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Quantitative, time-resolved detection of CH₄ concentrations in flows for injection analysis in CNG engines using IR absorption

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Abstract. The reduction of CO₂ and other greenhouse gas emissions is an important driving force for the development of modern engines. Especially in the transport sector, the use of alternative fuels like methane, the main component of compressed natural gas (CNG), is an applied measure to achieve this goal. This work describes the development of an optical measurement system for accurate quantification of CH₄ densities in gas flows based on broadband absorption of infrared light, i.e. non-dispersive IR absorption spectroscopy (NDIR). We demonstrate the capability of the system to achieve high time resolution as well as high measurement accuracy and precision. The optical set-up of the system is designed for usage at the inlet manifold of CNG-fuelled spark ignition engines. It allows for detailed analysis of the mixture formation during single engine cycles. CH₄ densities can be determined by monitoring the infrared light attenuation around 3.3 μ m caused by the ν_3 antisymmetric C-H-stretch vibration. We calculate the nonlinear relation between transmittance and CH₄ density from absorption cross sections calculated from the HITRAN database. The theoretical transmittance signals are corrected for spectral influences of the bandpass filter, the detector sensitivity, the fibre transmittance and the emission spectrum of the light source in order to calculate CH₄ densities directly from the measured transmittance. A calibration function corrects remaining differences between experimental and simulated values and improves the accuracy. We show that the sensor system is capable for determination of air-fuel ratios (λ -values) and demonstrate the dynamic quantification of a CH₄ injection into a flow channel under various flow conditions. Furthermore, we present the first measurements with a prototype probe capable of measurements inside the inlet manifold of a four-stroke spark ignition engine. We validate the detection strategy in experiments with premixed gases using a modified inlet geometry and demonstrate its application under standard engine operation with port fuel injection while varying the injection parameters.

1 Introduction

The worldwide climate change calls for changes and new developments in almost all areas of technology and society. One of the most important tasks is the emission reduction of greenhouse gases. Especially the reduction of carbon dioxide (CO_2) emissions, which is one of the primary products of combustion processes, is a significant challenge since combustion of fossil fuels is still one of the greatest energy sources used today (International Energy Agency,

2016). Common strategies to reduce the overall emissions are a continuous improvement of combustion system efficiencies as well as the use of alternative fuels that inherently emit less greenhouse gases.

Transportation nowadays consumes a large part of primary energy resources and thus produces significant greenhouse gas emissions (International Energy Agency, 2016). Therefore, sustainable mobility is one of the most important tasks of our time concerning technology and society. Besides the development of modern, fuel saving combustion engines, a higher number of battery electric vehicles (BEVs) can significantly reduce greenhouse gas emissions from transportation (Faria et al., 2012). Through technological development and policies favouring electric mobility, this presents a rising competition to internal combustion engine vehicles (ICEVs; Dijk et al., 2013). Nevertheless, BEVs still struggle with short ranges, long charging times and higher capital costs than ICEVs (Ma et al., 2012; Yilmaz and Krein, 2013). Furthermore, their CO₂ balance only becomes more favourable than conventional fuels if the electricity originates from renewable sources (Ma et al., 2012). In conclusion, combustion engines are likely to stay the standard driving technology for the next years. Consequently, the European Union set new limits for CO_2 and NO_x emissions of cars, which result in higher technological requirements for spark ignition (SI) engines (European Parliament and Council, 2009). Increasing the efficiency and lowering the emissions of conventionally fuelled car engines need more and more effort. Therefore, the use of alternative fuels such as compressed natural gas (CNG) is an attractive opportunity for emission reduction (Edwards et al., 2011; Turrio-Baldassari et al., 2006). Already based on its chemical structure (carbon-hydrogen ratio), it is capable of reducing CO2 emissions by 25 % in certain scenarios (Deutsche-Energie-Agentur, 2011). In conclusion, CNG can serve as a bridging technology before electric mobility becomes competitive. Moreover, CNG replaced by or blended with biogas allows for a striking CO₂ balance (Deutsche-Energie-Agentur, 2011; Kramer et al., 2015). However, CNG-fuelled engines do not yet reach efficiencies of gasoline-fuelled engines and still require significant improvement. For optimization of CNG-fuelled engines, detailed knowledge of the air-fuel mixture formation prior to the combustion is essential since the process determines properties of combustion (Korakianitis et al., 2011).

