Physikalisch-Technische Bundesanstalt
Braunschweig and Berlin
National Metrology Institute

Laser-spectrometric AMC detection

- *methods, uncertainties, metrological traceability*

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Olav Werhahn, Volker Ebert

Workshop on airborne chemical contamination, 17th November 2020

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

Electricity

Chemical Physics and Explosion Protection

Optics

Precision Engineering

Ionizing Radiation

Legal and International Metrology

Cross-Sectional Services

Administrative Services

QUEST Institute at PTB

Fundamental Physics for Metrology

Berlin

Temperature and
Synchrotron Radiation

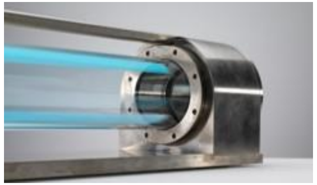
Medical Physics and Metrological
Information Technology

About us

3 Chemical Physics
and
Explosion Protection

3.4 Analytical chemistry of the gas phase

3.42 Spectrometric gas analysis

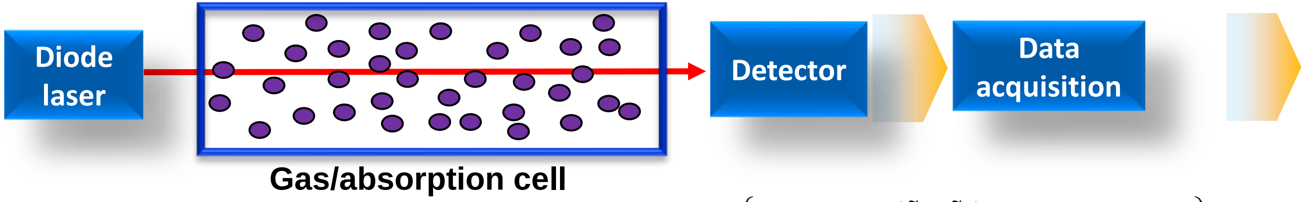


— Capabilities in 3.42 —

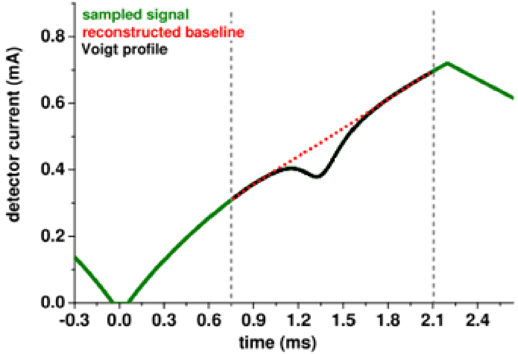
Laser spectroscopy

- Direct traceable spectroscopy techniques for amount fraction measurements
  → direct TDLAS = "dTDLAS" = absolute, calibration-free, full physical model TDLAS evaluation
- According to the TILSAM method
- Tunable diode laser absorption spectroscopy (TDLAS) – full development of spectrometers
- Cavity-enhanced (CRDS/CEAS)
- 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)
- Comb-assisted wavenumber axis definition

Direct tunable diode laser absorption spectroscopy = dTDLAS



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



Time to frequency conversion via Etalon measurement

Amount fraction

$$x_{HCl} = \frac{k_B \cdot A \cdot T}{S \cdot p \cdot L}$$

measured, constants, molecular data

Measured line absorbance via I(λ)

