Physikalisch-Technische Bundesanstalt
Braunschweig and Berlin
National Metrology Institute

Progressing dTDLAS-based HCl Optical Gas Standards
- towards meeting type approval requirements of EN 15267-4

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IMPRESS2 Stakeholder Workshop, 11th January 2021

About PTB

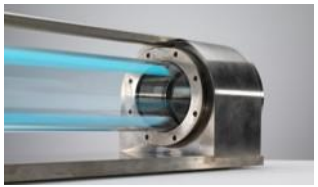
- **National Metrology Institute of Germany**, under the authority of the Federal Ministry for Economic Affairs and Energy (BMWi)
- approx. 1900 staff members,
  700 scientific papers per year,
  185 Mio. € annual budget

About us

3 Chemical Physics and Explosion Protection

3.4 Analytical chemistry of the gas phase

3.42 Spectrometric gas analysis



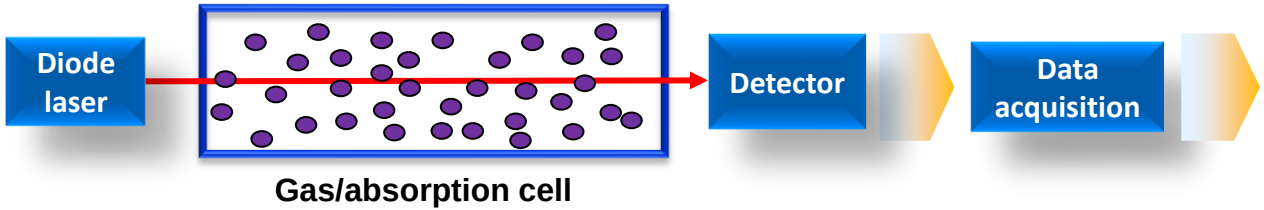
—Working Group 3.42—

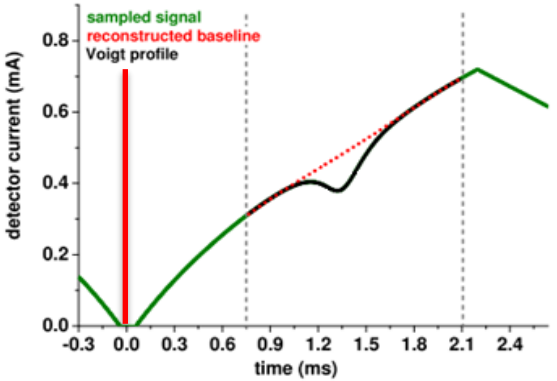
We are representing the PTB in CCQM and EURAMET committees on gases; with our national and international partners we are working on

- linking gas metrology & molecular spectroscopy
- developing methods and instrumentation for metrology, environmental science and industry
- employing IR laser-spectrometric measurement techniques as potential primary methods in gas metrology, i.e. developing optical gas standards
- determining and disseminating spectral line parameters

TDLAS technique combined with TILSAM*

= direct Tunable Diode laser Absorption Apectroscopy (dTDLAS)