One of the best-known methods to achieve time-resolved measurements of mixture formation is gas sampling followed by analysis in a flame-ionization detector (FID; Turrio-Baldassari et al., 2006; Collings, 1988; Cheng et al., 1989; Galliot et al., 1990). However, this method suffers from a time delay caused by the length of the sampling pipe, a drawback that can be overcome by optical sensor technologies (Grosch et al., 2011). Beside gas sampling systems, there are different optical methods to analyse mixture formation. Laser-induced fluorescence (LIF) allows spatially resolved measurements of temperature and air-fuel ratios but requires sufficient optical access. Additionally, LIF experiments are very time-consuming, need thorough preparation, including a careful selection of a fluorescent tracer molecule, and often do not allow real-time measurements (Luong et al., 2008; Schulz and Sick, 2005). Another laser-based detection technique employs the 3.392 µm emission of a He-Ne laser to determine fuel concentrations from absorption measurements. However, the pressure and temperature dependent absorption cross sections of hydrocarbons (in conventional fuels or of CH₄) can make quantification difficult regarding the varying conditions in engines (Tomita et al., 2003a, b; Klingbeil et al., 2006). Tuneable diode laser absorption spectroscopy (TDLAS) uses scanning of a specific molecular absorption line for fast measurements of temperature and species concentration and is widely applied in combustion diagnostics (Bolshov et al., 2015). In TDLAS experiments, it is crucial to select the respective absorption line with great care, and the zero emission line has to be controlled thoroughly regarding effects of light scattering and beam steering. Wavelength modulation techniques overcome part of these problems, but need sophisticated computational modelling, which introduces additional uncertainties (Bolshov et al., 2015). Overcoming problems of temperature and pressure dependence as well as selection of appropriate tracer molecules or absorption lines, sensor systems based on nondispersive infrared (NDIR) absorption to measure the local fuel concentration and exhaust gas recirculation at the spark plug of an engine were developed (Hall et al., 2001; Hall, 1999; Koenig and Hall, 1998, 1997). Using broadband infrared light sources, concentrations of several molecular species can be measured simultaneously by selecting their absorption range with infrared bandpass filters. Since NDIR systems usually cover the complete absorption band of a molecule, pressure and temperature influences are much weaker than in the case of narrow band detection of single absorption lines. A high time resolution and acquisition rate can be achieved allowing for single-cycle-based measurements. However, in situ calibration using a gas of well-defined concentration is necessary to calculate species concentration from transmission signals (Grosch et al., 2007; Hall, 1999).

In this work, we present the derivative of a measurement system based on NDIR absorption developed previously for mixture formation analysis at the spark plug in gasolinefuelled engines (Grosch et al., 2010, 2011, 2014, 2007). The system allows crank-angle resolved measurements of fuel concentration for single engine cycles. In contrast to prior work, we develop a quantification strategy to determine methane concentrations under known temperature and pressure conditions that does not require any in situ calibrations. Instead, a direct calculation of air-fuel ratios based on pressure and temperature dependent absorption cross sections taken from the HITRAN database (Rothman et al., 2013) is applied. We show that it is crucial to describe all spectral properties of the detection system as well as possible. In detail, we not only consider the transmittance spectrum of the IR bandpass filter in our model, but also detector sensitivity, fibre transmittance and emission spectrum of the light source. An ex situ calibration in pressure cell experiments efficiently removes small deviations that remain between experimental and calculated values. Typically, CNG-fuelled engines are operated with port fuel injection where the mixture formation already starts in the inlet manifold. Therefore, we show the development of a flexible optical measurement system for adaption to different inlet manifolds. We test a new optical set-up at a flow channel representing idealized con-



Figure 1. Schematic overview of the optical measurement system.

ditions and transfer the principle geometry into a first prototype inlet probe. The prototype sensor system is tested at an SI engine fuelled with methane performing validation experiments with premixed gases as well as standard engine operation with port fuel injection.

