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Effects of the spatial heterogeneity of gas matrix and thermal boundary layers on absolute TDLAS HCl measurements in hot flue gases

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Introduction

The project [1]:

- Metrology for air pollutant emissions
- EMPIR 16ENV08 IMPRESS2
- Budget: 2.3 M€
- Time: 05.2016 - 05.2020
- Providing **metrology** to enable the enforcement of the Industrial Emissions, Medium Combustion Plant and the EU's Emissions Trading Scheme

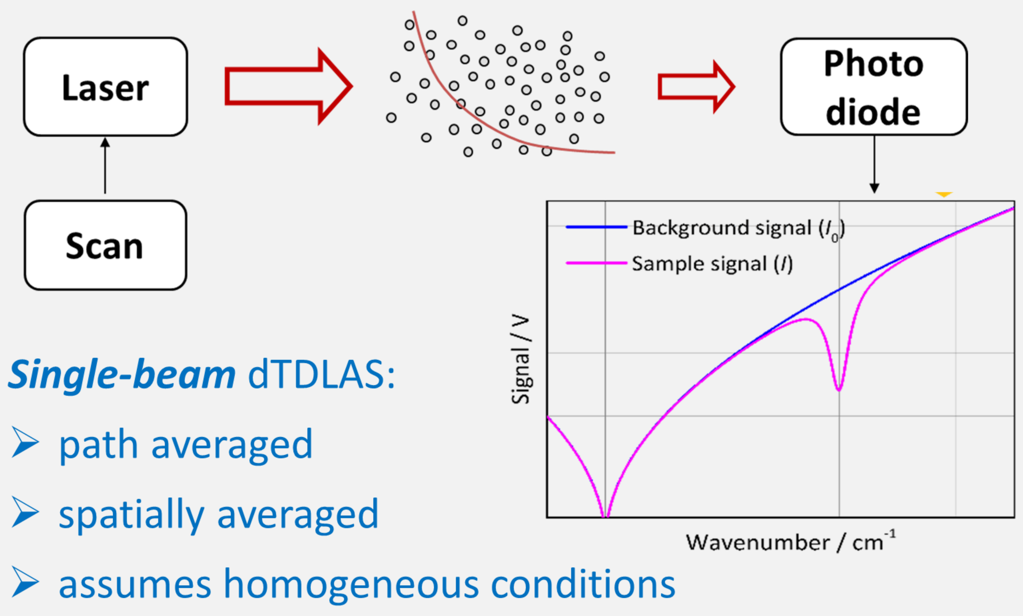
PTB tasks:

- Accurate measurement towards for HCl emissions from industrial combustion processes
- To meet lower emission limit values (2 mg/m³ ~1.4 ppm HCl @23⁰C, 1 atm)
- To achieve directly traceable measurements

Methodology:

- Direct tunable diode laser absorption spectroscopy (dTDLAS)

Line-of-sight dTDLAS



Single-beam dTDLAS:

- ➢ path averaged
- ➢ spatially averaged
- ➢ assumes homogeneous conditions
- ➢ spatial heterogeneity may skew the results

Amount fractions (concentration) from the Beer-Lambert law can be described as:

$$x = \frac{k_B \cdot T \cdot A_{line}}{S(T) \cdot L \cdot P}$$

Uniform *T, gas compositions* along the beam path

Quantify effects of boundary layers!

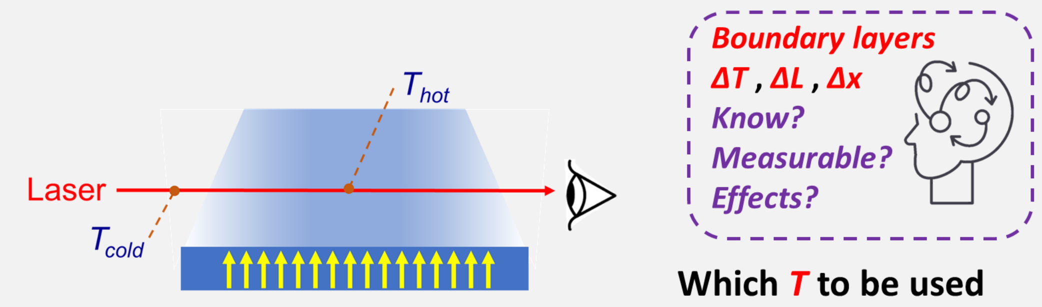
A	Line area (path integrated)
k_B	Boltzmann constant
T	gas temperature
L	optical path length
p	gas pressure
S_T	line strength of the probed molecular transition at *T*