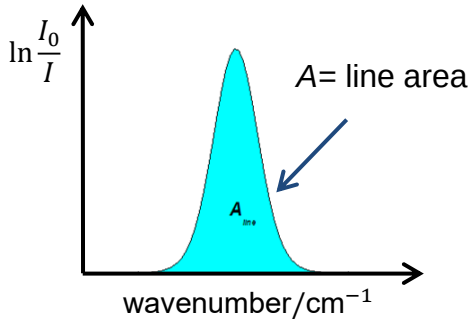




Amount fraction

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

measured, constants, molecular data



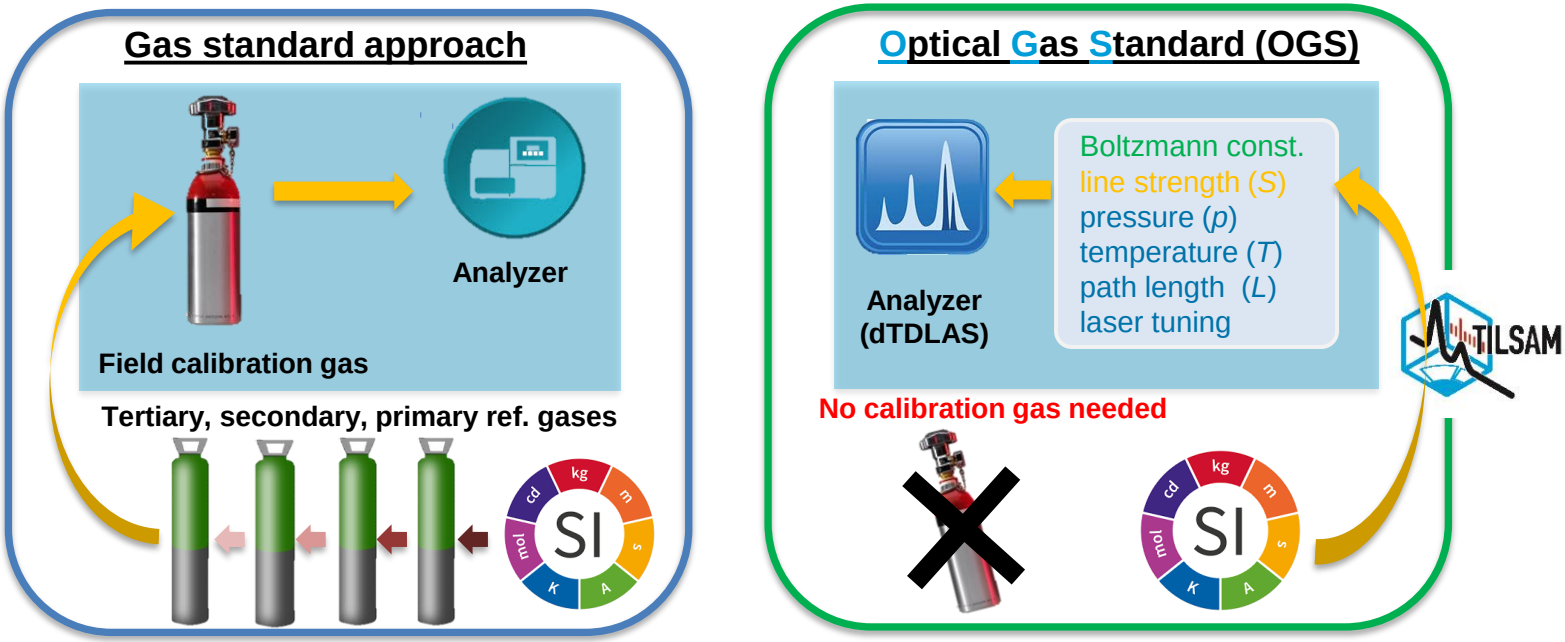
Time to frequency conversion via Etalon measurement

dTDLAS Advantages:
robust, linear, absolute, calibration-free, 1st principles model, in situ compatible

EN15267-4: Test of linearity

*Traceable Infrared Laser-Spectrometric Amount fraction Measurement

Optical gas standard (OGS)



An **Optical Gas Standard** is **a laser spectrometer** that can provide amount of **substance fractions (concentration)** that are **directly traceable to the SI**

Why HCl - OGS ?

- ***Current HCl reference method***

  emissions from stacks (EN1911)> indirect measurements via wet-chemistry
  - extractive gas sample / drying / filtration > systematic effects
  - stable gas standards for calibration (none for flue gas)

- ***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

18NRM04 Heroes

- ***HCl – OGS***
  - TILSAM compatible > no calibration by gas standards needed > low maintenance costs,
  - dTDLAS > first principle physical model > ***traceable to the SI*** *>> OGS!*
  - to complement calibration gases (Certified Reference Materials) > which cannot be provided in static gas cylinders

IMPRESS2 project

„Metrology for air pollutant emissions“

<u>WP1 task 1.4:</u> Next generation techniques and supporting spectroscopy

PTB contributions:

- Develop a dTDLAS spectrometer for HCl measurement for **stack emission monitoring** (flue gas matrix, high in CO_2, CO and H_2O)
- Analyze the potential and capability of the spectrometer for underpinning future emission limits (**~ 1 µmol/mol range**)

Physikalisch-Technische Bundesanstalt Braunschweig und Berlin

INO-CNR Istituto Nazionale di Ottica

DTU Technical University of Denmark

NPL National Physical Laboratory

HCl - OGS instrument within IMPRESS2

dTDLAS: direct tunable diode laser absorption spectroscopy

Light source:

- ICL laser (Nanoplus) at 3.6 µm
- Swept at 140 Hz

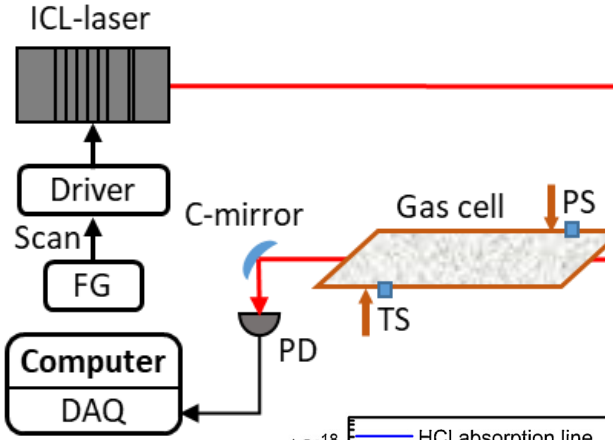
Gas cell:

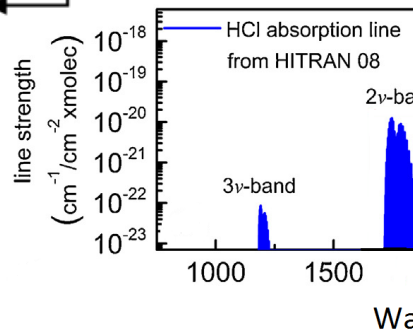
- single pass 0.77 m

Detector/Sensors:

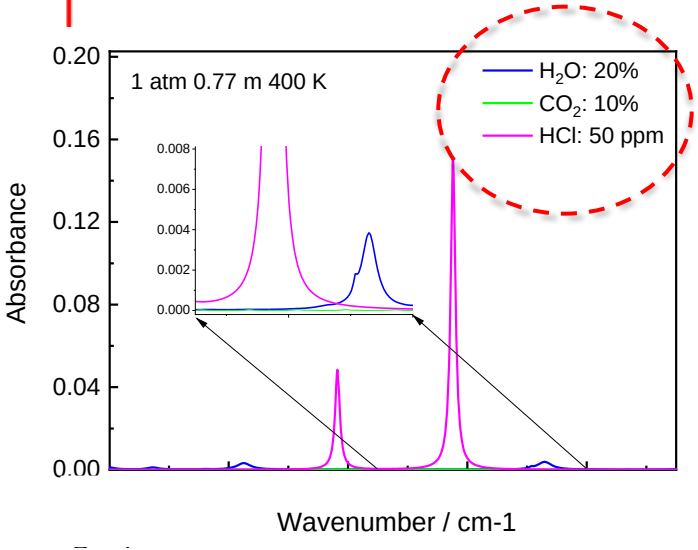
- T sensor: PT-100
- P sensor: MKS baratron
- Mid-IR detector (Vigo)

Manufactures' names are not to advertise them but only to document our instrument's realisation



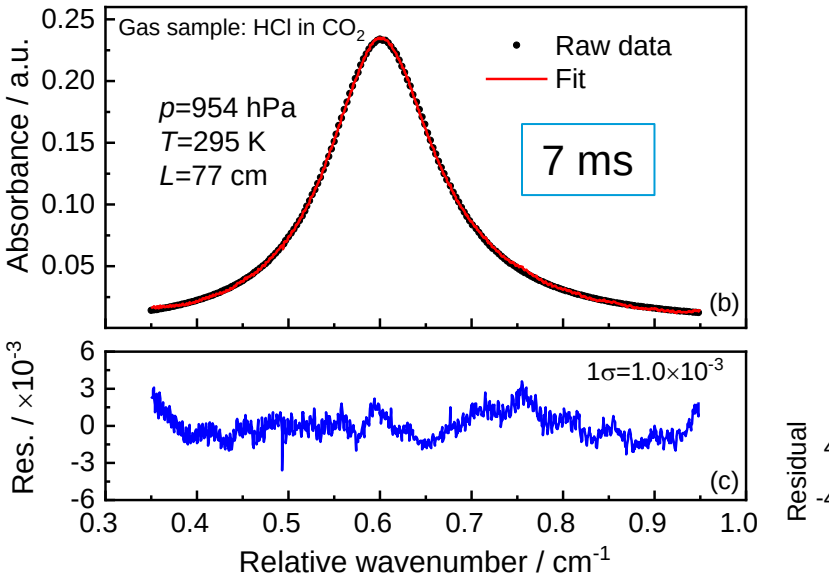


EN15267-4: 20-30% H_2O



HCl – OGS (industrial emission)