2 Experimental section

2.1 Measurement system

The detection system used in this work was originally developed to measure simultaneously air-fuel ratios and exhaust gas recirculation (EGR) rates inside the combustion chamber of a gasoline-fuelled SI engine (Grosch et al., 2007, 2011, 2014). The schematic concept is shown in Fig. 1. The light of a 150W quartz-tungsten-halogen (QTH) lamp is coupled into a ZrF₄ fibre through a chopper wheel that applies a 30 kHz modulation. This allows a constant measurement and subtraction of background infrared radiation, e.g. from hot surfaces or a flame during combustion. The fibre guides the light to a sensor probe where the gas in the absorption path causes a wavelength dependent attenuation of the incident radiation. The remaining light is coupled into a second ZrF₄ fibre and guided to the detection unit. The latter consists of a cascade of four mercury-cadmium-telluride (MCT) detectors covered by different IR bandpass filters. Each detector produces a voltage output according to the incident light intensity. Division of the detector signal with absorbing species present inside the measurement volume by the signal without absorbing species gives a broadband transmittance value, τ . The quantification method presented in this work is then able to assign a specific τ -value to the corresponding CH₄ density for given pressure and temperature. Hereinafter, each combination of filter and detector is referred to as a "channel" or a "detection channel". The bandpass filters select a detection frequency range matched to the molecule of interest and are



Figure 2. Absorption bands with marked detection regions for H_2O , H_2O+CO_2 , CO_2 and CH_4 of the prototype system used. The H_2O and CO_2 absorption enables determination of EGR rates but is not considered here. The H2O spectrum was calculated using HI-TRAN (resolution: 0.01 cm⁻¹ at 100 kPa, 298 K, 40 cm absorption path length). CH4 and CO2 spectra were measured with a FTIR spectrometer (Bruker Vector 33, resolution 0.9 cm^{-1}) in a pressure cell (400 kPa, 298 K, 6 cm absorption path length, 0.2 and 0.02 % mole fractions, respectively).

shown in Fig. 2. We note that the system used in this work is a prototype system for developing quantification strategies, i.e. the two filters around 2.7 μ m marked as "CO₂+H₂O" and "H₂O" as well as the filter around 4.2 µm marked as "CO₂" enable the determination of EGR rates. The quantification of exhaust gas concentrations is not considered in this work but will be presented in a future publication. Here, we focus on the ability of the filter at 3.3 µm (marked as "CH₄") to determine air-fuel ratios. The spectral region around 3.3 µm corresponds to the v_3 vibrational band of CH₄, which represents the anti-symmetric C-H-stretch vibration and is present in all hydrocarbons. Consequently, the same bandpass filter may be used for the detection of different hydrocarbon molecules, e.g. fluid hydrocarbon fuels, as well. Nevertheless, the quantification procedure is different for CH₄ because its small molecular structure results in an absorption spectrum with distinct peaks that exhibit strong influences of pressure and temperature.

A major issue of NDIR detection is the selection of an appropriate bandpass filter regarding sensitivity and reduction of cross sensitivity to other molecular species, i.e. CO_2 and H_2O . Figure 2 illustrates that the CH_4 channel shows no overlap with CO_2 and only a very weak overlap with H_2O absorption lines. We estimated that even in the case of 100 % humidity at room temperature (~ 3 % H₂O vapour) and the whole beam path exposed to ambient air, the absorption of H₂O vapour will only reduce the integrated transmittance to a value of $\tau \approx 99.7$ %. This value is of the order of the signal-



Figure 3. Schematic drawing of the flow channel with details of the mixing module and the optical set-up.

to-noise ratio (typically ~ 250) of the detector and thus can be neglected in our quantification method.

Since the sensor system was developed for usage in engines, where significant background radiation may be present, the signal is constantly modulated by the chopper wheel at 30 kHz while acquiring a crank angle (CA) resolved trigger and an additional trigger once or twice every cycle. After each measurement, the acquisition software maps the data to the trigger signals according to the desired resolution, typically 1° CA. In our flow channel and pressure cell experiments there are no trigger signals available. In this case the system simulates a user defined engine speed and maps the data accordingly.

