Physikalisch-Technische Bundesanstalt
Braunschweig and Berlin
National Metrology Institute

Progressing Optical Gas Standard concepts

- from environmental measurements to industrial process control and AMC monitoring

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Olav Werhahn, Volker Ebert

About PTB

- National Metrology Institute of Germany, under the authority of the Federal Ministry for Economic Affairs and Energy (BMWi)
- approx. 1900 staff members,
  700 scientific papers per year,
  185 Mio. € annual budget

Braunschweig

Mechanics and Acoustics (1)

Electricity (2)

Chemical Physics and Explosion Protection (3)

Optics (4)

Precision Engineering (5)

Ionizing Radiation (6)

Legal and Inter-national Metrology (9)

Cross-Sectional Services (Q)

Administrative Services (Z)

QUEST Institute at PTB

Fundamental Physics for Metrology (FPM)

Berlin

Temperature and
Synchrotron Radiation

Medical Physics and Metrological
Information Technology

About us

3

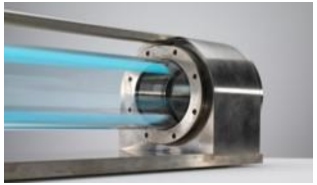
Chemical Physics
and
Explosion Protection

3.4

Analytical chemistry of the gas phase

3.42

Spectrometric gas analysis



— Capabilities in 3.42 —

Laser spectroscopy

- Direct traceable methods for amount fraction measurements → the TILSAM method
- Direct laser absorption spectroscopy (TDLAS/QCLAS) – development of spectrometers
- Field TDLAS instruments (ground based, balloon, airplanes)
- Cavity-enhanced (CRDS/CEAS) and comb-assisted techniques
- Optical isotope ratio spectroscopy (OIRS)
  - Thermo ($\delta^{13}C$-CO_2 *and* $\delta^{18}O$-CO_2)
  - Picarro ($\delta^{13}C$-CO_2 *and* $\delta^{13}C$-CH_4)
  - Los Gatos (triple water analyser)

Current running projects

Laser spectroscopy

16ENV08-IMPRESS2

17IND09-MetAMC2

CCQM-Kxx
key comparison

30 µmol/mol HCl in N_2

EURAMET 1498 - pilot study
bilateral comparison

100 µmol/mol HCl in N_2

METROLOGY FOR BIOMETHANE

16ENG05-BioMethane

HCl related

16ENV06-SIRS
CO_2 isotopes

MefHySto
Metrology for Advanced Hydrogen Storage Solutions

19ENG03-MefHySto
H_2O in H_2

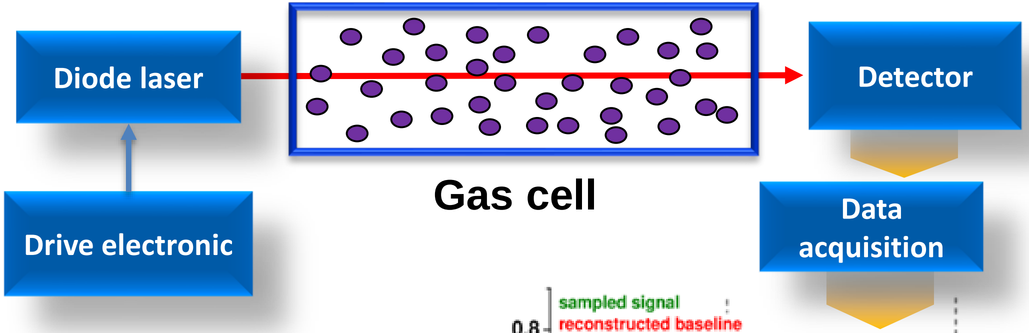
19ENV05-STELLAR
CH_4 /CO_2 isotopes

DFG SPP1924-HALO
H_2O in atmosphere

19ENV09-MetroPEMS
NO_2 emission

Technique – dTDLAS

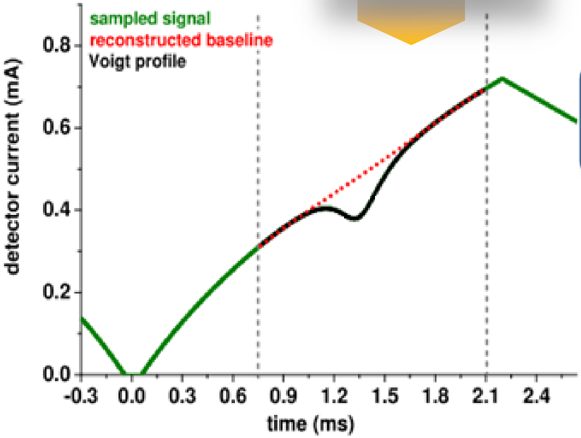
dTDLAS: direct tunable diode laser absorption spectroscopy



