

DOI: 10.7795/810.20191119A  
<https://doi.org/10.7795/810.20191119A>

This work was presented (Poster) at:

### 29. Deutscher Flammentag

17 – 18 Sep, 2019, Bochum

#### Workshop Website

<http://www.lead.rub.de/index.php?do=Flammentag.html>

#### Acknowledgement

This work was supported by IMPRESS2 within EMPIR.

<http://empir.npl.co.uk/impres/>



EMPIR



EURAMET

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

#### The authors are with the PTB working group

Spectrometric Gas Analysis (3.42)



<https://www.ptb.de/cms/en/ptb/fachabteilungen/abt3/fb-34/ag-342.html>

#### Contact:

Dr. Zhechao Qu, Dr. Olav Werhahn  
Phone: +49 531 592 -3112, -3420  
E-mail: [olav.werhahn@ptb.de](mailto:olav.werhahn@ptb.de)  
Physikalisch-Technische Bundesanstalt  
Bundesallee 100  
D-38116 Braunschweig

## Mid-IR ICL based TDLAS spectrometer dedicated to monitor HCl concentration in combustion emissions

Z. Qu, O. Werhahn and V. Ebert

### Abstract

We present our direct tunable diode laser absorption spectroscopy (dTDLAS) approach targeting accurate HCl measurements in different matrices motivated by combustion emissions such as large-scale power stations or biomass burning domestic boilers. The system is based on a Mid-IR interband cascade laser (ICL) at 3.6  $\mu\text{m}$  probing a HCl transition line in its fundamental band in a 38 cm single pass cell. The dTDLAS system is projected to directly derive absolute HCl concentrations in hot gas plumes with enriched  $\text{H}_2\text{O}$  vapor and  $\text{CO}_2$ . The system achieves a noise-equivalent ( $1\sigma$ ) sensitivity of  $1.0 \times 10^{-5} \text{ cm}^{-1} \text{ Hz}^{-1/2}$  for HCl. Integration over 60 s yields a sensitivity of 38 ppb at a meter path length.

### Introduction

Hydrogen chloride (HCl) is a harmful gas which is released to the atmosphere from fossil fuel power plants and waste incinerators. It is also a process gas in many industries such as the electronic or textile industry. HCl is highly toxic and corrosive. In the EU, HCl emissions from the industry are covered by Industrial Emissions Directive 2010/75/EU. The EMPIR project IMPRESS2 [1] is carrying out technical development work as well as underpinning spectroscopy in support of monitoring and enforcing Emission Limit Values (ELVs) in future European legislation for key air pollutants and regulating emissions. The project addresses current technological obstacles to enhance the control of emissions thus supporting industry and regulators as well as new CEN/ISO standards.

The HCl emission measurement, as described in EN-standard 1911: 2010, does not fully extend down to concentration levels consistent with the increasingly stringent ELVs that have / will come into force. On the other hand, it is a wet chemistry-based extractive method. The sample extraction and preparation (cooling, dehumidification and filtration of particulates) significantly delay the time response and may have unexpected losses.

The laser-based optical techniques offer key features for combustion emission measurements such as high sensitivity, sufficient molecular selectivity and compatibility with online in-situ measurement applications. The availability of accurate optical measurement systems as well as gaseous and optical calibration standards allowing the monitoring of HCl emissions is a necessary prerequisite for the efficient implementation of the EU directive. Currently, stable reference materials with the required uncertainties of typically better than 5 % at HCl concentration levels of 1-10 ppm are difficult to realise. The European metrological infrastructure for measuring HCl is still to

improve. There is a pressing need for the development of traceable HCl measurement systems and reference materials to enable accurate on-site measurements for HCl emission monitoring.

Tunable diode laser absorption spectroscopy (TDLAS) is frequently applied in combustion monitoring, in research and in industry to determine species concentrations [2]. In this work, we present our TDLAS-based HCl spectrometer developed within the IMPRESS2 project. The system combines a Mid-IR ICL with a single pass cell and takes advantage of the selected absorption line having a stronger line strength as compared to Ref. [3, 4], and less/hardly any CO<sub>2</sub>/H<sub>2</sub>O interference. It should be noted that the spectrometer described in this paper is been operated as an optical gas standard for absolute traceable HCl concentration measurements without any calibration by reference gas mixtures [5-7]. instrument response using a calibration gas [4, 5, 6].