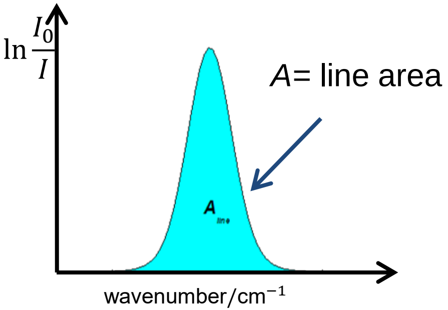
Laser tuning

Integrated Line area, *A*

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

TILSAM*

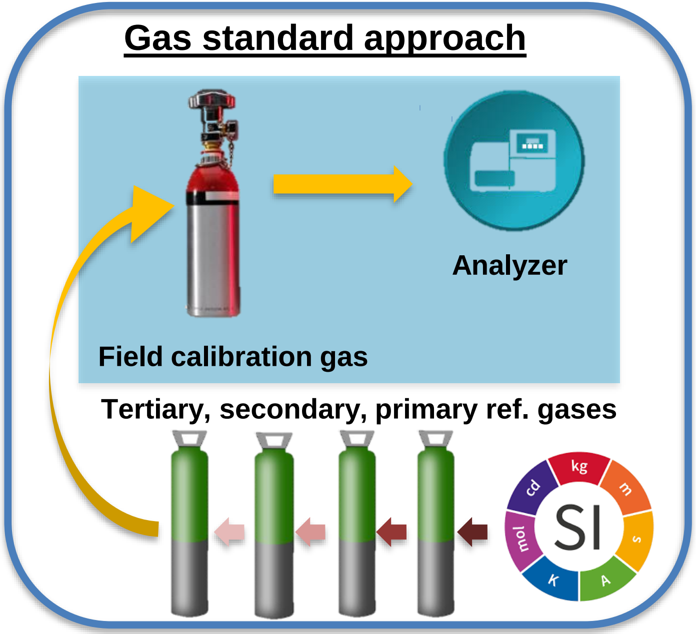
traceable amount fraction, x_{HCl}

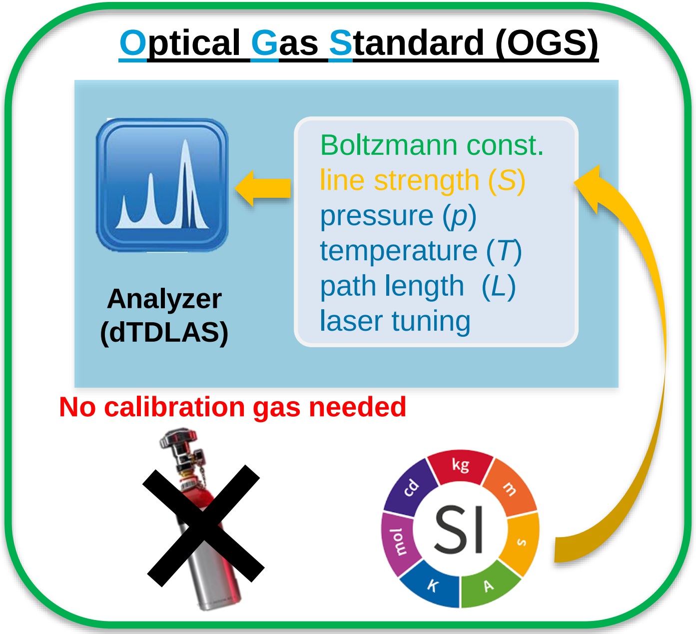


dTDLAS Advantages:
robust, linear, absolute,
calibration-free
1st principles model
in situ compatible

*Traceable Infrared Laser-Spectrometric Amount fraction Measurement (TILSAM) > metrological description

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**

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 entirely described by **first principle physical model**
  → *Input parameters + OUTPUT = 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*

dTDLAS uncertainties

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), $u \sim 1$ %

T : gas temperature, $u < 0.1$ %

p : gas pressure, $u < 0.2$ %

L : optical path length, $u \sim 0.1$- 0.4 %

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

Mixture	3 µmol/mol CO in Air		
Quantity	Value	Relative Standard Uncertainty /%	Index of Contribution to the Uncertainty of x_{CO} /%
L	76.643 m	0.021	0.0
T	295.09 K	0.08	1.3
p	838.63 hPa	0.15	1.1
S	$2.718 \cdot 10^{-19}$ cm/molecule	0.96	46.6
A_{line}	0.13222 cm^{-1}	1.00	50.9
x_{CO}	3.073 µmol/mol	1.4	–