2.2 Flow channel

The flow channel depicted in Fig. 3 serves as idealized model geometry for an inlet manifold of an SI engine. Note that the time-resolved quantification of CH_4 in an inlet manifold is the primary goal of the presented measurement technique here. Nevertheless, a transfer to other environments and geometries is possible with only little effort.

A fan draws ambient air from the laboratory into the channel through a filter as shown in Fig. 3. The air passes a flow meter and then enters a mixing module. The module enables addition of gas via a mass flow controller (MFC) to the stream of air and produces a homogenous mixture. A draft of this module is sketched in the lower part of Fig. 3. The module comprises three stages. Each stage consists of a separating plate splitting the flow channel into consecutive sections. The air flow has to pass each of these separation plates through a particular aperture influencing the flow behaviour. The gas is introduced to the air flow in front of the first separating plate. This plate's aperture has an oval shape and is aligned close to the plate's edge to induce a rotation in a plane parallel to the flow channel. The plate of the second stage has an aperture in the centre and is equipped with baffle plates to produce a swirl around the flow channel centre line. The first two stages serve for the mixing of the gas. The third plate has regularly arranged holes, like a strainer, and serves to align the mixture flow. Along 50 cm downstream of the mixing module, the flow channel is continued in a straight line to settle down the flow before the gas-air mixture reaches the detection region.

The optical set-up shown in Fig. 3 starts with an optical fibre guiding the incident light to the flow channel, where a lens collimates it to a ~ 8 mm wide beam. After collimation, the light passes a 50 % beam splitter, enters and exits the flow channel through two quartz windows and is reflected back to the beam splitter passing the flow channel a second time. A second lens couples the light to a second optical fibre guiding it to the detection unit. The geometry described here is chosen instead of a simple transmittance set-up, because it is more compact and in its final form (see Sect. 2.4) only requires optical access from one side. Thus, it is easier to adapt to an SI engine where free space around the inlet manifold is limited.

All experiments were performed under ambient conditions (298 K, 100 kPa). The flow channel has a profile area of $28 \times 38 \text{ mm}^2$ and the light passes through the short side. Due to the optical set-up with reflector and beam splitter, the light passes the flow channel twice, leading to an absorption path length of 56 mm. The maximum flow velocity in the flow channel is about 13 m s^{-1} , leading to a pressure drop of the order of 1 kPa inside the channel. The temperature was monitored via a type K thermocouple measuring the room temperature inside the laboratory. For acquisition of calibration data, we use MFCs to mix a defined amount of CH₄ into the air flowing through the channel. In engine applications, the air-fuel ratio is typically stated as the λ -value. This value is defined as the mass ratio of air to fuel divided by the ratio under stoichiometric conditions, but can also be converted to a volumetric ratio. For CH₄ a stoichiometric mixture with an air-to-fuel volume ratio of 9.52 : 1 corresponds to $\lambda = 1$. This ratio is equivalent to the flow ratio of air and CH₄ flowing through the channel. Therefore, we can adjust the λ -value of the mixture inside the channel by measuring the flow of air and adjusting the flow of CH₄ through the MFC accordingly.

We perform the calibration measurements with a fixed air flow of 0.66 and 1.1 m s⁻¹. Further experiments with higher air flows showed no influence of flow velocity on the measured signal (see inset in Fig. 7). The flow through the MFCs is adjusted equivalent to values of $\lambda = 0.25$ -4. Prior to each measurement, we measure the ambient air signal without CH₄ in the flow channel. Each pair of ambient air and air– CH₄ mixture is measured six times. Each measurement consists of 36 000 consecutive data points with a time resolution of ~ 0.17 ms (~ 5.9 kHz acquisition rate) resulting in a measurement duration of 6 s. A repetition of the experiment minimizes the influence of small variations in the experimental conditions, e.g. fluctuation of the light source emission, and ensures a good quality of the measurements. All measure-

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Figure 4. Experimental set-up for engine validation measurements with premixed gas. The optical set-up is covered by a housing and screwed into the inlet manifold via a threaded stainless steel tube. The latter is sealed by a 2 mm thick sapphire window which is level with the inlet manifold's wall. This set-up can either be used with a closed inlet with premixed gases or opened inlet and regular injection and air flow.

ments are averaged and the 95 % confidence interval is taken as uncertainty.