## Method

**Tunable diode laser absorption spectroscopy.** In TDLAS, the wavelength  $\lambda$  of a tunable laser is rapidly scanned across a narrow region of the optical spectrum covering one or several electronic, vibrational or rotational-vibrational absorption lines. The intensity of the laser light,  $I(\lambda)$ , focused onto a photodetector after passing the sample with absorbers can be described by the extended Lambert-Beer law according to

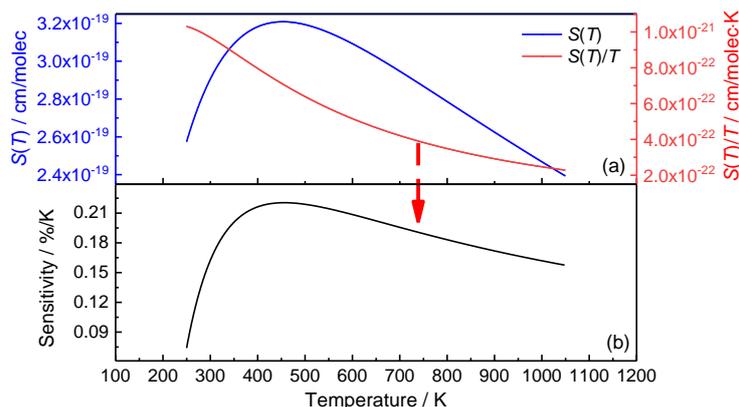
$$I(\lambda) = E(t) + I_0(\lambda) \cdot T(t) \cdot \exp[-S(T) \cdot g(\lambda - \lambda_0) \cdot n \cdot L] \quad (1)$$

with the background emission  $E(t)$  at time  $t$ , initial laser intensity  $I_0(\lambda)$ , and the broadband transmission losses  $T(t)$  which are synchronously derived from the individual raw signals and absorption profiles. The exponential term embraces the absorption line strength  $S(T)$  at gas temperature  $T$ , the normalised (area=1) line shape function  $g(\lambda - \lambda_0)$  (centered at the wavelength  $\lambda_0$ ), the absorber number density  $n$  and the optical path length  $L$ .

By combining Eq. 1 and the ideal gas law, the gas concentration  $x$  is

$$x = k_B \cdot T \cdot A_{line} / [S(T) \cdot L \cdot p_{total}] \quad (2)$$

where  $k_B$  is the Boltzmann constant,  $p_{total}$  is the total pressure of the gas sample, and  $A_{line}$  is the line area determined by spectral integration of the measured absorption line over the wavenumber axis. Note that number density  $n$  in Eq.1 is converted to concentration  $x$  (amount fraction) in Eq.2. Considering the uncertainty contributions of the input parameters for Equation 1, the uncertainties of the line strength  $S(T)$ , e.g. from HITRAN database, and the measured line area  $A_{line}$  are normally the two most significant contributors.



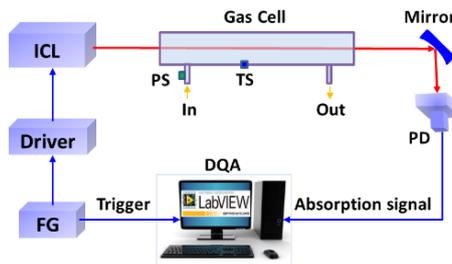
**Figure 1.** Temperature behavior of the line strength for the selected HCl transition line, the line data are from HITRAN [8]; (a) blue:  $S(T)$ -cm/molec; red:  $S(T)/T$ -cm/molec-K. (b) temperature coefficient of  $S(T)/T$

**Line temperature dependence.** To develop a TDLAS spectrometer, it is very important to study the temperature dependent line strength  $S(T)$  of the candidate lines especially in time-varying temperature combustion or stack conditions. Figure 1(a) shows two forms of the temperature dependence of the targeted HCl transition line, one is the number density normalized temperature dependence  $S(T)$  with the unit of cm<sup>-1</sup>/molecules·cm<sup>-2</sup> (blue), the other is  $S(T)/T$  with the unit of cm<sup>-1</sup>/molecules·cm<sup>-2</sup>·K (red). According to Eq. 2, if the species concentration  $x$  is to be measured, the temperature dependence of  $S(T)/T$  should be analyzed. Otherwise, number density normalized temperature dependence  $S(T)$  is used when measuring the number density  $n$ . In the temperature range shown in Fig. 1,  $S(T)/T$  is decreasing as the temperature is increasing.