Gas cell

$$x_{\mathrm{HCl}} = \frac{k_{\mathrm{B}} \cdot A \cdot T}{S \cdot p \cdot L}$$

measured parameters
constants
molecular line data



Measure spectral absorbance (via laser intensity)

Laser tuning

Line area, *A*

Traceable inputs: ***p*, *T*, *L*, *S*, k_B**

TILSAM*

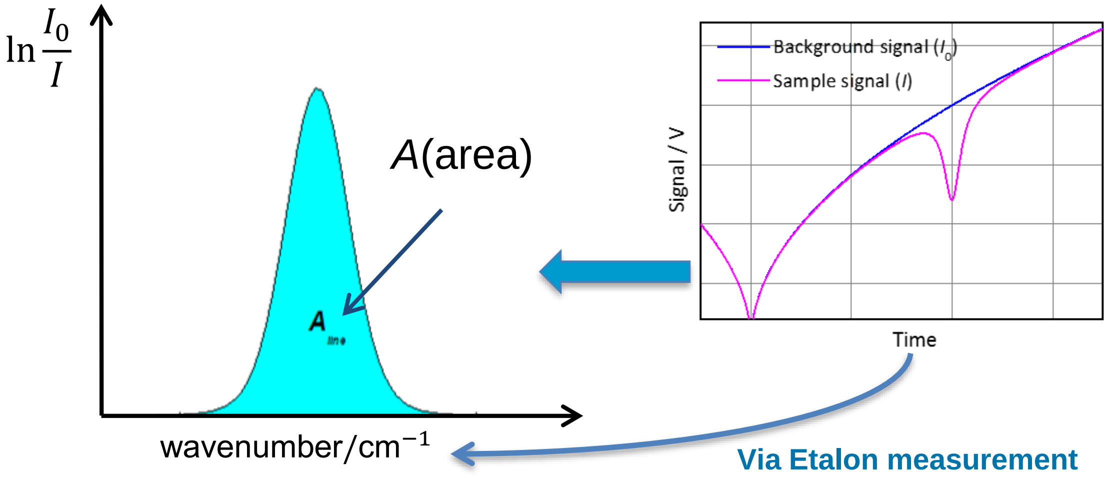
Calculate traceable amount fraction, x_{HCl}

***Traceable Infrared Laser-Spectrometric Amount fraction Measurement (TILSAM)**| https://www.euramet.org/Media/docs/projects/934_METCHEM_Interim_Report.pdf

dTDLAS uncertainty

Amount fraction (concentration):

$$x_{\mathrm{HCl}} = \frac{k_{\mathrm{B}} \cdot A \cdot T}{S \cdot p \cdot L}$$



Quantities:

k_B : Boltzmann constant

A : integrated absorbance (area), u ~ 1 %

T : gas temperature, $u < 0.1$ %

p : gas pressure, $u < 0.2$ %

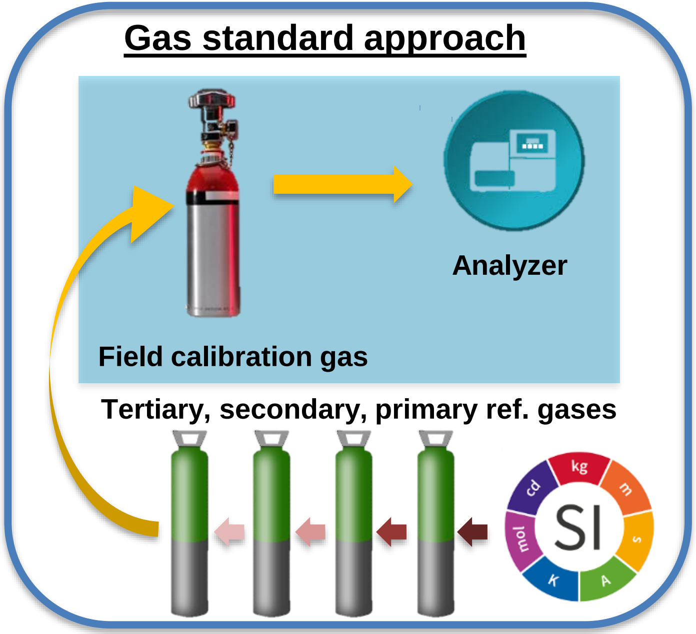
L : optical path length, u ~ 0.1- 0.4 %

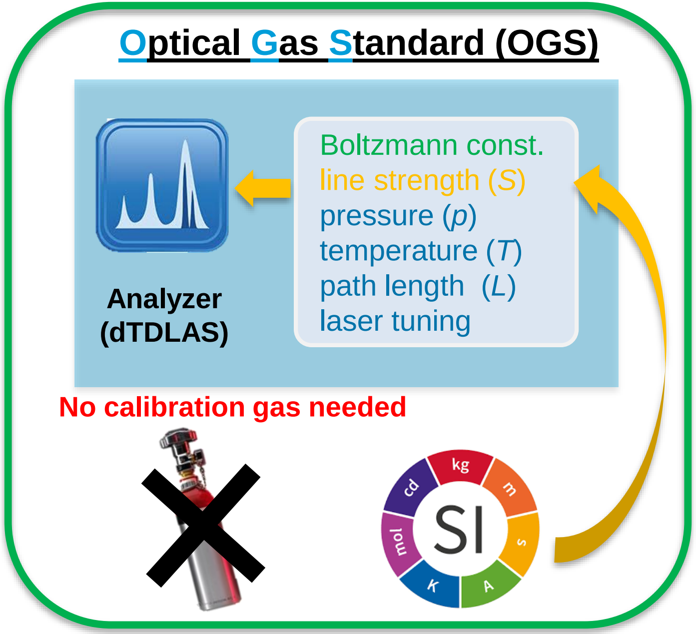
S_T : line strength of the probed molecular transition at T, u_{HITRAN} ~ 2-20 %, $u_{\mathrm{PTB}} < 1$-3 %

Advantages of dTDLAS-TILSAM:

robust, simple, in situ, linear, calibration-free

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**

→ **TILSAM***

***Traceable Infrared Laser-Spectrometric Amount fraction Measurement (TILSAM)|** https://www.euramet.org/Media/docs/projects/934_METCHEM_Interim_Report.pdf

Optical gas standard

Current realisation:

- Based on direct tunable diode laser absorption spectroscopy (dTDLAS)
  → *accurate and reliable amount fraction measurements*

- Calibration-free (no gaseous standards needed > low maintenance cost)
  → *no need for calibration procedures … just validation*

- dTDLAS-based amount fraction measurement instrument can be entirely described by a first principle physical model – TILSAM compliant
  → *all input parameters are directly traceable to the SI >> OGS!*

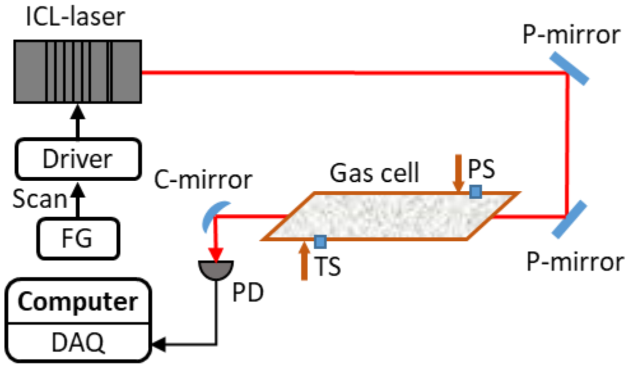
- Especially for sticky and reactive gases which cannot be provided in static gas cylinders (Certified Reference Materials)
  → *to complement calibration gases*

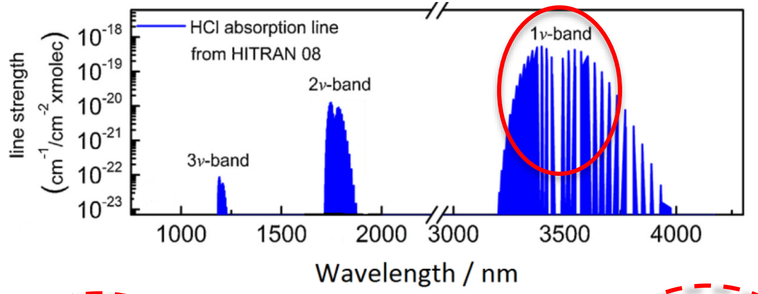
Current and future HCl - traceability ?