To perform measurements with injection of CH₄, the mixing module and the MFC in Fig. 3 are removed and we install a CNG injector from a standard SI engine 5 mm upstream to the detection region. The time resolution of the experiment again is ~ 0.17 ms and the duration of a measurement cycle with one injection is 1200 ms. The injection starts 200 ms after the beginning of a cycle, to monitor the signal level prior to injection. The injector is backed with a CH₄ pressure of 700 kPa and opens for 7 ms in this experiment. Every measurement consists of 50 recorded cycles where the first 10 are without injection of CH₄. This procedure allows one to take the first 10 cycles of every recording as a background signal. The signal with CH₄ injection is divided by the averaged background signal, resulting in a broadband transmittance value. We average these values over the 40 cycles with injection, which minimizes the effect of small variations of single injections, and repeat every measurement three times.

2.3 Pressure cell

The environmental conditions inside an engine differ from those inside the flow channel as mentioned above, e.g. regarding dynamical changes in pressure and temperature. Additionally, the optical system does not include quartz windows, which results in different spectral calculations. Therefore, we performed a series of calibration measurements on pressure cells with highly purified premixed gases. The mixtures were composed of 2.62%, 9.5% and 30% CH₄ (99.9995 %) in N₂ (99.9999 %), corresponding to λ -values of 3.9, 1.0 and 0.25, respectively. The pressure cell is capable of enduring pressures up to 400 kPa and temperatures up to 500 K. It serves not only as a calibration environment for the inlet manifold, but also for the combustion chamber. The calibration data covers a pressure range from 50 to 350 kPa at temperatures of 300 and 473 K. Here, we consider only the data at low pressures important for measurements in the inlet manifold. Pressure and temperature in the inlet manifold are not expected to reach higher values than in the pressure cell experiments. Since in a combustion chamber typical temperatures are higher than in our pressure cell experiments, we validated that the calibration is independent of temperature (see Fig. 10 and the description). Further experiments with quantification of CH₄ densities inside the combustion chamber are subject to current research and will be considered in future publications. We repeat each measurement six times and calculate the average value with a 95 % confidence interval. At the start of the measurements, the cell is evacuated to determine the background signal without any absorber present. Afterwards, the cell is filled with the premixed gas and evacuated again, after the signal at maximum pressure was measured.

2.4 Prototype engine inlet probe and engine conditions

For experiments at the inlet manifold of an SI engine, a prototype probe was built by LaVision GmbH. It has the same optical design already used in the flow channel experiments, but is housed and equipped with a stainless steel tube sealed by a 2 mm thick sapphire window at the end. An M12 thread at the tip of the probe allows attachment to the inlet manifold of an SI engine. In contrast to the flow channel experiments, the reflector is mounted inside the inlet manifold as shown in Fig. 4. We performed all experiments in a four-stroke engine with four cylinders and port fuel injection that has been modified for switchable operation with gasoline or CNG. It is important to note that the CNG injection in the test engine occurs rather far away from inlet valves ($\sim 20 \,\mathrm{cm}$). A length adapter is placed between cylinder head and actual inlet manifold to gain a certain distance required by the geometry of the test station. The measurement position was located 5 cm away from the injector between the point of injection and the engine's inlet valve. Furthermore, we made some modifications to the inlet manifold adapter (Fig. 4). The set-up can be used with the injector in regular engine operation or by using the adapter with premixed gases, which allows validation measurements. For the validation experiments, the inlet of one cylinder of the engine was closed and connected to a separate gas supply instead. The gas supply is equipped with two valves enabling the induction of either premixed gas or ambient air from the laboratory. The average temperature in the inlet manifold was monitored using a 1 mm thick type K thermocouple, whereas pressure was recorded with a time resolution of 1° CA by a piezo resistive pressure sensor (Kistler type 4007B). Both, thermocouple and pressure sensor, were located close to the detection position at a distance of 1.5 cm. The premixed gases consisted of 2.52 and 9.51 % CH₄ (99.9995 %) in N₂ (99.9999 %) giving λ -values of 4.06 and 1.0, respectively. Background measurements with ambient air were performed before and after every measurement and both mixtures were measured six times at 800 rpm engine speed. At this speed 1° CA corresponds to a time resolution of ~ 0.21 ms, resulting in an acquisition rate of ~ 4.8 kHz. Each measurement acquires 100 single engine cycles that are averaged for further analysis. For measurements with injection of CH₄ under standard engine operation, the modifications of the air and gas input shown in Fig. 4 were removed.