Nwaboh, J.A., Qu, Z., Werhahn, O. and Ebert, V., Applied Optics, 56(11), 2017

dTDLAS uncertainties

Line parameter (line strength) determination at PTB

$$S = \frac{k_B \cdot A \cdot T}{x_{HCl} \cdot p \cdot L}$$

HCl line strength (1.7µm)

$S(T_0)$ [cm^{-1}/(molec cm^{-2})]

Relative error [%]

Deviation to our measurement [%

Ortwein, P., Woiwode, W., Wagner, S., Gisi,

Pogány, A., Ott, O., Werhahn, O., Ebert, V., JQRST, 130, 2013

Uncertainty component		P36e line: Relative expanded uncertainty	P36e line: Relative contribution to the uncertainty of the line strength	P34e line: Relative expanded uncertainty	P34e line: Relative contribution to the uncertainty of the line strength
p		0.24 %	*5.3 %*	0.24 %	*3.5 %*
T		0.16 %	*2.4 %*	0.16 %	*1.6 %*
L		0.26 %	*6.1 %*	0.26 %	*4.0 %*
x	X_0	0.01 %	*0.0 %*	0.01 %	*0.0 %*
	K_{leak}	0.4 %	*14.7 %*	0.4 %	*9.6 %*
	K_{evac}	0.23 %	*4.8 %*	0.23 %	*3.2 %*
A_{line}	A_{line}^{fit}	0.2 %	*3.7 %*	0.2 %	*2.4 %*
	$K_{\tilde{\nu}}$	0.8 %	*58.7 %*	1.1 %	*72.8 %*
	K_{zero}	0.35%		0.35%	
K_T		0.21 %	*4 %*	0.21 %	*2.7 %*
r_{iso}		0.1 %	*0.3 %*	0.1 %	*0.2 %*
S_0		**1.0 %**		**1.3 %**	

HCl - OGS instruments

dTDLAS: direct tunable diode laser absorption spectroscopy

Light source:

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

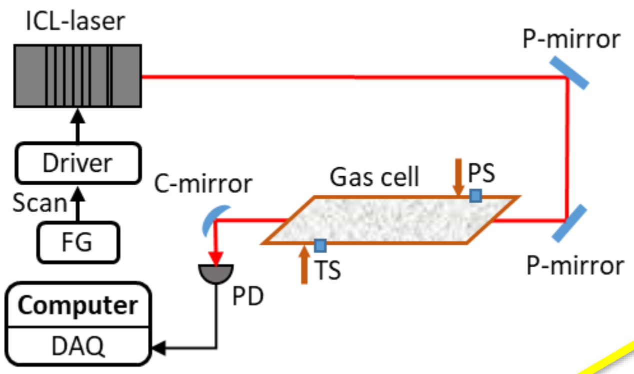
Gas cell:

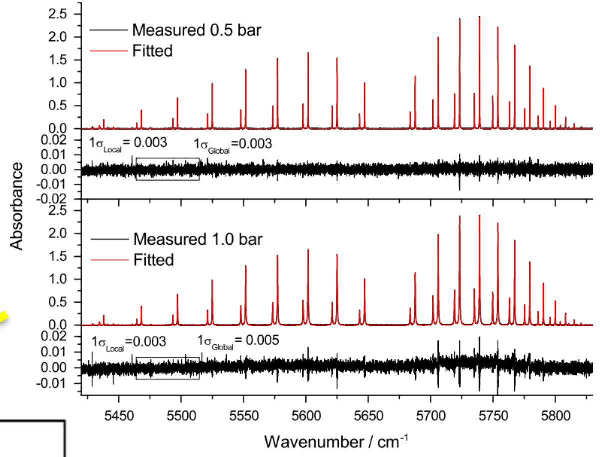
- single pass 0.82 m (instr. A)
  0.77 m (instr. B)
- Multi-pass 31 m (instr. C) (Thorlabs)