- ***Current HCl reference method***
  - **Biomethane** : Reference method for HCl measurements is unavailable
  - **Combustion**: emissions from stacks (EN1911)> indirect measurements via wet-chemistry
    - extractive gas sample / drying / filtration > systematic effects
    - stable gas standards for calibratoin (none for flue gas)
  - **Semiconductor**: HCl in nmol/mol (ppb) to pmol/mol (ppt)
    - no gaseous reference materials for instrument calibration
- ***HCl metrology***
  - no HCl CMC for amount fractions below 10 µmol/mol
  - existing HCl CMCs
    - NPL (UK): 10 – 1000 µmol/mol HCl in N_2
    - VNIIM (Russia): 20 – 1000 µmol/mol HCl in N_2

HCl - OGS instruments

dTDLAS: direct tunable diode laser absorption spectroscopy





Light source:

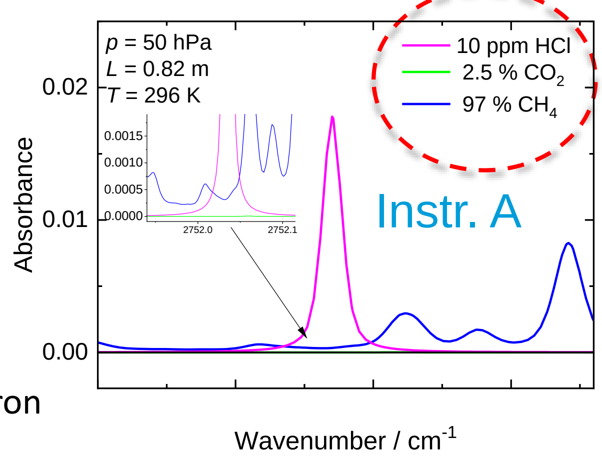
- ICL laser at 3.6 µm - Swept at 140 Hz

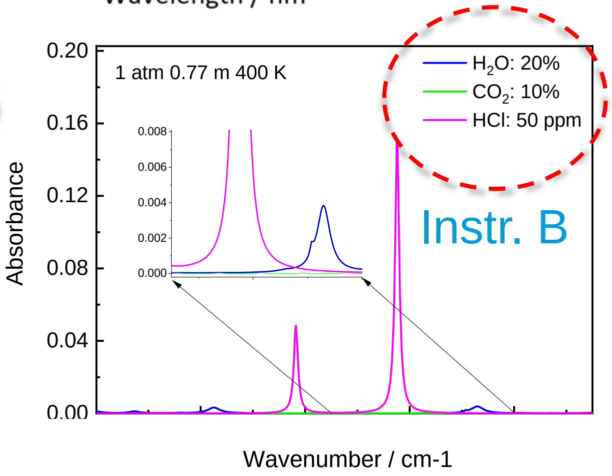
Gas cell:

- single pass 82 cm (instr. A)
  77 cm (instr. B)

Detector/Sensors:

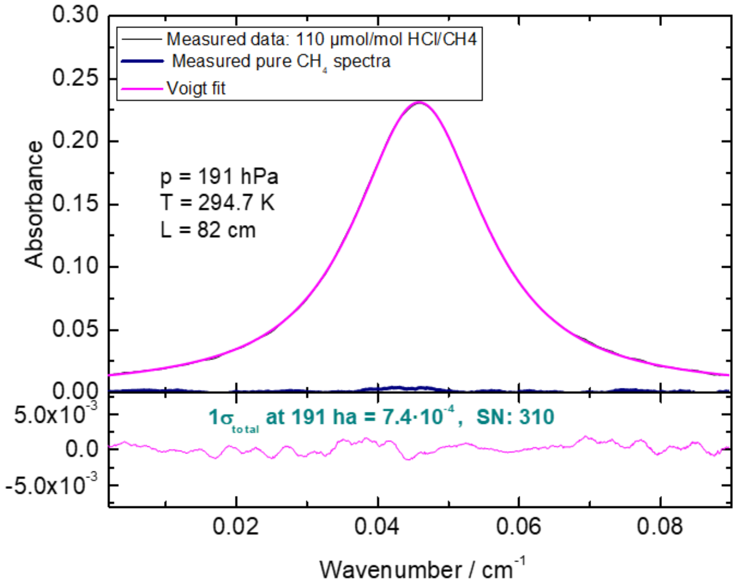
- T sensor: PT100b -P sensor: MKS baratron
- Vigo Mid-IR detector



