Physikalisch-Technische Bundesanstalt
Braunschweig and Berlin
National Metrology Institute

Diode laser spectrometer for NO_2 quantification: Absolute laser spectroscopic and direct NO_2 concentration measurements for atmospheric monitoring within the EMPIR project $MetNO_2$

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Due to the situation with Covid-19, DFM could not provide results to this presentation

Overview

1. Introduction

2. direct Tunable Diode Laser Absorption Spectroscopy (dTDLAS)

3. Nitrogen dioxide (NO_2) measurements

4. Conclusions

1. Introduction

- Nitrogen dioxide (NO_2) **air pollutant** e.g. from fuel combustion → human health risk

- **Standard reference method** (SRM) for NO_2 emissions: **Chemiluminescence** (European standard EN 14211:2012)

- Using chemiluminescence, **NO_2 is measured** only **indirectly**, i.e. NO_2 calculation: difference between NOx and NO after conversion of NO_2 to NO
  - Issue: other species (e.g. NOy: HNO_3, HNO_2, N_2O_5) converted to NO, can cause an overestimation in the NO_2 results

1. Introduction

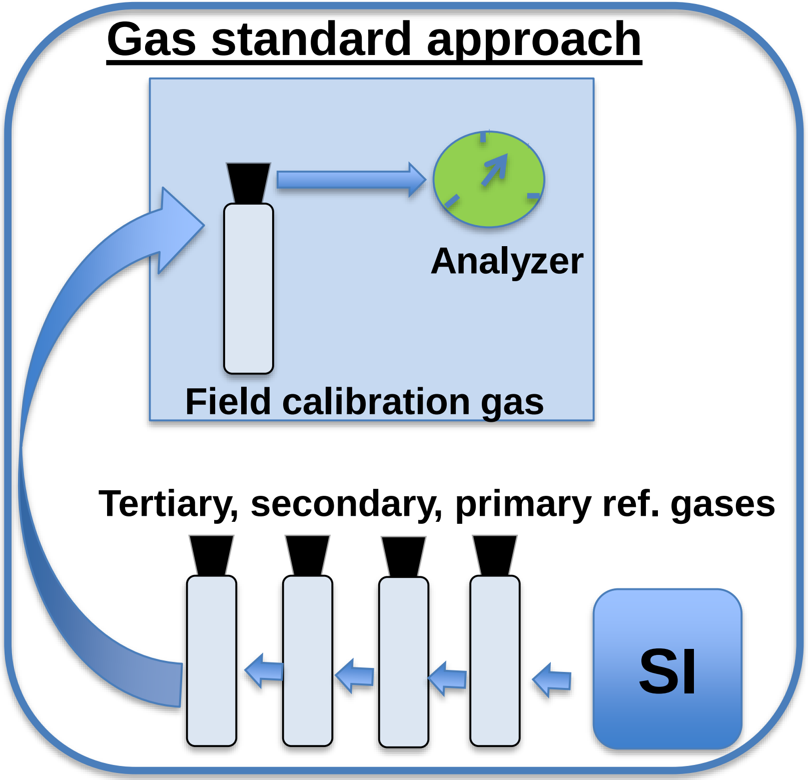
- Alternative instruments for **direct highly specific** NO_2 detection required