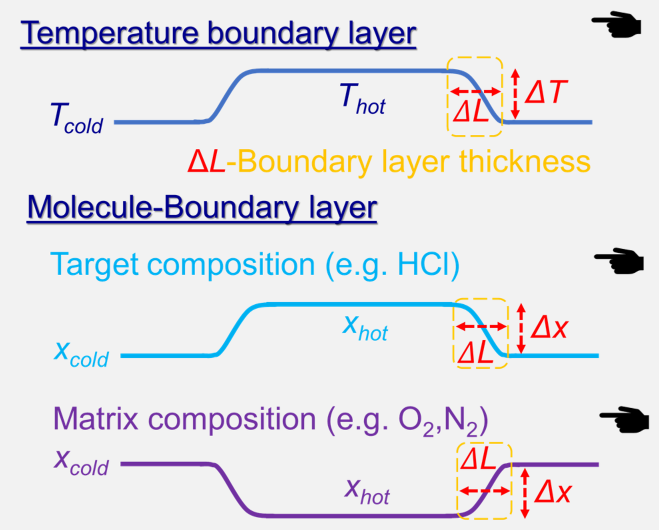
Spatial heterogeneity

The spatial heterogeneity includes:

- ○ Thermal boundary layers
- ○ Gas compositions varying along the beam path
  - Target molecule (e.g. analyte HCl) distribution
  - Gas matrix (e.g. N_2, CO_2) distribution

Mimic real conditions by simulations



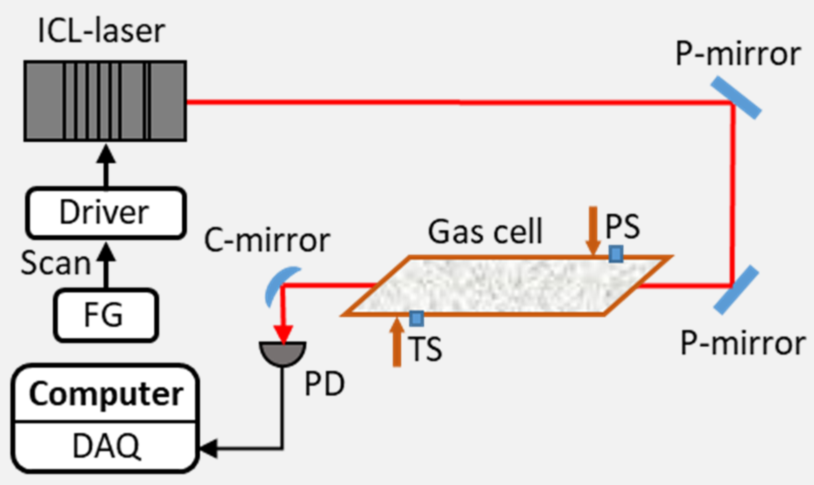


Which *T* to be used to compute concentrations? *T_{hot}, T_{cold}, mean or path average*