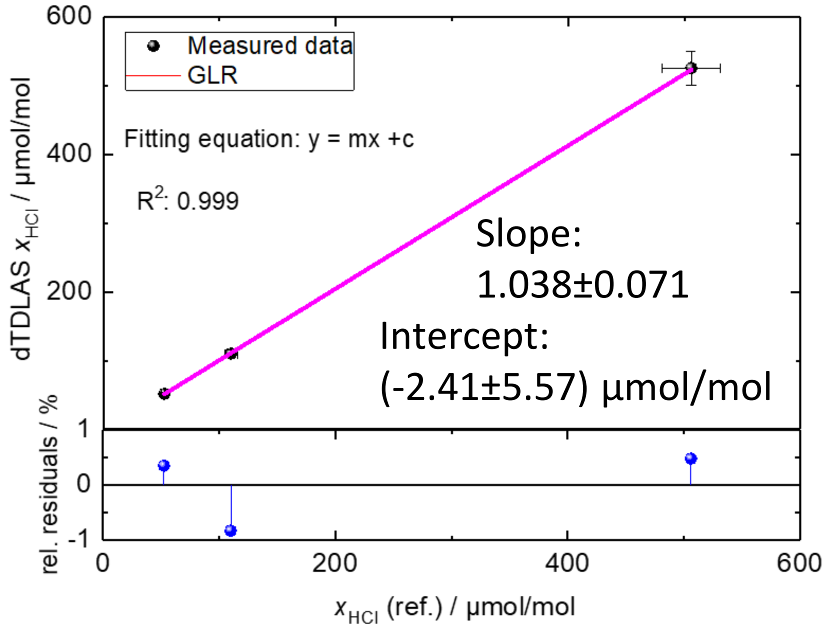


BioMethane: HCl - in CH_4 OGS

Typical HCl dTDLAS signal in CH_4



HCl/CH_4: 50-500 µmol/mol



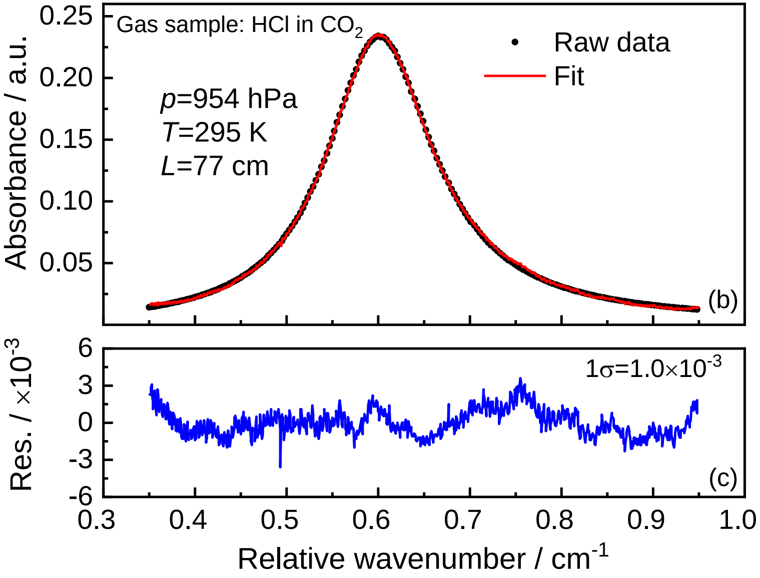
The detection limit of this HCl-OGS system is 29 nmol/mol at Δt= 54 s