2.5 Quantification method

Inside the detection volume, the CH₄ molecules absorb parts of the infrared light according to Beer–Lambert's law, resulting in an attenuated intensity of light I(v) compared to the initial intensity $I_0(v)$:

$$I(\nu) = I_0(\nu)e^{-\sigma(\nu, p, T) \times \rho(p, T) \times L},$$
(1)

where $\sigma(v, p, T)$ is the pressure and temperature dependent absorption cross section at a specific frequency ν , $\rho(p,T)$ is the density of the absorbing molecule, L is the length of the absorption path and p and T are pressure and temperature, respectively. Our quantification method uses absorption cross sections calculated from the spectroscopic parameters of the HITRAN database (Rothman et al., 2013) by a Lab-View program. The program generates absorption cross sections in the respective spectral range for pressures from 20 to 400 kPa in increments of 20 kPa and temperatures from 250 to 1000 K in 5 K steps. The simulated resolution of the absorption cross sections is 0.01 cm^{-1} for 20–280 kPa and 0.1 cm^{-1} from 300 kPa and the frequency ranged from 2500 to $3500 \,\mathrm{cm}^{-1}$. Note that the transmittance $\tau(\nu) = I(\nu)/I_0(\nu)$ in Eq. (1) is a function of frequency, whereas the detection system measures only integral broadband transmittance values τ . Consequently, we integrate Eq. (1) over the simulated spectral range, considering the transmittance of the system τ_{sys} comprised of filter transmittance, detector sensitivity, fibre transmittance and the emission spectrum of the QTH lamp:

$$\tau = \frac{\int e^{-\sigma(\nu, p, T) \times \rho(p, T) \times L} \times \tau_{\text{sys}} \, \mathrm{d}\nu}{\int \tau_{\text{sys}} \, \mathrm{d}\nu}.$$
 (2)

Here, the system transmittance is defined as multiplication of filter transmittance $\tau_{\text{filter}}(\nu)$, detector sensitivity $S_{\text{detector}}(\nu)$, fibre transmittance $\tau_{\text{fibre}}(\nu)$ and lamp intensity $I_{\text{QTH}}(\nu)$.

$$\tau_{\rm sys}(\nu) = \tau_{\rm filter}(\nu) \times S_{\rm detector}(\nu) \times \tau_{\rm fibre}(\nu) \times I_{\rm QTH}(\nu)$$
(3)

The black line in Fig. 5 shows a transmittance spectrum of the methane v_3 absorption band from 2600 to 3300 cm⁻¹



Figure 5. Principle of broadband transmittance measurements for a CH_4 spectrum: the grey area corresponds to the voltage output of the detector.

measured with a FTIR spectrometer (Bruker Vector 33) in a pressure cell filled with 0.2 % CH₄ at 500 kPa and 298 K. The different peaks in the spectrum correspond to different rotational transitions. Especially in the case of CH₄, pressure and temperature have a severe influence on the spectrum. At constant density, higher pressures lead to broader but lower peaks (pressure broadening), whereas high temperature mainly broadens the whole spectrum. The latter is a result of the occupation of higher rotational quantum states through thermal excitation. As a result, the same CH₄ density can cause different values of τ when pressure and temperature change. This can be taken into account by measuring the pressure and estimating the temperature. Fortunately, the pressure and temperature inside the inlet manifold are rather low and normally do not exhibit strong dynamic changes. They typically range around 20-250 kPa and 280-470 K depending on the location inside the inlet manifold. The highest temperatures are reached closest to the cylinder head where exhaust gas from a previous engine cycle may enter the inlet manifold through an open inlet valve. The determination of fast changing pressure is possible with piezo resistive pressure sensors and available at typical engine test stations. Facing the problem of dynamical temperature changes is subject to current research.