Detector/Sensors:

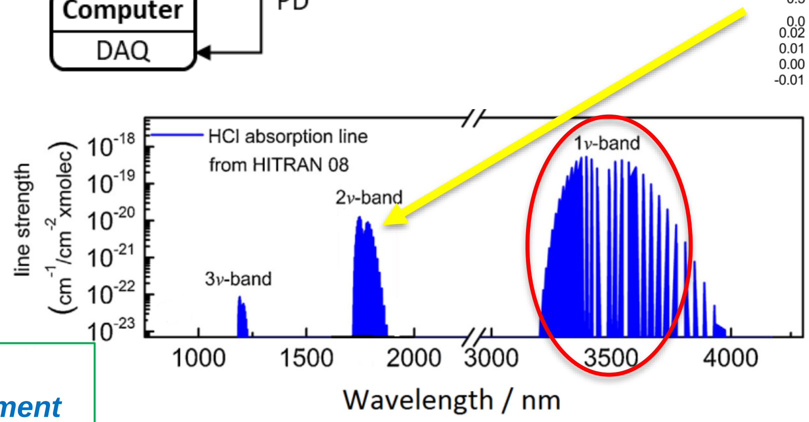
- T sensor: PT100b
- P sensor: MKS baratron
- Mid-IR detector (Vigo)

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



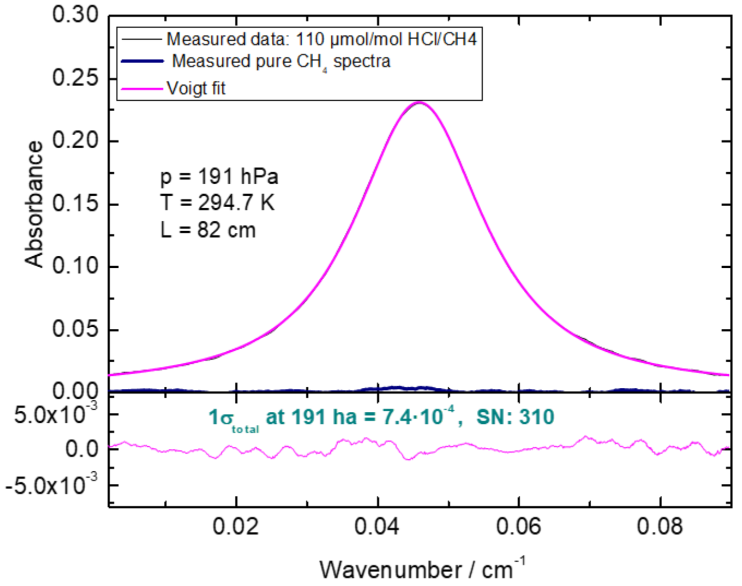


Li, G., Serdyukov, A., Gisi, M., Werhahn, O., Ebert, V., *JQRST, 165, 2015*



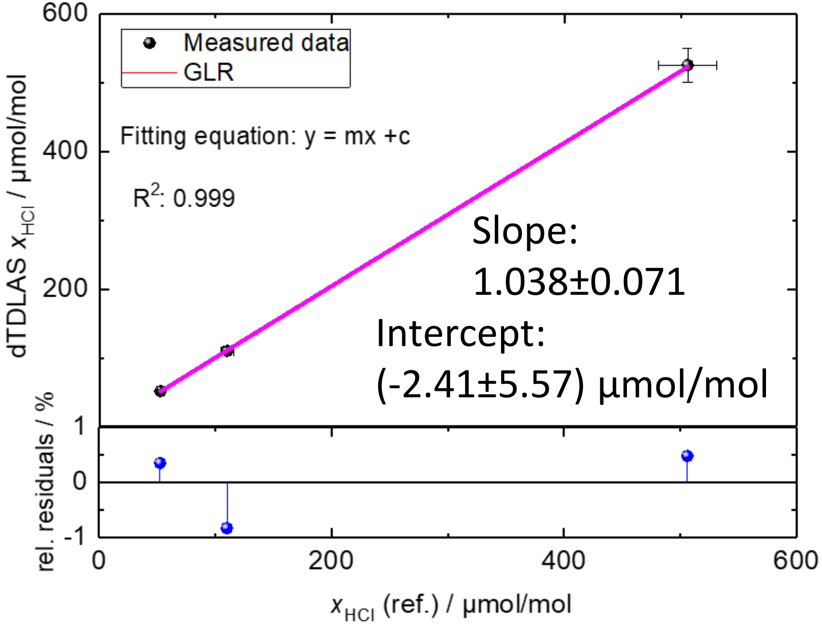
HCl – OGS (energy gas impurity)