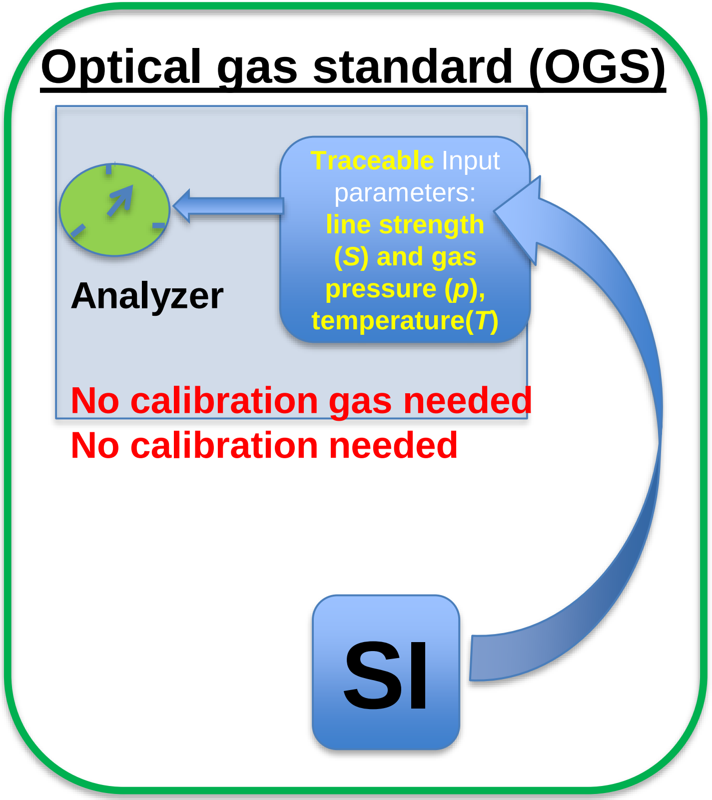
  - e.g. **an Optical gas standard" (OGS)** based on **direct** tunable diode laser absorption spectroscopy (dTDLAS)

An OGS:

- a dTDLAS **spectrometer** directly providing **SI-traceable gas concentration**
- can **complement gaseous standards for calibrations**, as an instrumental reference **(similar to the Ozone Standard Reference Photometer)**

2. dTDLAS: Optical gas standard (OGS)





„An optical gas standard is a laser spectrometer that can provide amount of substance fraction (concentration) results that are directly traceable to the SI“

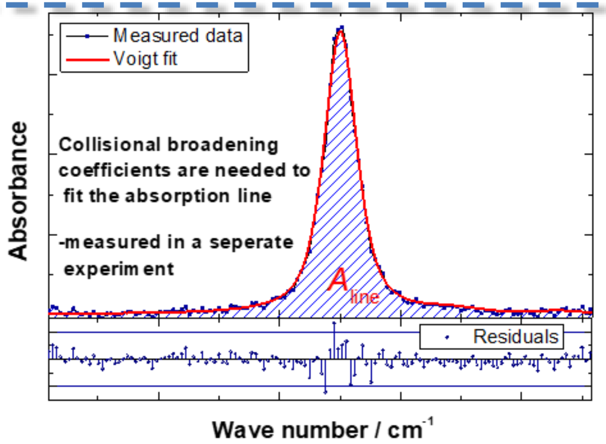
2. dTDLAS: measurement method

dTDLAS:

- **Standardized measurements method**

Measurement of spectral absorbance

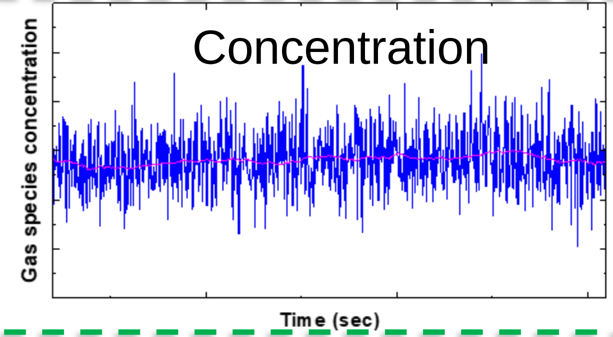
Derivation of the line area



Traceable input quantities: *p*, *T*, *L*, S_T, k_B

$$x_{\text{species}} = \left(\frac{A_{\text{line}} \cdot k_B \cdot T}{L \cdot S \cdot r_{\text{iso}} \cdot p} \right)$$