Regarding the quantification of CH_4 densities, Fig. 5 shows an overview of all known optical elements of the detection system with major spectral influence on the broadband transmittance measurements of CH_4 . The figure demonstrates that besides the bandpass filter, detector sensitivity, fibre transmittance and the emission spectrum of the light source need to be considered in the calculations. In addition, the transmittance spectrum of the quartz windows of the flow channel, which are passed four times by the light beam before reaching the detector, have to be included in the system transmittance as well. The resulting system transmittance is shown as a purple curve in Fig. 5 and the effectively measured spectrum (orange curve) is the multiplication of the spectral transmittance of CH_4 by the system transmittance. The detector's voltage output is proportional to the grey area under the curve corresponding to the numerator of Eq. (2). The area decreases with increasing CH_4 density at constant temperature and pressure. Previous publications only considered the influence of the filter in the calculations (Grosch et al., 2011). We find that inclusion of the detector sensitivity, the light source emission, the fibre transmittance and, in the case of flow channel experiments, the quartz window transmittance, significantly improves the quantitative agreement with the experimental data.

We use Eq. (2) to build a database of expected broadband transmittance values as a function of pressure, temperature and mole fraction $x_{\rm m}$ of CH₄. The CH₄ density $\rho(p, T)$ for a given pressure p and temperature T results from the ideal gas law.

$$\rho(p,T) = x_{\rm m} \frac{p}{RT} \tag{4}$$

This constructed database works as a three-dimensional look-up table and allows us to connect the measured integrated transmittance signal to a corresponding CH_4 density with pressure and temperature as additional input parameters. Since the grid of the look-up table is still rather coarse, we use the built-in scattered interpolant function of MAT-LAB from MathWorks to perform a trilinear interpolation based on a triangulation algorithm. This allows us to obtain the CH_4 density for any combination of the three input parameters within the range of the look-up table.

To calculate λ -values at every measurement point, we need to set the density of air in relation to the density of CH₄ and calculate the ratio to the stoichiometric value for ideal combustion. The total gas density $\rho_{tot}(pT)$ can be calculated by the ideal gas law employing measured pressure and temperature. Subtracting the measured CH₄ density ρ_{CH_4} yields the density of ambient air, and thus the λ -value is

$$\lambda = \frac{\rho_{\text{tot}} - \rho_{\text{CH}_4}}{9.52 \times \rho_{\text{CH}_4}}.$$
(5)

In applications, it is possible that the available light intensity changes over time or even during a single measurement due to impurities (e.g. oil droplets), intensity fluctuations of the light source, beam steering or vibrations. Since these effects do not depend on the radiation frequency, we use the signal from the filter marked as " CO_2+H_2O " in Fig. 2 as an offline reference to correct signal variations that are not due to a changing absorber density. Note that we can only apply this correction if the amount of CO_2 and H_2O in the ambient air remains constant during a single measurement within the resolution of the detection. This assumption should be fulfilled very well under our conditions since we draw ambient air from the laboratory environment for only a few seconds.

For the validation experiments performed with an SI engine, the correction is straightforward, because all gas in the inlet manifold is taken from premixed CH_4-N_2 gas bottles.

Figure 6. Integrated transmittance values as calculated from FTIR

measurements of 9.5 % CH₄ in N₂ compared to calculations using

We validate our calculations by comparison to experimental CH₄ spectra acquired in a pressure cell by a FTIR spectrometer (Bruker Vector 33). The cell was subsequently filled up to different pressures at room temperature with a CH₄–N₂ mixture equal to $\lambda = 1$, where N₂ is used as an IR inactive buffer gas to reach the desired pressure conditions. After acquisition of the spectra, we calculated broadband transmittance values using the same system transmittance as for the look-up table described in Eqs. (2) and (3). From the lookup table, we calculated the expected broadband transmittance values with temperature, pressure and the respective CH₄ density as input parameters. The comparison of measurement to calculations in Fig. 6 shows a very good agreement with a maximum absolute deviation of ~ 1.3 % in the transmittance value at the highest measured density.

3 Results and discussion

3.1 Flow channel

the HITRAN database.