Target gas HCl: **Path averaged concentration, or column density**

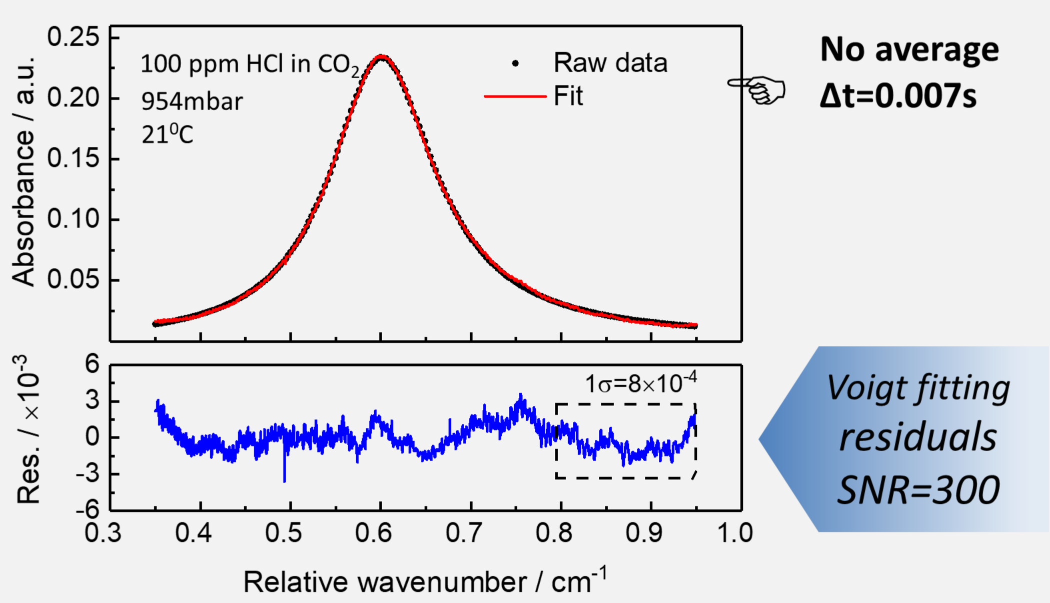
Different broadening effects on the target molecule

dTDLAS HCl spectrometer



- Mid-IR ICL laser at 3.6 µm (Nanoplus)
- Swept at 139 Hz (time resolution 0.007s)
- Single pass gas cell 77 cm (passivated)
- Mid-IR detector (VIGO)
- T-sensor: PT100 P-sensor: capacitive pressure gauge

Typical signal

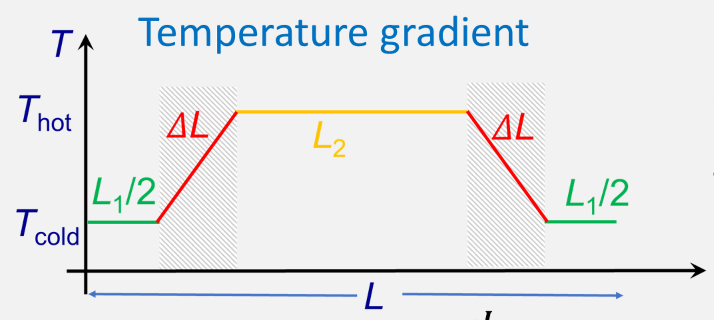


Limit of detection (LOD):

- 0.33 ppm (@0.77 m, 0.007 s)
- 0.02 ppm (@1 m, 1 s) << EU emission limit (1.4 ppm)

Simulation1 (HCl in CO_2 background)

Spatial heterogeneity info:

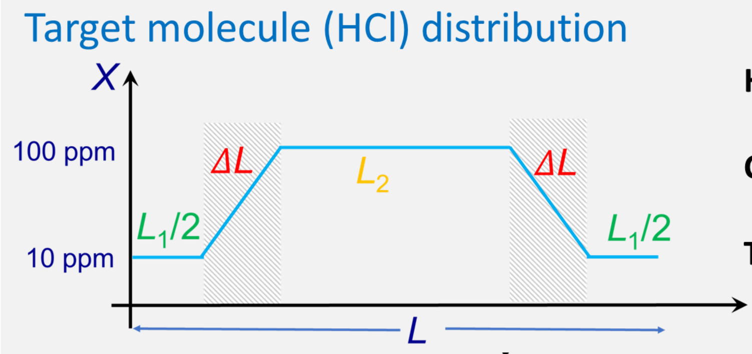


Hot zone L_2: 60 cm
Cold zone L_1: 20 cm
Transition zone ΔL: 10 cm

True path-average *T*: $T_{ave} = \int_0^L T_i \mathrm{d}L_i / L$ ← **technically unavailable**