Typical HCl dTDLAS signal in CH_4



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

HCl/CH_4: 50-500 µmol/mol

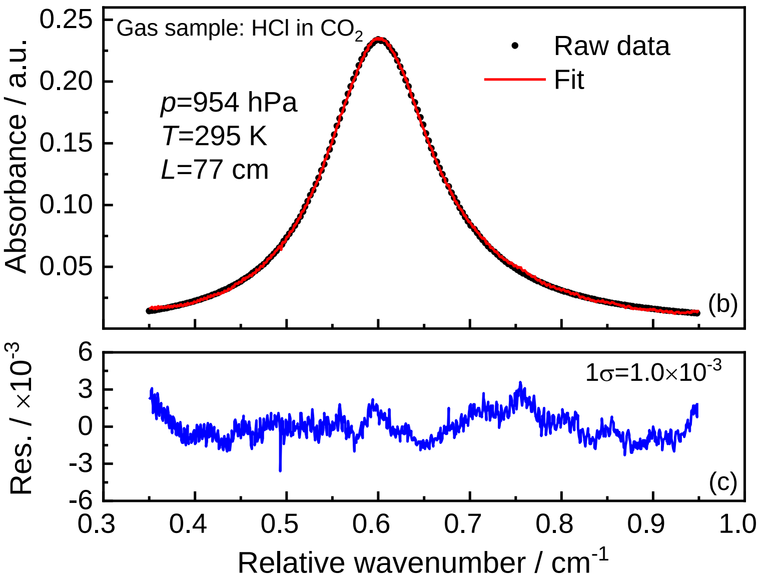


Relative uncertainty of HCl dTDLAS results: 4.6 %, k = 2

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

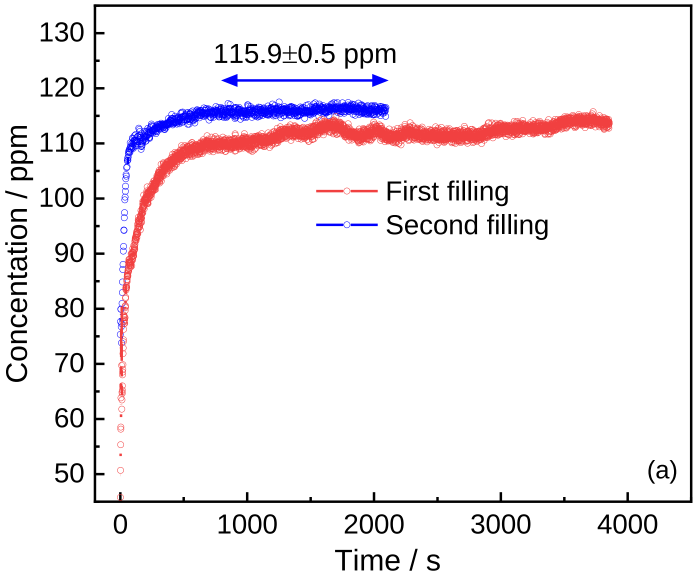
HCl – OGS (industrial emission)