Relative uncertainty of HCl dTDLAS results: 4.6 %, k = 2

J. Nwaboh, Z. Qu, B. Buchholz, O. Werhahn and V. Ebert, ***OSA 2020 Optical Sensors and Sensing Congress***

IMPRESS2: HCl - in flue gas OGS

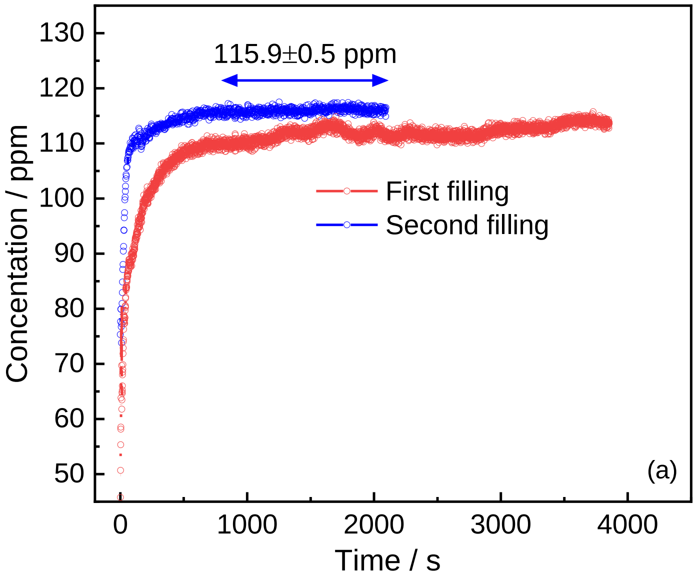
Typical HCl dTDLAS signals in CO_2



Instrument detection limit: 0.02 µmol/mol @1 s, 1 m

< EU emission limit 1.5 µmol/mol

Improved system response by passivation

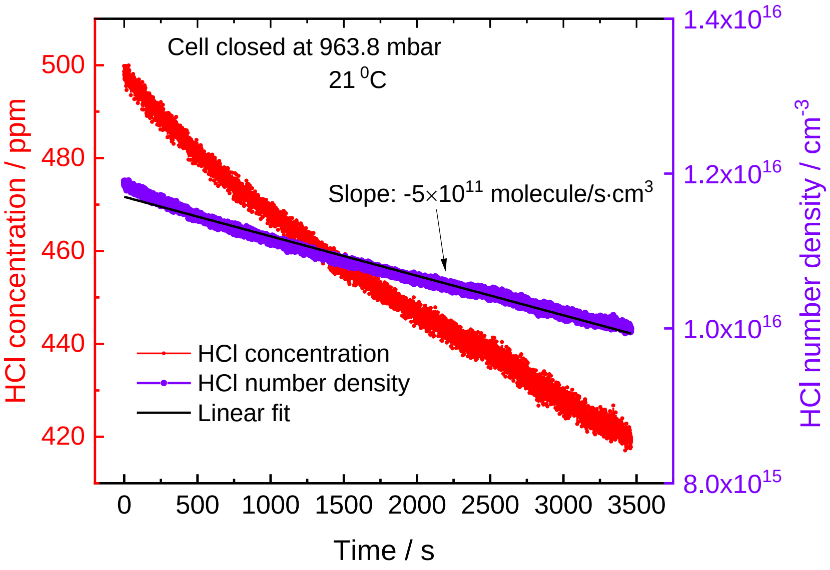


Passivation time more than 1000 s for the first filling @ instrument inner surface coated !

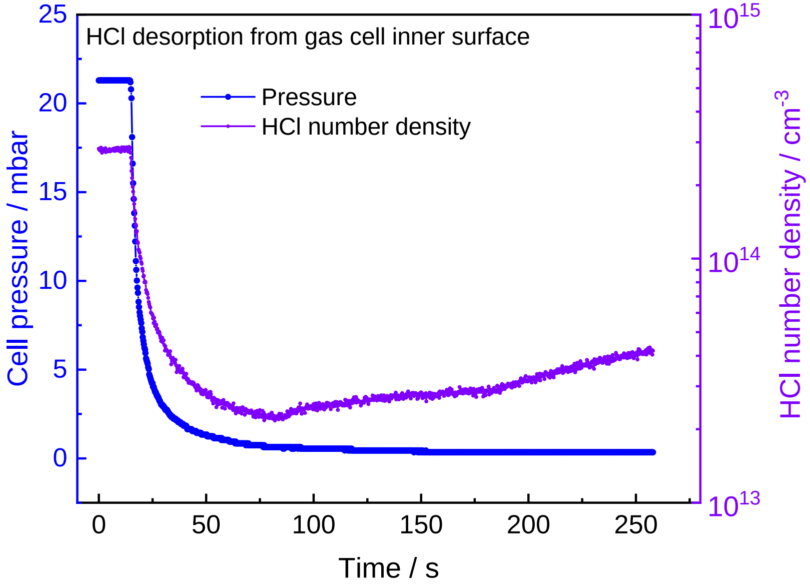
*Z. Qu, J. Nwaboh, O. Werhahn and V. Ebert, **Flow, Turbulence and Combustion 2020** accepted*