This paper focuses on the concentration measurement, so that the sensitivity (temperature coefficient) of  $S(T)/T$  is shown in Fig. 1(b). The sensitivity shows that, the line strength  $S(T)/T$  changes from 0.08 to 0.22 %/K in the full range. For example, the sensitivity is around 0.2 %/K at 600 K in Fig. 1(b), there will be about 2% concentration deviation when the temperature is varying 10 K. This is beneficial to estimate whether a transition line is good enough for certain applications, especially under conditions with varying temperature.

### Spectrometer setup

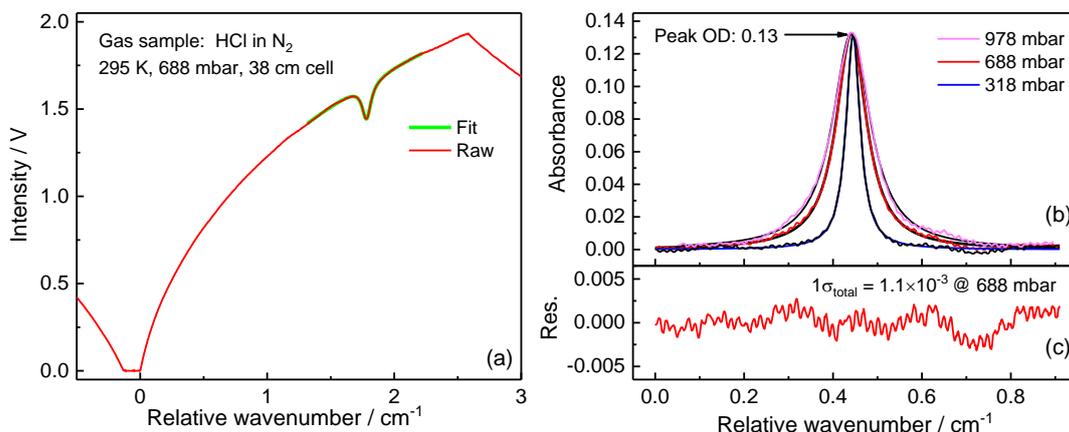
A schematic drawing of the experimental setup is shown in Fig. 2. An IC Laser at 3.6  $\mu\text{m}$  (Nanoplus GmbH) is employed to scan across the one HCl absorption line. The laser injection current was supplied by a low-noise driver, which also controlled the diode temperature. The scan was achieved by varying the laser current with a 140 Hz triangular wave generated by a function generator. The laser beam was directed through the gas cell and then focused onto a photodetector. The detector signal is sampled at 600 kHz.



**Figure 2.** Schematic drawing of the experimental TDLAS setup, PS-pressure sensor, TS-temperature sensor, PD-photodetector, FG-function generator, DQA-data acquisition card.

### Results

Typical measured absorption profiles with fitted Voigt profiles are shown in Fig. 3, as well as the residuals between the measured data and the fitting function. The residuals and the peak absorptions on the optical density ( $OD = -\ln(I/I_0)$ ) scale are depicted in Fig. 3(b). The residuals can be quantified by the statistical standard deviation of the residual across the scan range,  $1\sigma = 1.1 \times 10^{-3}$  (noise equivalent absorption coefficient). The signal-to-noise ratio (SNR) where the signal is defined as the OD peak ( $OD=0.13$ ) value and the noise as the  $1\sigma$  value of the residuals, were calculated as 118 for the spectrum measured at 688 mbar of total gas pressure. It is common to normalize the noise equivalent absorption ( $1\sigma$ ) coefficient with respect to the path length (38 cm) and the square root of the temporal bandwidth (0.125 s), which yields in this case  $1.0 \times 10^{-5} \text{ cm}^{-1} \text{ Hz}^{-1/2}$ .



**Figure 3.** (a) The typical measured raw signal with laser offset subtraction, (b) The measured spectral at different pressure and the Voigt fitting, (c) the fitting residual of 688 mbar spectrum.

The stability of the HCl spectrometer was investigated by means of a time series of the measured concentration as in Figure 4 (a). A histogram plot of concentrations depicting an approximate normal distribution around the mean value is plotted in Fig. 4(b). A Gaussian profile is fitted to the distribution histogram, resulting in a sigma value of 0.99 ppm – the standard deviation of the time series of HCl concentration measurement.