Mean *T*: $T_{mean}=(T_{cold}+T_{hot})/2$

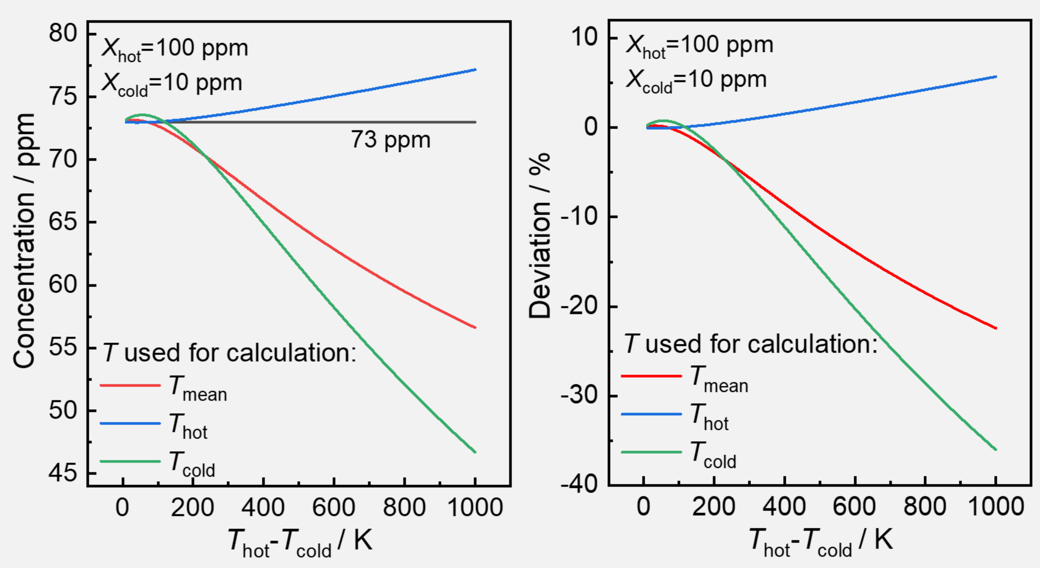
Target molecule (HCl) distribution



Hot zone x_{HCl}: 100 ppm
Cold zone x_{HCl}: 10 ppm
Transition zone : linear increasing