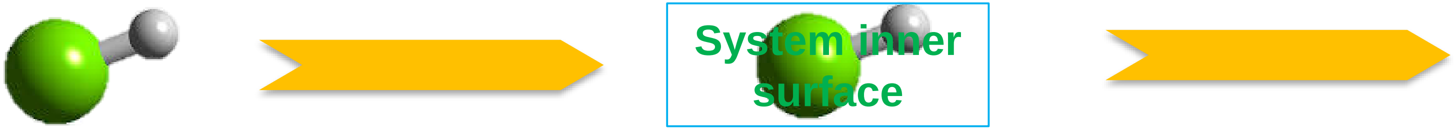
Absorption/desorption of reactive gas - HCl

HCl gas mixture in closed cell



Evacuation process



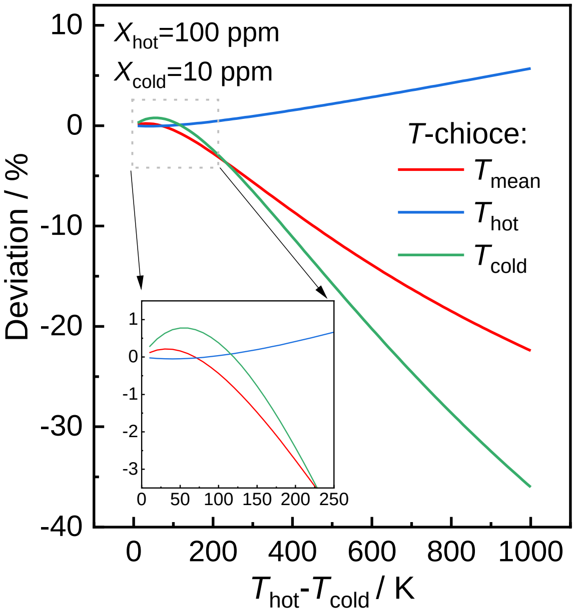


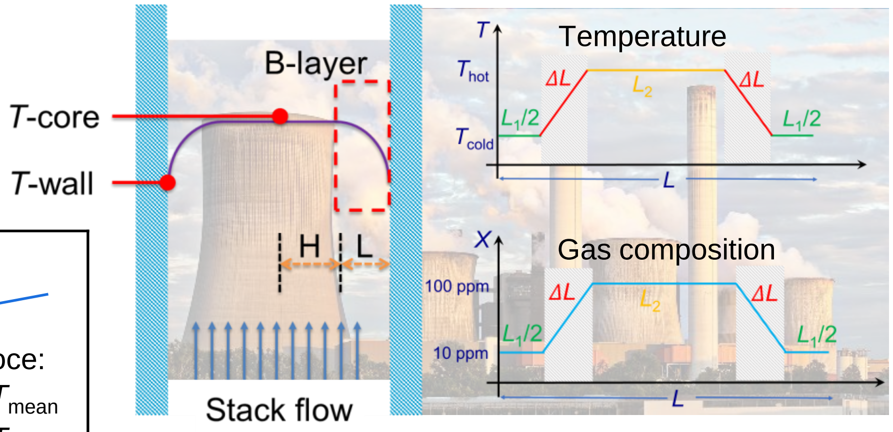
Stack emission monitoring applications

Heterogeneity effects on dTDLAS

$$x_{\mathrm{HCl}} = \frac{k_{\mathrm{B}} \cdot A \cdot T}{S(T) \cdot p \cdot L}$$

Boundary layers
ΔT , ΔL , Δx
Known?
Measurable?
Effects?





Heterogeneity effects on dTDLAS depends on:

- transition line, $S(T)$
- boundary layers
  - temperature
  - gas compositions
- temperature choice
  - calculation temperature used in
  - T_{hot}, T_{cold}, T_{mean}

MetAMC2 project

„Metrology for Airborne Molecular Contaminations 2"

WP1: Spectroscopy instrumentation

- Develop an OGS system based on a combined dTDLAS/WMS to measure HCl **in cleanrooms** (air matrix)
- Design a bypass calibration system to bridge dTDLAS and WMS techniques
- Target detection of < **1 nmol/mol (ppb) in 1 minute**

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VSL Dutch Metrology Institute
MIKES METROLOGY
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MetMAC2: HCl - in air OGS

Target: trace HCl in Air (Cleanroom)