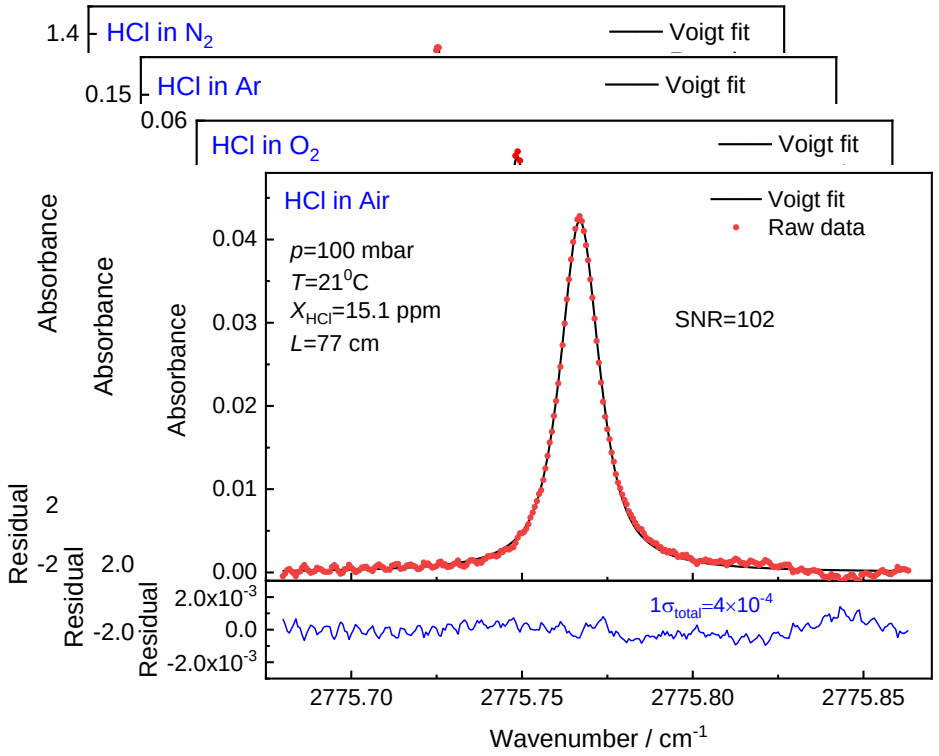
Typical HCl dTDLAS signals in CO_2



Instrument detection limit: 0.02 µmol/mol @1 s, 1 m
< EU emission limit 1.5 µmol/mol

