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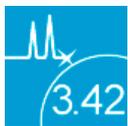


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Laser detection of HCl in biomethane for combustion engines

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Abstract

To quantify HCl impurity in biomethane, a new matrix-specialized laser spectrometer has been developed based on direct-tunable diode laser absorption spectroscopy (dTDLAS). The spectrometer is equipped with a 3.6 μm interband cascade laser, a single pass gas cell, and can determine absolute HCl gas species concentration in CH_4 or biomethane with a relative standard uncertainty of 2.3 %. For HCl concentration measurements at 161.7 mg/m^3 , the dTDLAS HCl concentration result agrees with the HCl in CH_4 reference gas mixture, demonstrating the capability of the sensor. The repeatability of the dTDLAS HCl concentration results was determined to be 0.05 mg/m^3 .

Introduction

Biogas and biomethane (upgraded biogas: mainly methane) are energy gases which are easily used in applications that are designed for natural gas such as internal combustion engines. Biomethane contains a variety of impurities such as hydrogen chloride (HCl) and Hydrogen fluoride (HF) [1]. The presence of gaseous hydrogen chloride in biomethane can cause potential corrosion problems in the combustion process and thus needs to be minimized to ensure a long lifetime of the process installation. The specifications for biomethane (i.e. EN 16723-1 for injection into natural gas grids), which can subsequently be used for combustion applications, provide limit values for chlorinated compounds ($< 1 \text{ mg}/\text{m}^3$) and maximum HCl values. Therefore, highly accurate HCl in biomethane test methods are required for quality control.

For HCl measurements in biomethane, so far, there is no specific standard reference method published. For other applications, e.g., stack emissions, there is the standard DIN EN1911 published to support the determination of mass concentration of gaseous chlorides expressed as HCl. Therefore, in order to support policy makers and quality control in the supply and utilization of biomethane, it is becoming indispensable to realize a standardized test method for HCl and other chlorinated compounds in biomethane.

Tunable diode laser absorption spectroscopy (TDLAS) is an interesting diagnostic technique for accurate HCl quantification. However, to calibrate sensors, a major problem is a lack of stable HCl standards. An approach to solve this problem is to use direct-TDLAS (dTDLAS) sensors, which are suitable to reduce the need for calibration gases and frequent calibration processes. dTDLAS, which is a variant of TDLAS that combines this spectroscopic technique with a special, first principles data evaluation approach to directly extract absolute species concentration without calibration of the sensor with a reference gas

[2 - 3]. Due to its independence from calibration, a dTDLAS sensor can serve as an “optical gas standard (OGS)”. An OGS is an optical analyzer providing absolute gas species concentrations which are traceable to the international system of units (SI), ideally without a requirement for an initial or a cyclic calibration with a reference gas as shown in [2 - 4]. dTDLAS sensors have been used to measure gaseous concentrations without the need of any prior calibration of the sensor with a calibration gas and have been demonstrated for accurate gas species concentration measurements in a variety of applications [2 - 10]. Laser spectrometers based on dTDLAS are non-contact sensors, highly selective, have near real time response, are very sensitive towards the ppb level [11].

In this paper, a new development towards absolute HCl detection in biomethane using dTDLAS is reported. The system is equipped with a mid-IR interband cascade laser and specifically designed for HCl measurement in biomethane. Measurement results of HCl in biomethane mixtures and rigorous uncertainty evaluation following GUM principles are presented, to demonstrate the current capability of the system.

Direct tunable diode laser absorption spectroscopy (dTDLAS)

In dTDLAS, the beam of a tunable laser source is transmitted through an absorbing medium, e.g. gas species in a cell. The transmitted radiation Φ is expressed by the extended Beer Lambert law,

$$\Phi(\tilde{\nu}, L) = Tr(t) \cdot \Phi_0(\tilde{\nu}) \cdot \exp\{-S_T \cdot r_{iso} \cdot g(\tilde{\nu} - \tilde{\nu}_0) \cdot L \cdot n\} + E(t) \quad (1)$$

where Φ_0 is incident radiation, L is the path length of the light beam transmitted through the absorbing medium, S_T is the line strength of the probed molecular transition at gas temperature T , and g is a normalized line profile centered at ν_0 [2], [10]. Briefly, as described elsewhere [2], [12], the quantities $Tr(t)$ and $E(t)$ describe the effect of variations of the cell transmission and an additive detector signal (like background radiation) with time t , respectively. By means of the ideal gas law, the absorber number density n is expressed via the partial pressure p_{partial} of the absorbing molecules and the gas temperature T . The partial pressure is related to the total pressure p_{total} using the concentration of the absorbing species x_{species} , i.e., $p_{\text{partial}} = x_{\text{species}} \cdot p_{\text{total}}$. Making use of the area-normalization of g , Eq (1) can also be written in its integral form