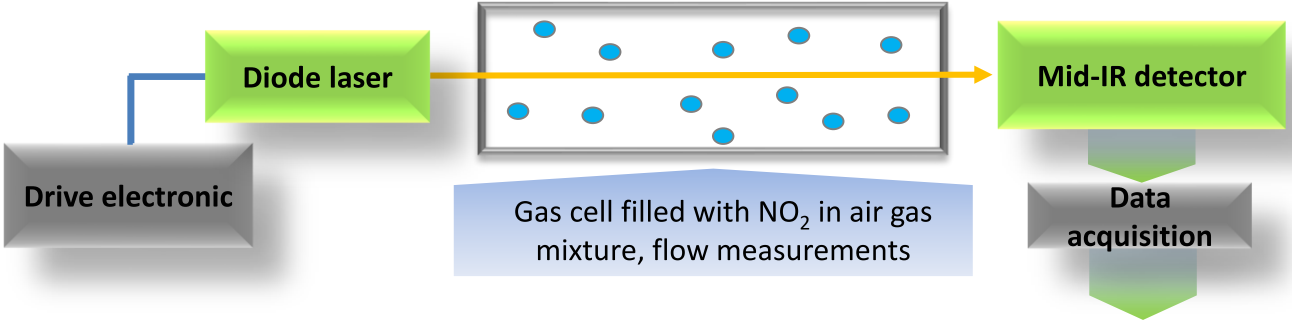
Calculation of a traceable amount fraction result



TILSAM: traceable infrared laser spectrometric amount fraction measurement), available at:
http://www.euramet.org/fileadmin/docs/projects/934_METCHEM_Interim_Report.pdf

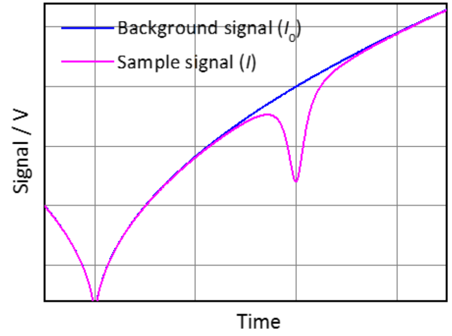
2. dTDLAS: schematic

dTDLAS



- From the Beer-Lambert-law

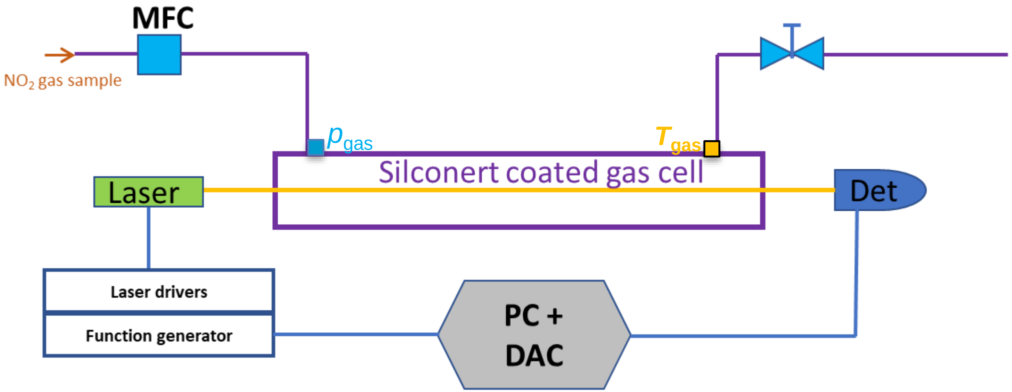
$$I(\tilde{\nu},L) = I_0(\tilde{\nu}) \cdot Tr(t) \cdot \exp\left\{\frac{-S_T \cdot r_{\mathrm{iso}} \cdot g(\tilde{\nu}-\tilde{\nu}_0) \cdot L \cdot x_{\mathrm{species}} \cdot p_{\mathrm{total}}}{(k_{\mathrm{B}} \cdot T)}\right\} + E(t)$$



