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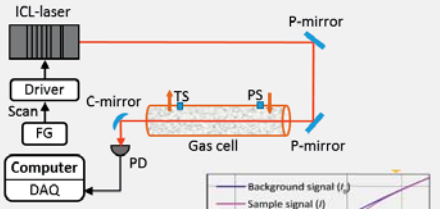
Towards a TDLAS based optical gas standard for the absolute HCl measurements in flue gases from combustion process

Introduction

Accurate measurement of emissions of pollutants from industrial combustion processes to the atmosphere is vital in enabling action to control and reduce air pollution. Industry needs to measure and report emissions for regulatory purposes including assessing stack emissions against concentration limit values.

The EMPIR IMPRESS 2 project [1] goes beyond state of the art in measuring the emissions of HCl with lower emission limit values (2 mg/m³~1.4 ppm HCl), to achieve directly traceable measurem ents. Here, we present the spatial heterogeneity effects on the method of direct TDLAS (dTDLAS) method for absolute HCl conc entration measurement in real applications.

dTDLAS spectrometer for HCl



Light source:
- ICL laser at 3.6 µm
- Swept at 139 Hz
  (time resolution 0.007s)

Gas cell:
- single pass 77 cm (coated)

Detector/Sensors:
- Vigo Mid-IR detector

Sensors:
-T-sensor: PT100
- P-sensor: capacitive pressure gauge

Operation ranges:
- Pressure:
  0- 1 bar
- Temperature:
  20-30 °C (gas in cell)
  (possible for high T)

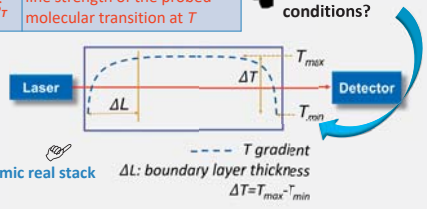
HCl line temperature dependence

dTDLAS is a first principle approach to directly get absolute gas concentrations. Amount fractions from the Beer-Lambert law can be described as:

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

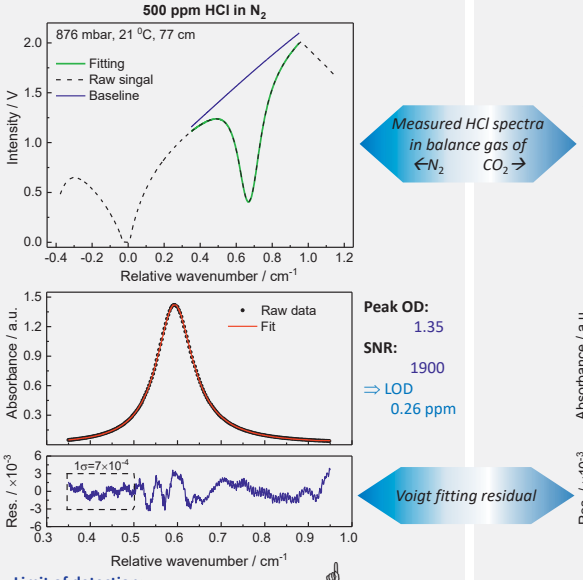
A	Line area / cm^{-1}
k_B	Boltzmann constant
T	gas temperature / K
L	optical path length / m
p	gas pressure / Pa
S_T	line strength of the probed molecular transition at T

Which temperature to use under heterogeneous conditions?



HCl in N_2 spectra

- Gas sample: HCl in N_2 (#2735703, N_2 6.0, HCl 5.5)
- Flow rate: 200 sccm (constant gas flow through the cell)
- Temperature: 294 K



Measured HCl spectra in balance gas of ←N_2 CO_2→

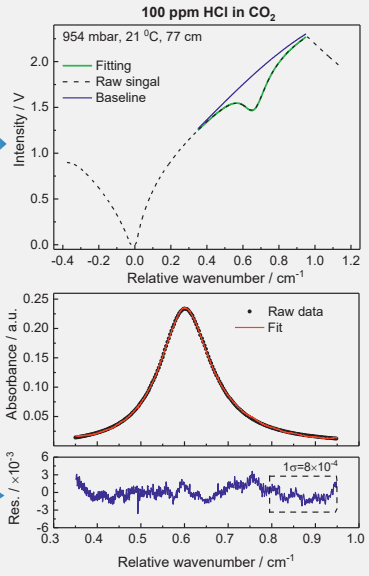
Voigt fitting residual

Limit of detection:
- 0.016 ppm·m·Hz$^{-1/2}$
- our 0.26 ppm is lower than EU emission limit values
- can be scaled with pathlength to even lower LOD

Single shot without average, 7ms

HCl in CO_2 spectra

- Gas sample: HCl in CO_2 (#2733740, CO_2 5.3, HCl 5.5)
- Flow rate: 200 sccm (constant gas flow through the cell)
- Temperature: 294 K

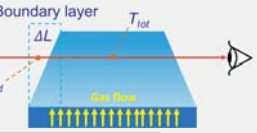


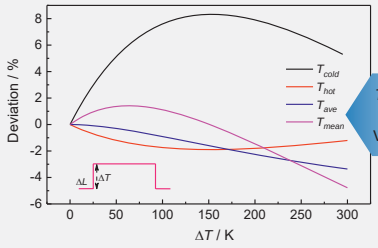
The selected HCl line :
- fundamental band with strong absorbance→ high sensitivity
- well isolated from CO_2 and H_2O lines→ good specificity

Heterogeneity simulation-HCl in Air

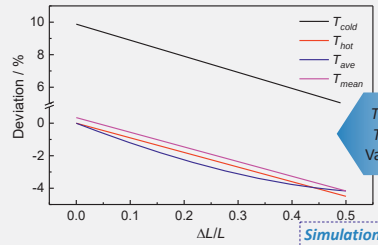
- TDLAS: **line-of-sight technique**
- Temperature gradient: **systematic error/deviation!**

Path-averaged:
$T_{ave} = \int_0^L T_i dL_i / L$
Mean T_{mean}:
$T_{mean} = (T_{cold} + T_{hot})/2$





T_{cold}=300K, $\Delta L/L$=0.2, Varying T_{hot}



T_{cold}=300K, T_{hot}=500K, Varying $\Delta L/L$

The systematic error/deviation is
- transition lin-depended, $S(T)$
- thermal boundary depended

Simulation info:
- 100 ppm HCl in Air
- Our target HCl line
- L= 100 cm
- Pressure 1 bar

Heterogeneity effects

We developed a heterogeneity effect simulation model and applied to our 2.7 µm CO_2- and 4.6 µm CO-TDLAS systems.

Molecules	Our work	Concentration deviation	Note
CO_2	Experiment & simulation	3% ($\Delta L/L$=0.34, ΔT=100 K, T_{ave})	Ref [4]
CO	Experiment & simulation	15% ($\Delta L/L$=0.34, ΔT=100 K, T_{ave})	Ref [8]
HCl	Simulation	2% ($\Delta L/L$=0.34, ΔT=100 K, T_{ave})	This work

Summary

❖ **Results**
- a dTDLAS spectrometer was developed for absolute HCl concentration measurements
- a LOD of 0.26 ppm at 0.007s time resolution was achieved
- the temperature gradient effects on the dTDLAS HCl concentration measurement was analyzed using our simulation model showed a max. 8 % deviation of T gradient

❖ **Plans**
- bring this HCl Optical Gas standard in operation
- to improve the measurement uncertainty

References

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[5] G. Li et al., *JQSRT*, **203**, 434-349 (2017).
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