$$x_{\text{species}} = \frac{k_B \cdot T}{S_T \cdot r_{iso} \cdot L \cdot p_{\text{total}}} \int_{-\infty}^{\infty} A(\tilde{\nu}) d\tilde{\nu} = \frac{k_B \cdot T}{S_T \cdot r_{iso} \cdot L \cdot p_{\text{total}}} \cdot A_{\text{line}} \quad (2)$$

where the quantity $A(\tilde{\nu}) = -\ln(\Phi(\tilde{\nu}) / \Phi_0(\tilde{\nu}))$ is the spectral absorbance, and k_B the Boltzmann constant [2], [10]. The gas species concentration x_{species} can be traceable to the international system of units (SI), if all input quantities i.e. p_{partial} and T are traceable as well.

Experimental

The setup in Fig. 1 consists of an ICL (Nanoplus) emitting around 3.6 μm , a single pass, 0.82 m, gas cell, and a mid-infrared detector. The gas pressure and temperature are measured with an MKS Baratron pressure sensor and two PT100, respectively.

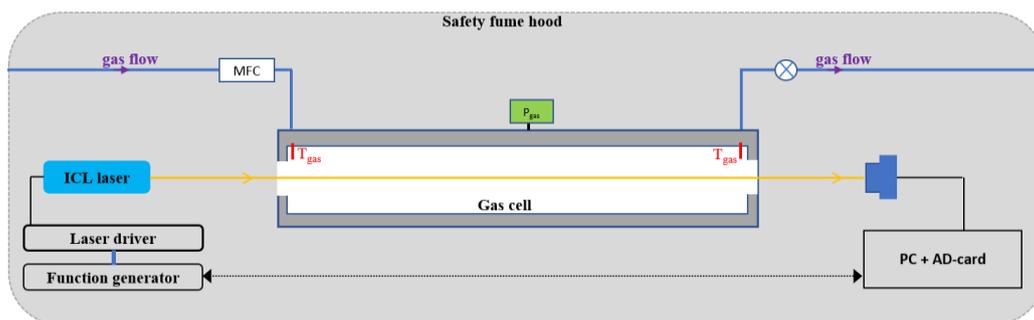


Fig.1: dTDLAS setup for HCl measurements in biomethane

For spectroscopic measurements, the gas cell in Fig. 1 is filled with a 110 $\mu\text{mol/mol}$ HCl in CH_4 gas mixture (corresponding to $161.7 \pm 8.1 \text{ mg/m}^3$, note: 1 ppm HCl $\sim 1.47 \text{ mg/m}^3$ at 25 °C and 1 atm). The laser wavelength is swept at 139.8 Hz across the HCl absorption line at 3.6 μm . Figure 2a depicts a typical absorbance spectrum measured with the dTDLAS system in Fig. 1. The data in Fig. 2a is fitted with a Voigt profile in order to derive the line area (A_{line} : area under the individual absorption line). The standard deviation of the Voigt fit residuals (Fig. 2b) is $1 \sigma_{\text{total}} = 2.3 \times 10^{-3}$. From the peak absorbance of 0.18 and $1 \sigma_{\text{total}}$, a signal to noise ratio (SNR) of 78 is derived for the data in Fig. 2. From the HCl concentration of 152 mg/m^3 (derived from the data, see Fig. 2c) and the SNR, a snapshot precision of 1.9 mg/m^3 is calculated at a time resolution of 0.13 seconds. In order to estimate the achievable SNR with optimized optics, $1 \sigma_{\text{total}}$ is utilized. By means of $1 \sigma_{\text{local}} = 1.3 \times 10^{-3}$ (Fig. 2b) and the peak absorbance of 0.18, a SNR of 138 and a snapshot precision of 1.1 mg/m^3 is derived.