The quantity x_{species} is the concentration of e.g. NO_2

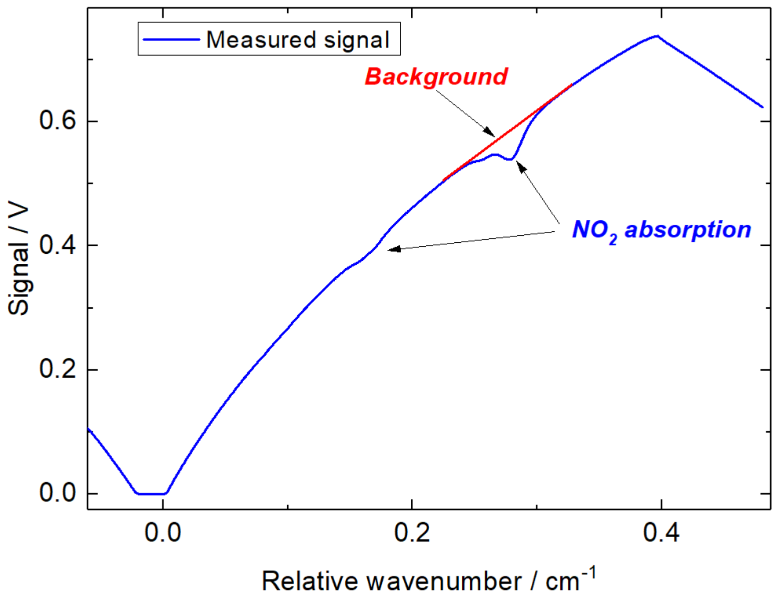
3. NO_2 measurements: setup, typical data

Setup



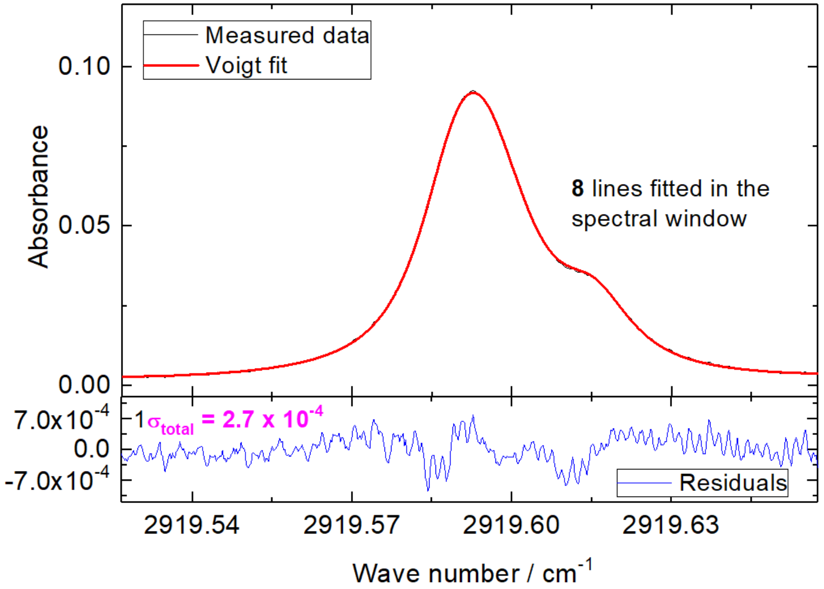
- Laser emitting in the mid-infrared
- Laser wavelength rapidly swept
- Sampling lines + cell →Silconert coated

Typical signal (979 µmol/mol NO_2/ air)



3. NO_2 measurements: spectra, uncertainty

Measured absorbance data (NO_2/air)



Uncertainty budget

Model

$$x_{NO2} = \frac{A_{\mathrm{line}} \cdot k_B \cdot T}{L \cdot S \cdot p_{\mathrm{total}}}$$