True path-average x_{HCl}: $x_{ave} = \int_0^L x_i \mathrm{d}L_i / L$ =73 ppm

Effect of temperature choice

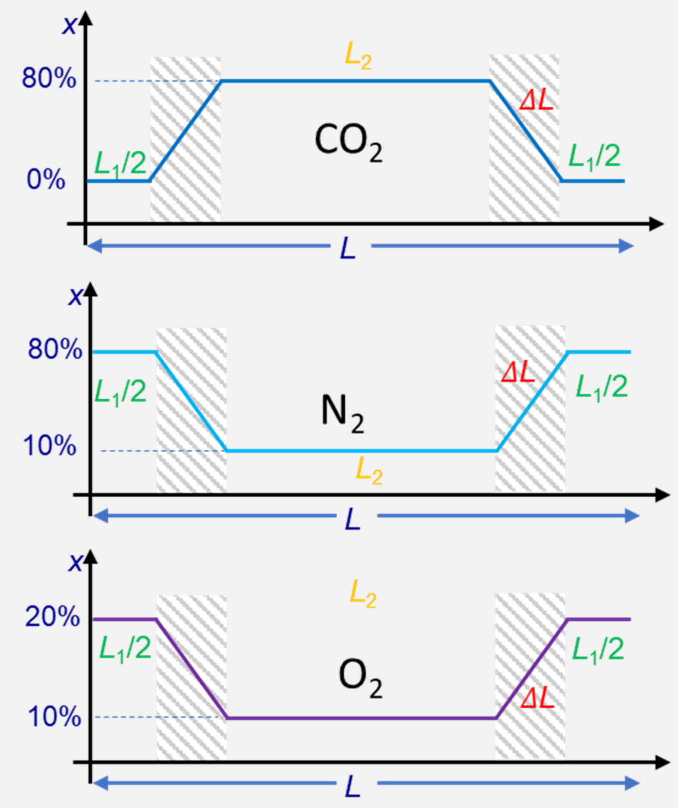


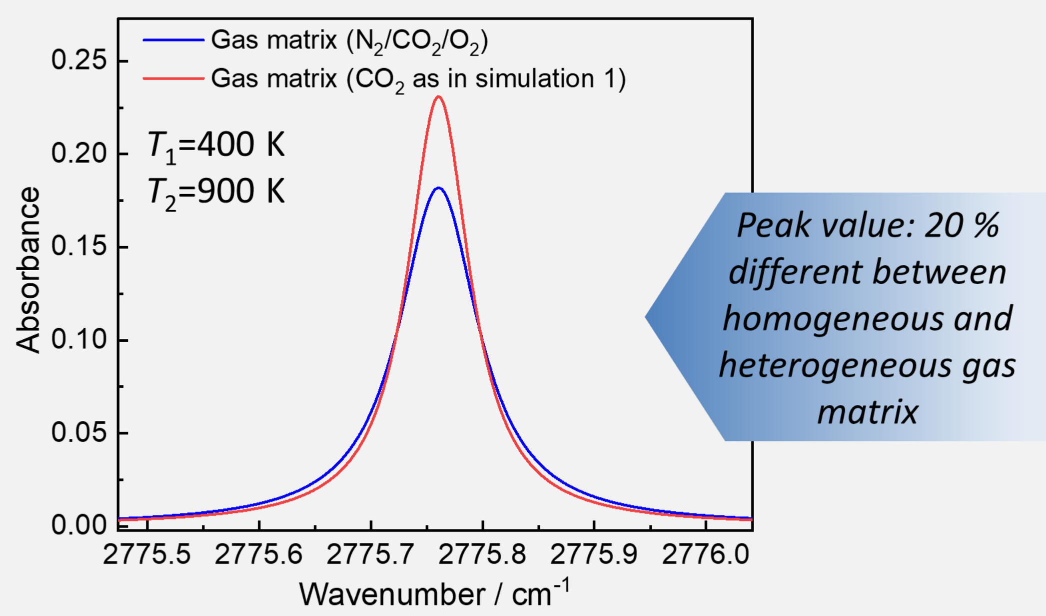
Left: concentration from simulation based on different temperature choice
Right: concentration deviation from the true path-average value (73 ppm)

Simulation2 (HCl in CO_2+N_2+O_2)

Spatial heterogeneity info:

- Temperature gradient and HCl distribution
  Same as Simulation 1
- Gas matrix
  (Varying along the beam path)
- HCl Broadening coefficients
  HCl-CO_2:
  0.076 cm⁻¹/atm
  HCl-N_2:
  0.061 cm⁻¹/atm
  HCl-O_2:
  0.034 cm⁻¹/atm
  (Thoes values are measured in PTB for our HCl line)





Heterogeneity effects

Heterogeneity effects on dTDLAS depends on:

- transition line, *S*(*T*) [7]
- thermal boundary [8]
  - ○ thickness and gradient
- target molecule distribution
- matrix gas composition
- Temperature choice
  - ○ calculation temperature used in $x = \frac{k_B \cdot T \cdot A_{line}}{S(T) \cdot L \cdot P}$
  - ○ T_{hot}, T_{cold}, T_{mean}

Summary

❖**Results**

- A Mid-IR dTDLAS spectrometer was developed for HCl concentration measurements
- a LOD of 0.02 ppm at 1 s time resolution was achieved
- Temperature choice is critical, i.e. in the plot above, if T_{cold} was chose, the deviation can be up to 40%
- Best temperature choice information can be obtained from simulation results

❖**Plans**

- to improve the sensitivity by using i.e. WMS
- to reduce the uncertainty by getting better line data

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EMPIR EURAMET
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CLIMATE AND OCEAN OBSERVATION

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