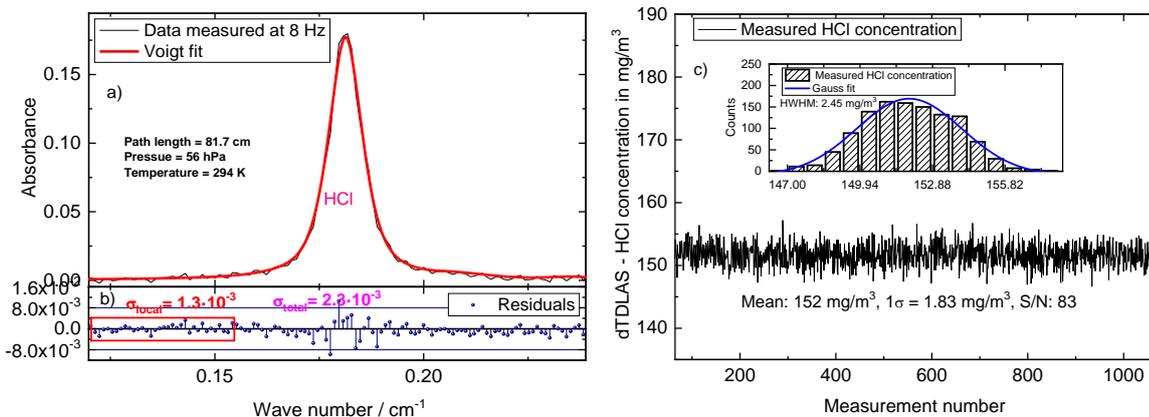


Fig. 2: a) Typical dTDLAS absorbance data measured with the setup in Fig. 1. b) Residuals of a Voigt fit to the data in Fig. 2a. c) Repeated measurements of HCl concentration results.

To determine the stability of the system, Fig. 2c depicts continuous dTDLAS HCl concentration measurements (time resolution of 0.13 seconds per individual HCl point) with a mean value of 152 mg/m^3 . From this, a stability of $1 \sigma = 1.83 \text{ mg/m}^3$ (1.2 %) is derived from the standard deviation of the HCl measurements, corresponding to a SNR of 83 ($152 \text{ mg/m}^3 / 1.83 \text{ mg/m}^3$). For this concentration level, this 1.83 mg/m^3 (1.2 %) stability is already better than the 2.5 % (max.) required for HCl measurements in stack emissions according to DIN EN1911. The repeatability, calculated as the standard deviation of the mean, of the concentration results in Fig. 2c is 0.05 mg/m^3 .

Table 1. Uncertainty budget

Parameter	Value	Relative standards uncertainty / %
Pressure	56.34 hPa	0.30
Temperature	294.4 K	0.10
Path length	0.8165 cm	0.24
Line strength	$1.92 \cdot 10^{-19} \text{ cm/ molecule}$	2.00
Line area	$2.25 \cdot 10^{-3} \text{ cm}^{-1}$	1.00
HCl concentration results	^a 152 mg/m^3	2.30 (combined uncertainty)

^aNote: The HCl concentration is 103.4 ppm (152 mg/m^3) using an estimated conversion factor of 1 ppm HCl $\sim 1.47 \text{ mg/m}^3$ at 25 °C and 1 atm

Table 1 shows a first example uncertainty (error) budget to evaluate the quality of the measured input (contributing) parameters such as the gas pressure and the temperature, and finally of the concentration results. As shown in Table 1, the relative standard uncertainty of the HCl concentration results delivered by the system in Fig. 1 is 2.3 % at 152 mg/m^3 . The input parameter that contribute the most to the final uncertainty of the concentration results is the HITRAN [13] line strength value with a relative standard uncertainty of 2 %. It could be noted here that upper range of the HITRAN line strength uncertainties for HCl of 2 % (range $\geq 1\%$ and $< 2\%$) is used and $k=1$ is assumed.

The HCl concentration of (152 ± 7) mg/m³, $k = 2$ (the uncertainty has been multiplied by 2, as typically expressed to enable a comparison [9]), delivered by the dTDLAS system is in good agreement with the (161.7 ± 8.1) mg/m³, $k = 2$, for the commercial HCl standard in the gas cylinder. The quantity k is a coverage factor expressing the probability that the true value of the measurand is contained within a specified interval of measured values based on the information available. If the possible values of the measurand are normally distributed, then $k = 2$ is producing an interval having a level of confidence of 95% that the true value is included [9]. Regarding the uncertainty of the individual input parameters in Table 1, it can be concluded that, in order to improve the uncertainty of the spectrometric results, more work has to be done to improve the uncertainty (2 %) of the HCl line strength value. Except for the line strength taken from HITRAN, the traceability of the concentration results to the SI is addressed via the traceability of the input parameters such as the gas pressure and temperature. Future work to improve the quality of the data delivered by the dTDLAS spectrometer will focus on the measurement of a metrologically compatible line strength value with a reduced uncertainty. With a SI-traceable line strength value, and if all other input parameters in Eqn. 2 are SI traceable as presented, SI-traceability of the dTDLAS HCl concentration results could be reached, with the potential of the spectrometer to be operated as an OGS.

Conclusions

We have developed a new application specific dTDLAS system for absolute HCl concentration measurements in CH₄ or biomethane. The results delivered by the system are in agreement with the certified value of the commercial HCl in CH₄ gas mixture used. The relative standard uncertainties of the HCl concentration results delivered by the system is 2.3 % ($k = 1$). The repeatability of the HCl concentration results is 0.05 mg/m³ (0.03 % at 152 mg/m³). Future work will be focused on the measurement of the HCl line strength aiming to achieve SI traceability of the concentration results, and subsequently to operate the dTDLAS system as an optical gas standard.

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