Parameter	Value	Relative standard uncertainty (k = 1) / %	Index (% uncertainty contribution)
Pressure	108.5 hPa	0.20	0.10
Temperature	294.3 K	0.10	≤0.05
Path length	0.82 cm	0.13	≤0.05
Line strength (HITRAN value)	$5.425 \cdot 10^{-21}$ cm/molecule	≥2 and <5.00*	96.00
Line area	0.001097 cm^{-1}	1.00	3.80
NO_2 concentration (x_{NO2}) result	**978.9 µmol/mol**	**5.10⁺ (combined uncertainty)**	**-**

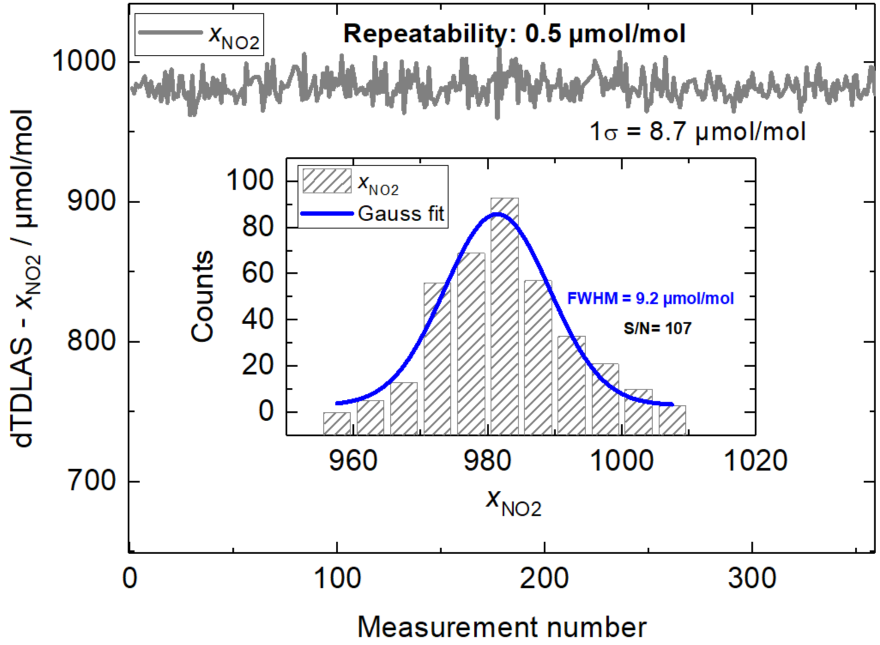
*HITRAN line strength uncertainty: ≥ 2 % and <5 %, upper limit used. ⁺Computed taken the line strength unceratinty as 5 %.

Commercial certified NO_2 concentration: (979±20) µmol/mol

Traceability: Traceability of the results is addressed via the traceability of input paramaters such as the gas pressure and temperature that are traceable to respective PTB standards

