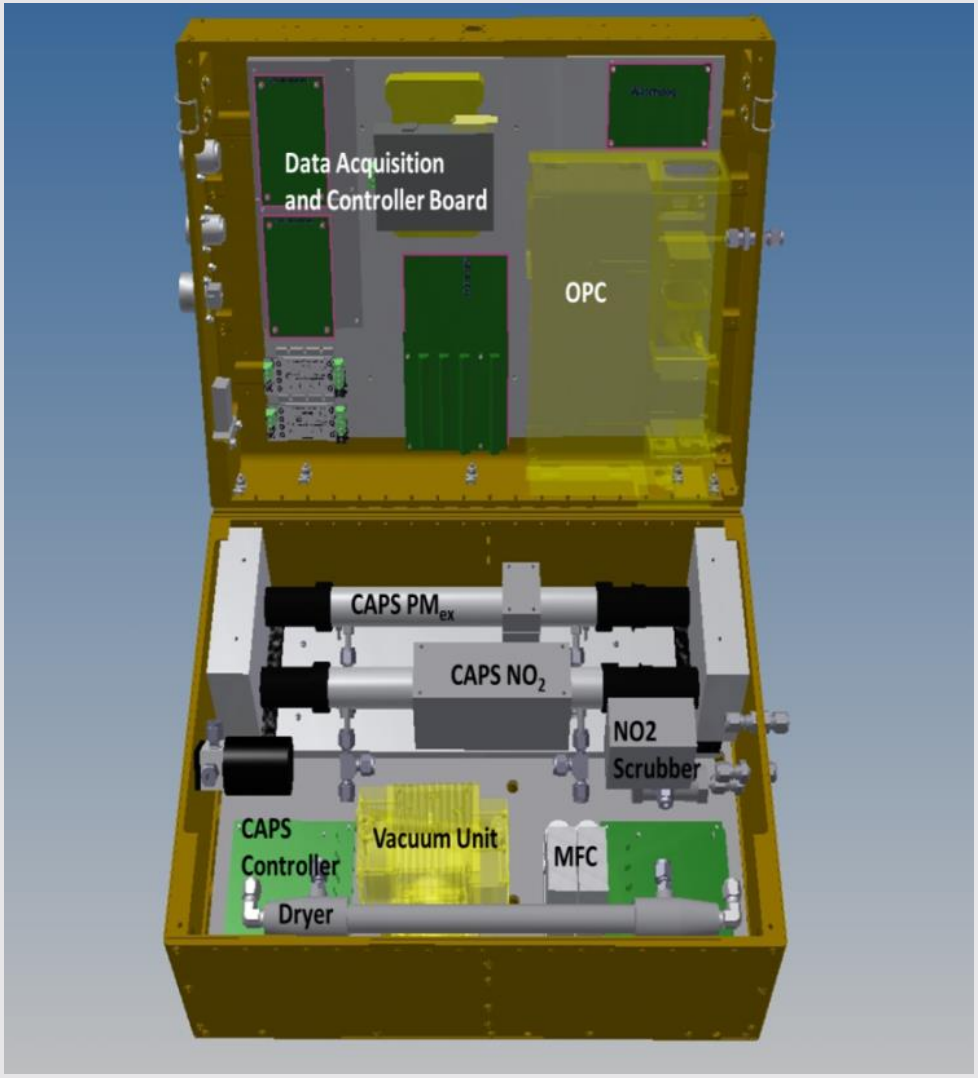


- Combines the measurement of $NO_2$, aerosol light extinction, and aerosol size distribution as proxy for aerosol mass.
- Allows measurement of regular profiles of key air quality parameters.