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

Improved system response by passivation

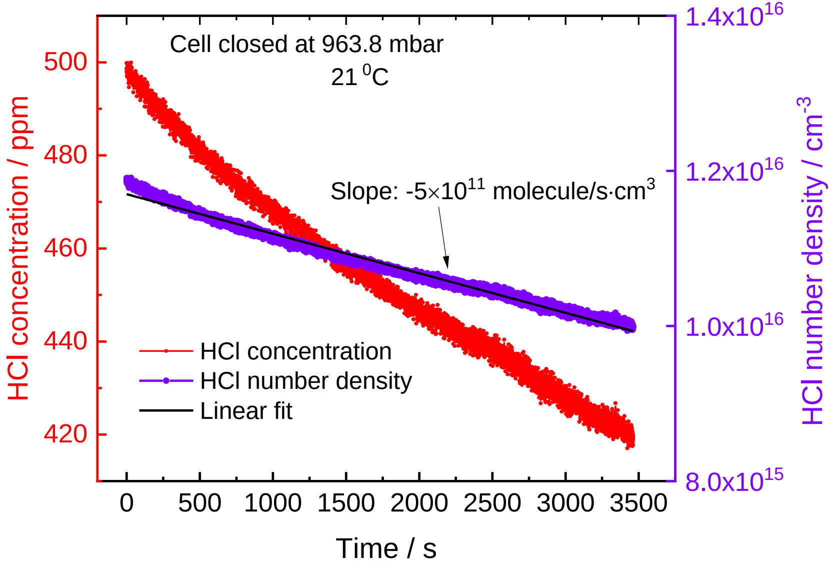


Passivation time more than 1000 s for the first filling @ instrument inner surface coated !

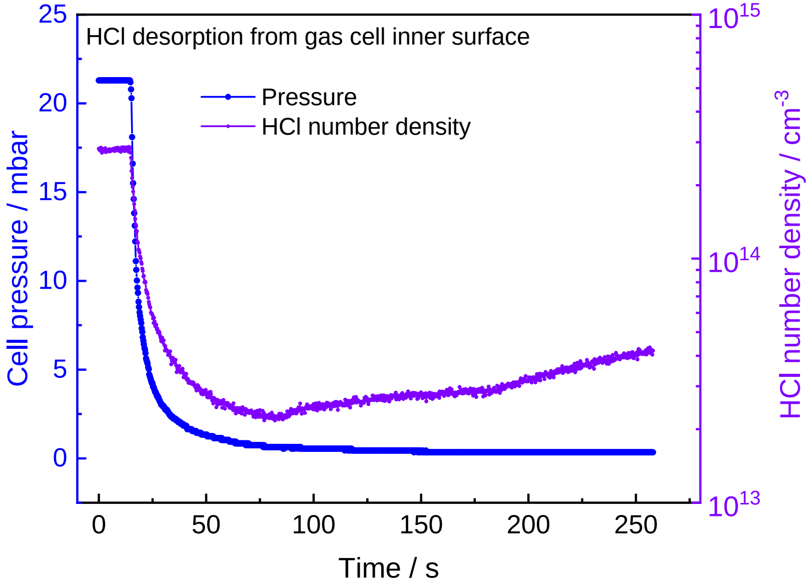
Z. Qu, J. Nwaboh, O. Werhahn and V. Ebert, ***Flow, Turbulence and Combustion 2020*** *accepted*

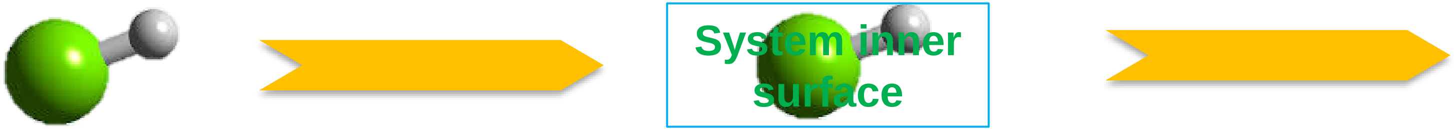
Absorption/desorption of reactive gas - HCl