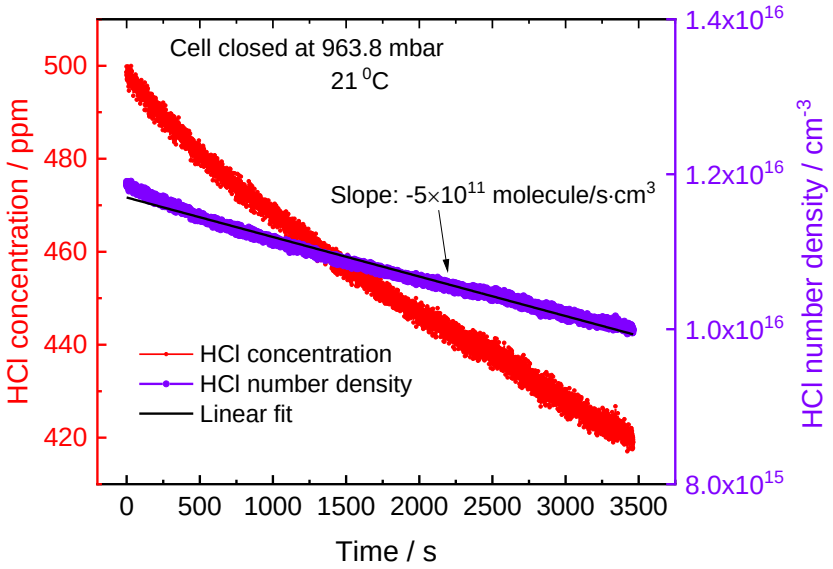
EN15267-4: 400s

Typical HCl dTDLAS signals in other gases

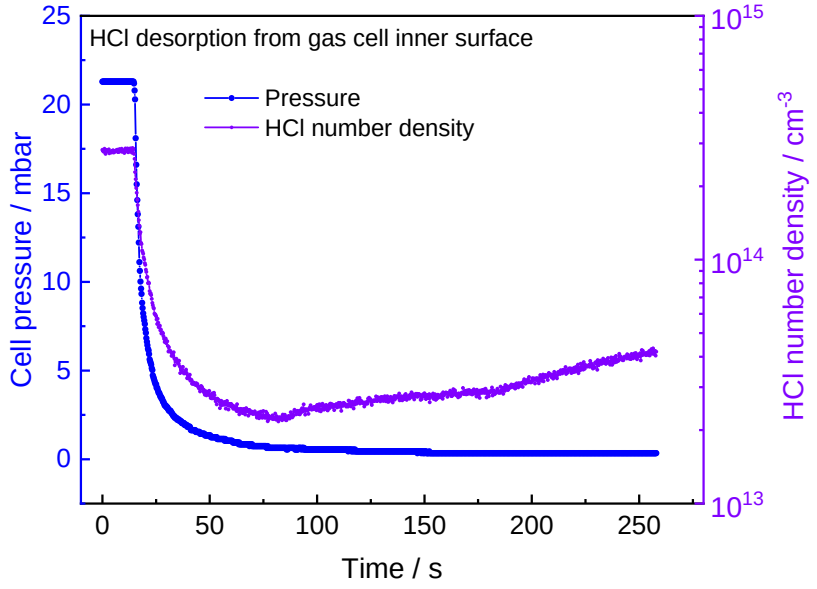


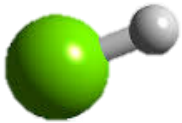
Absorption/desorption of reactive gas - HCl

HCl gas mixture in closed cell



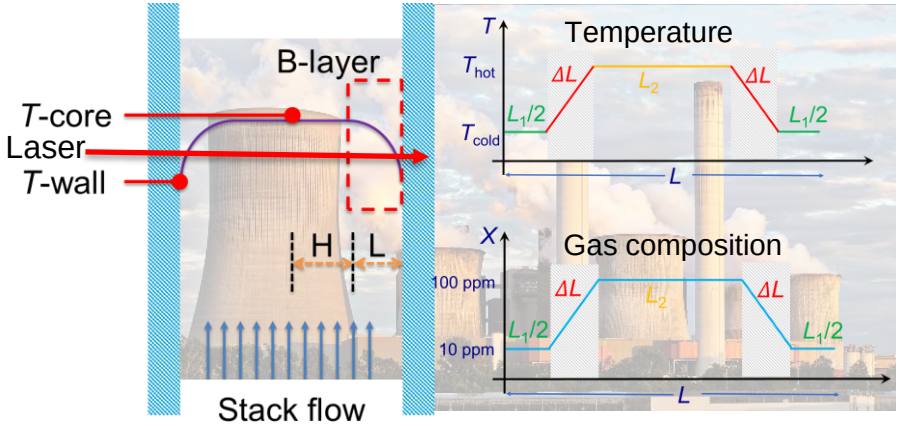
Evacuation process





System inner surface

In situ cross-stack applications

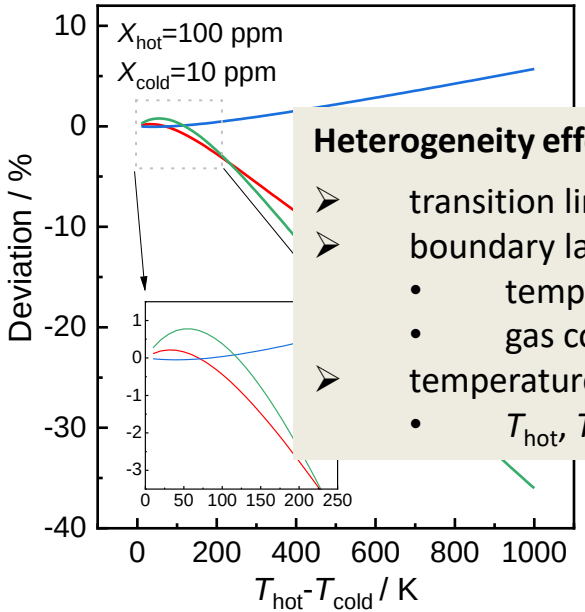


Heterogeneity effects!

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

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

Simulation model:



Heterogeneity effects depends on:

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

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

Summary and outlook

- A dTDLAS HCl-OGS instrument can
  - ✓ serve as **SI-traceable transfer standard** according to the TILSAM method,
  - ✓ is complementary to the calibration gas concept (CRMs),
  - ✓ directly applied in-field as an **instrument.**
- The HCl-OGS spectrometer developed within the IMPRESS2 project
  - ✓ was tested under different relevant conditions (varying temperature and gas matrix),
  - ✓ was quantified for **heterogeneity effects** > for in situ cross-stack applications.
- The achieved detection limit is far below the EU HCl emission limit value.
- Further development that would be necessary to meeting EN 15267-4.

Thanks for your attention!

Acknowledgements to

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