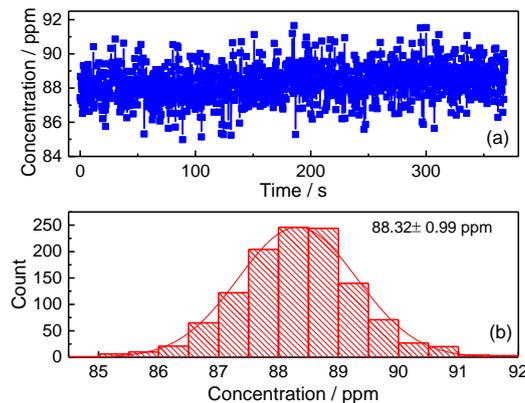


Figure 4. (a) Time series of HCl concentration measurement. (b) Histogram plot of the measured concentration, the red line depicts a Gaussian profile.

The Allan deviation plot shown in Fig. 5 is used to characterize the system stability of the dTDLAS spectrometer. The precision is improved with the integration time while white noise is reduced, then for the longer time periods the precision gets limited by the long-term instabilities like thermal drifts. At 1 min averaging time, a precision of 38 ppb at a meter pathlength (corresponding 100 ppb at 0.38 m in Fig.5) can be achieved by our HCl spectrometer.

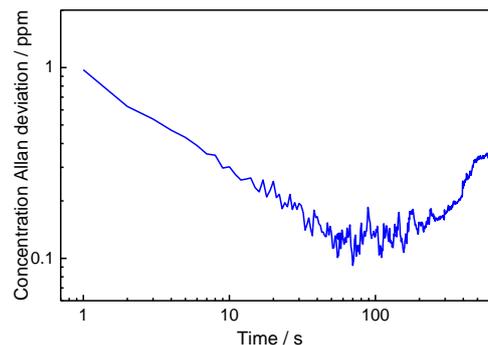


Figure 5 Allan deviation plot for the same time series concentration measurements shown in Fig. 4.

## Conclusion and outlook

We presented an ICL based TDLAS spectrometer for HCl measurements. Laboratory characterization and validation experiments showed a  $1\sigma$  precision of the HCl measurement of 0.99 ppm at 8 Hz resolution. The spectrometer was tested under different conditions from 100 mbar to 1000 mbar cell pressure, and higher cell temperature (the results are not shown here). As the targeted HCl line was selected for combustion atmosphere, this spectrometer can also accurately measure HCl in high CO, CO<sub>2</sub> (20%) and H<sub>2</sub>O (20%) contents conditions. In addition to a previous case study for thermal boundary layer effects on line-of-sight CO<sub>2</sub> detection [9], we are working on the application of our HCl spectrometer as an optical gas standard.

## References

- [1] IMPRESS2: <http://empir.npl.co.uk/impress/>
- [2] Ebert V., Fernholz T., Giesemann C., Pitz H., Teichert H., Wolfrum J., Jaritz H.: *Simultaneous diode-laser-based in situ detection of multiple species and temperature in a gas-fired power plant*, Proceedings of the Combustion Institute, 28(1), 423-430, 2000.
- [3] Ortwein P., Woiwode W., Fleck S., Eberhard M., Kolb T., Wagner S., Gisi M., Ebert V.: *Absolute diode laser-based in situ detection of HCl in gasification processes*, Experiments in fluids, 49(4), 961-968, 2010.
- [4] Li G., Serdyukov A., Gisi M., Werhahn O., Ebert V.: *FTIR-based measurements of self-broadening and self-shift coefficients as well as line strength in the first overtone band of HCl at 1.76  $\mu\text{m}$* , Journal of Quantitative Spectroscopy and Radiative Transfer, 165, 76-87, 2015.

- [5] Nwaboh J., Pratzler S., Werhahn O., Ebert V.: *Tunable diode laser absorption spectroscopy sensor for calibration free humidity measurements in pure methane and low CO<sub>2</sub> natural gas*, Applied spectroscopy, 71(5), 888-900, 2017.
- [6] Buchholz B., Ebert V.: *Absolute, pressure-dependent validation of a calibration-free, airborne laser hygrometer transfer standard (SEALDH-II) from 5 to 1200 ppmv using a metrological humidity generator*, Atmospheric Measurement Techniques, 11(1), 459-471, 2018.
- [7] Buchholz B., Böse N., Ebert V.: *Absolute validation of a diode laser hygrometer via intercomparison with the German national primary water vapor standard*, Applied Physics B, 116(4), 883-899, 2014.
- [8] HITRAN database: <https://www.cfa.harvard.edu/hitran/>
- [9] Qu Z., Werhahn O, Ebert V.: *Thermal Boundary Layer Effects on Line-of-Sight Tunable Diode Laser Absorption Spectroscopy (TDLAS) Gas Concentration Measurements*, Applied spectroscopy, 72(6), 853-862, 2018.