Instruments A and B

- Single pass cell < 1 m
- dTDLAS technique

sub µmol/mol range

Instrument C

- Multi pass cell 30 m
- dTDLAS + WMS

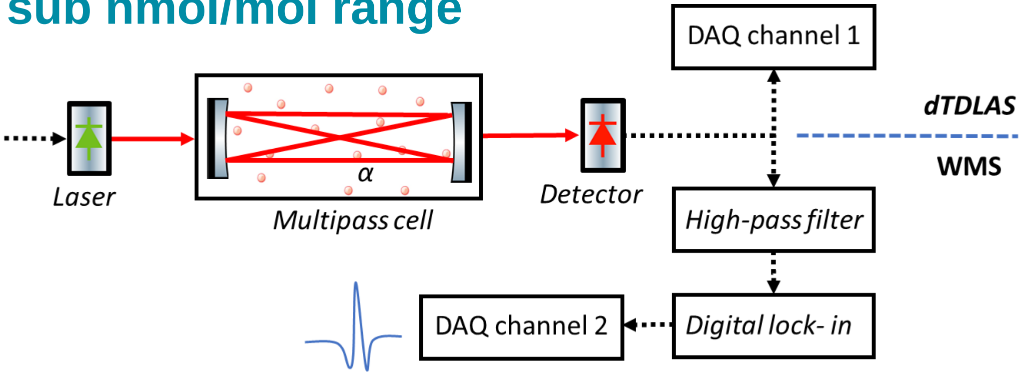
sub nmol/mol range

Detection limit improved by:

- Multipass gas cell
- Wavelength modulation spectroscopy

dTDLAS here:

- As an OGS to calibrate WMS



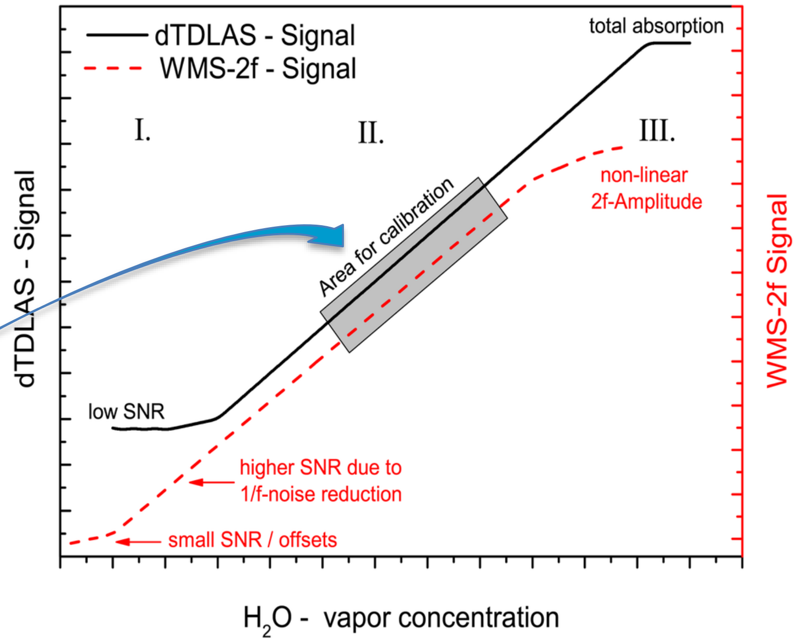
MetMAC2: HCl - in air OGS

HCl-OGS

dTDLAS + WMS

By-pass calibration system

non-certified but sufficiently 'high' concentration gas mixture



A. Klein, O. Witzel, V. Ebert. **Sensors** 2014, *14*(11)

Dilution device >> multi point calibrations

Summary and outlook

- We presented the concept of calibration free instruments **(dTDLAS based OGS)**.
- dTDLAS OGS instruments can
  - ✓ serve as **SI-traceable instruments complying with the TILSAM method**;
  - ✓ be used for **field measurements**, and also provide an **alternative field calibration approach** for sticky or reactive gases;
  - ✓ complement calibration gases (CRMs).
- **Three HCl-OGS** instruments have been progressed for different applications.
- dTDLAS/WMS HCl-OGS instrument will be validated by comparison to NPL HCl gas mixtures and dynamic dilution system.
- EURAMET 1498 **bilateral study with KRISS** on 100µmol/mol HCl in nitrogen, and CCQM HCl **key comparison** (2021) >> goal HCl CMC(s).

Thanks for your attention!

Acknowledgement

The EMPIR initiative is co-funded by the European Union's Horizon 2020 research and innovation programme and the EMPIR Participating States

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Supplementary