3. NO_2 measurements: system stability

Repeated dTDLAS NO_2 measurements

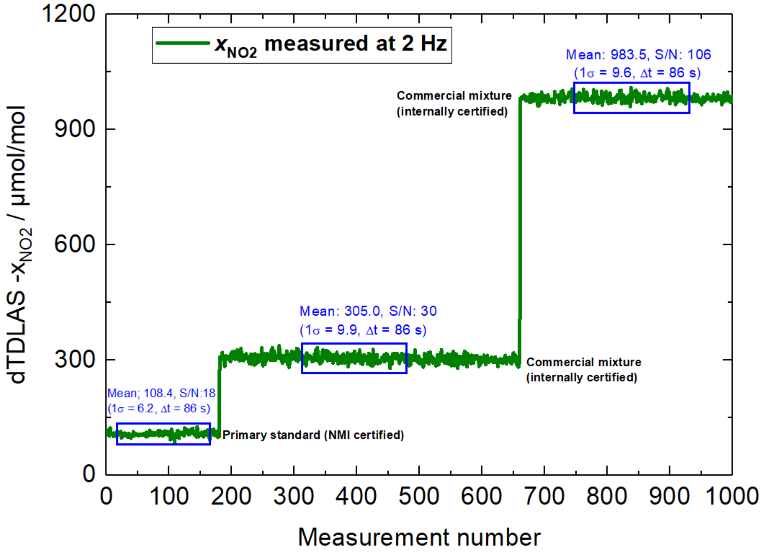


- Repeatability of 0.5 µmol/mol (0.05 %) @ 982.5 µmol/mol, absorbance: 10^{-4} range

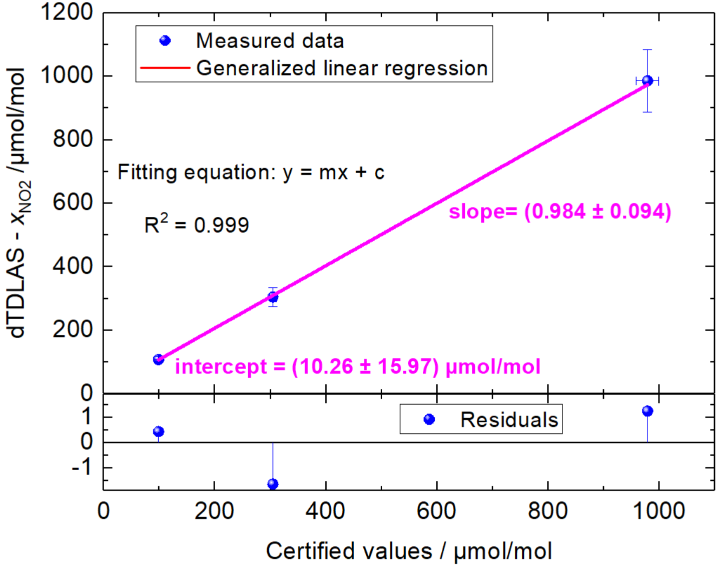
- Inset: a histogram depicting an approximate normal distribution around the mean value of the NO_2 concentration results. A gauss profile is fitted to the data, resulting to a full width at half maximum (FWHM) of 9.2 µmol/mol

3. NO_2 measurements: response, linearity

System response (NO_2 in air)



System linearity (NO_2 in air)



- System response – within 0.5 seconds
- A good linearity (slope = 0.984±0.095, k = 2) between measured dTDLAS -x_{NO2} vs. certified values

4. Conclusions

- We have presented a lab-based realization of a new calibration-free dTDLAS NO_2 spectrometer (specially designed for direct NO_2 concentration measurements in air)
- The standard uncertainty of the dTDLAS NO_2 concentration results is 5.1 %, and will be in the 2.0 % range if the lower bound HITRAN uncertainty (≥ 2 % and <5 %) was taken for the line strength
- Good agreement (slope: 0.984 ± 0.094, k = 2) was measured in a first validation exercise, such that the dTDLAS instrument comes as a high potential “OGS”

Outlook: next,

- adapt the spectrometer for in situ ambient NO_2 measurements by an adapted path length (30 m or 200 m $\rightarrow$ a few ppb range NO_2 resolution)
- PTB to improve uncertainty figures for the line strength $\rightarrow$ improving the accuracy of the NO_2 concentration results

Acknowledgement:

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PTB participates as an unfunded partner in the EMPIR MetNO$_2$ project (http://empir.npl.co.uk/metno2/)

References: J. Nwaboh, Z. Qu, O. Werhahn, V. Ebert, 3rd International Workshop on Oxy-Fuel Combustion, 04-05.03.2020, Montabaur, Germany (2020)

CLIMATE AND OCEAN OBSERVATION

PTB is member of the European Metrology Network for Climate and Ocean Observation (https://www.euramet.org/european-metrology-networks/climate-and-ocean-observation/)

Thanks for your attention!

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