HCl gas mixture in closed cell



Evacuation process





MetAMC2 project

„Metrology for Airborne Molecular Contaminations 2"

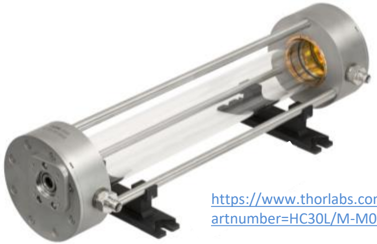
WP1: Spectroscopy instrumentation

- 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**

MetAMC2: HCl - OGS

Target: trace HCl in Air (Cleanroom)

30m Herriott cell from Thorlabs



https://www.thorlabs.com/thorproduct.cfm?partnumber=HC30L/M-M02#ad-image-0

Instruments A and B

Single pass cell < 1 m

dTDLAS technique

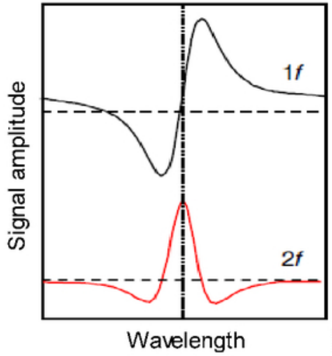
sub µmol/mol range

Instrument C

Multi pass cell 30 m

dTDLAS + WMS

sub nmol/mol range



WMS: Wavelength Modulation Spectroscopy

- modulation shifts absorption information to harmonics of f_m (extracted via lock-in)
- noise-rejection

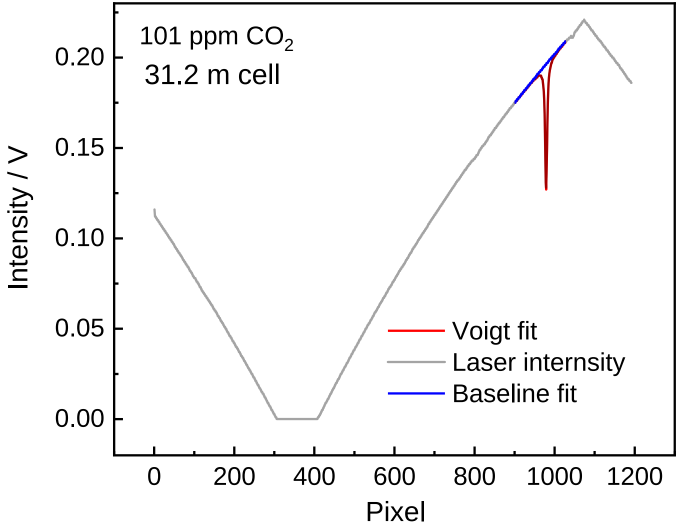
MetAMC2: HCl - OGS

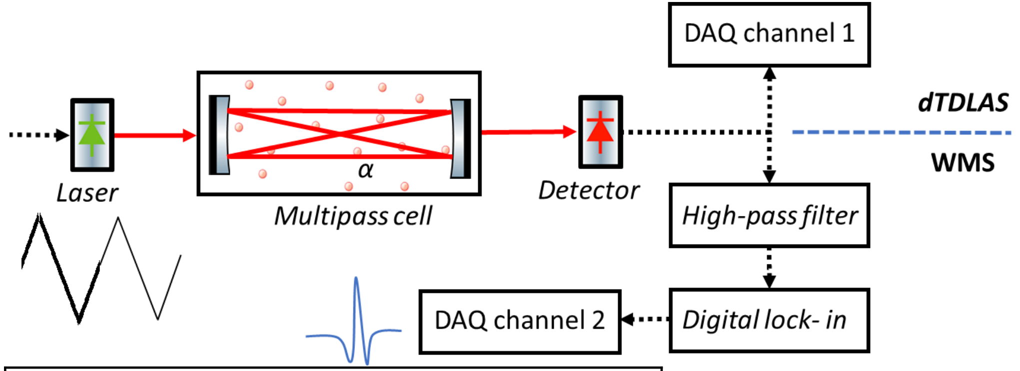
Detection limit improved by:

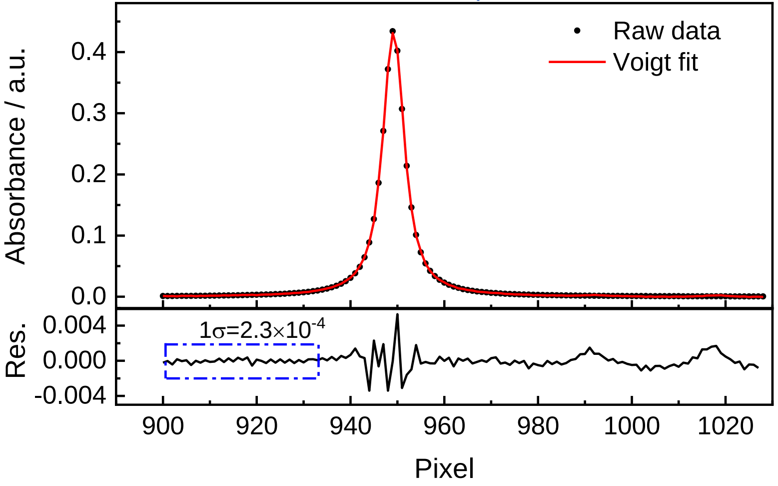
- Multipass gas cell
- Wavelength modulation spectroscopy

dTDLAS here:

- As an OGS to calibrate WMS







Baseline noise:

1σ=2.3× 10^{-4}

***LOD:* (dTDLAS)**

50 ppb CO_2

(2 ppb HCl)

WMS

sub ppb HCl

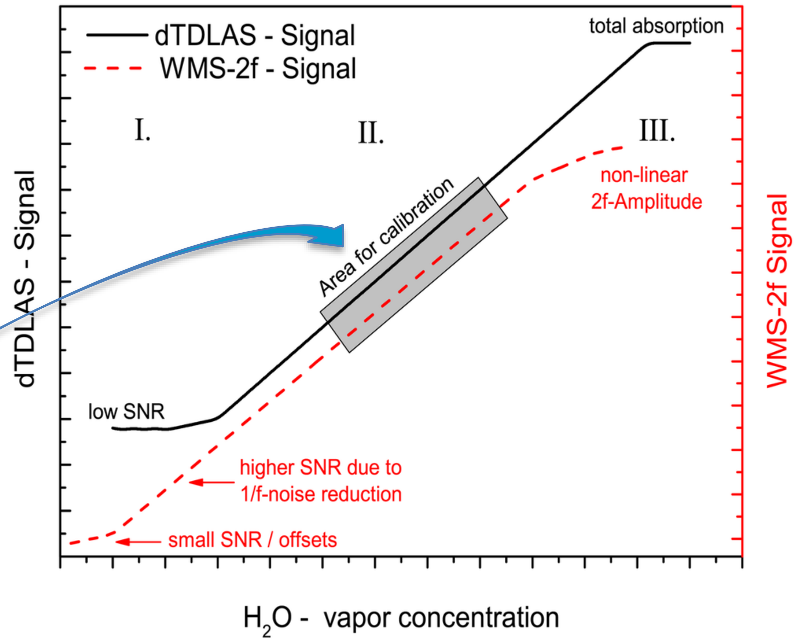
MetAMC2: HCl - in air OGS

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 **dTDLAS based OGS** as calibration-free instrument
- dTDLAS OGS instruments can
  - ✓ serve as **SI-traceable transfer standard** providing **alternative field calibration approach** for sticky/reactive gases;
    - ✓ Complementary to calibration gas concept (CRMs).
  - ✓ dTDLAS OGS instruments can also serve as field **instrument**
- dTDLAS calibrated WMS HCl-OGS: to be compared to **NPL: HCl gas mixtures** + 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!

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Supplementary