Figure 7 shows the results of the calibration measurements performed with defined CH₄-air mixtures prepared in the mixing module. In general, the time dependent signal intensities indicated a good homogeneity. The peak-to-peak fluctuation during a measurement was less than 0.6 and 2.2 % of the detection signal for ambient air and CH₄-air mixtures in the worst case. Averaging the signal over the acquisition time, the standard deviation corresponds to 0.27 % of the detection signal. The red curve in Fig. 7 shows a comparison of the experimental results to a calculation based on the model described in Sect. 2.5. The green curve in Fig. 7 shows that





Figure 7. Results of the calibration measurement (black dots) as well as calculated (green: only filter; red: all spectral influences) and calibrated values (blue). The inset shows in a line-of-sight-geometry measured transmittance values for different air flows.

including only the filter in transmittance calculations leads to significantly larger deviations from the measurements. Since the quartz windows of the flow channel have a spectral influence as shown in Fig. 5, their transmittance spectrum was added as a factor to the system transmittance in Eq. (3). As a result of this additional spectral influence, the flow channel experiments require a separate calibration compared to engine measurements with the prototype sensor probe. The calculated curve in Fig. 7 shows the same behaviour as the measured data and the relative deviation is at the maximum ~ 1.1 % with a mean relative deviation of 0.5 % (see Fig. 8). Relative deviation is defined here as the absolute value of 1 minus the ratio of calculated to measured value. However, we found that even small errors in the calculated transmittance values can have a strong impact on the quantification, especially at high λ-values corresponding to low CH₄ concentrations. Therefore, we apply an empirical calibration procedure successfully used in previous work (Grosch et al., 2011). We note that differences between calculations and measurements may result from errors determining the exact absorption path length or unknown spectral influence of the different optical elements, e.g. frequency dependent fibre coupling. All these influences are assumed to be considerably weak compared to the ones considered, but can still sum up and explain the deviations between calculation and experiment. Furthermore, we cannot exclude errors resulting from the HITRAN simulations as suggested by the small deviations observed in comparison to FTIR data (Fig. 6). In addition to possible errors in the quantification model, the λ -uncertainty at high λ -values increases because the MFC reaches its lower flow limit, which could explain the increasing difference between measurement and calculation. The inset of Fig. 7 shows further measurements with defined λ -values for different flow



Figure 8. Relative deviation of calculated to measured transmittance values before (black squares) and after (red dots) calibration. Inset: relation between measured and calculated broadband transmittances for several methane densities in flow channel experiments. The green line illustrates the behaviour for perfect agreement.

velocities inside the flow channel. These were done using an optical set-up in line-of-sight geometry where the light beam is directly coupled into the detection fibre on the opposite side of the channel. Consequently, the light passes the detection region only once, resulting in a shorter absorption path and explaining higher transmittance values compared to the calibration measurements. The data demonstrate that there is no influence of flow velocity on measured transmittance.

We find that the agreement between experimental and calculated data can be further improved by an empirical calculation. In our calibration procedure, we plot measured over calculated transmittance for all densities of the calibration experiment. The inset of Fig. 8 shows the plot and the linear relation between measured and calculated values as well as the expectation for perfect agreement (green line). A slight deviation from the linear fit occurs at high transmittance values, but overall the linear fit matches the data well. The fit yields a linear function linking measured transmittance τ_{meas} to calculated transmittance τ_{calc} :

$$\tau_{\rm meas} = 0.9441 \times \tau_{\rm calc} + 0.0458. \tag{6}$$

The blue curve in Fig. 7 shows that the calibrated calculations match the measured data better than the uncalibrated ones. This results in a lower relative deviation below 0.5% (red circles in Fig. 8). The average deviation is 0.18%, demonstrating the working function of the calibration procedure.

The next step is the quantification under dynamic conditions, i.e. of a pulsed injection into the flow channel. The upper panel of Fig. 9 displays the different behaviour of the measured transmittance signal for different flow velocities.



Figure 9. (a) Broadband transmittance values for a CH_4 injection into the flow channel for different flow velocities. (b) Data analysis results of the injection measurements. The inset shows a zoom into the injection from 200 to 250 ms.

Independent of the flow velocity, the transmittance drops sharply directly after the injection at 200 ms followed by a flow velocity dependent increase in transmittance due to removal of CH₄ from the detection region. The curves in Fig. 9 show clearly that the latter process becomes slower at lower flow velocities. At the slowest flow speeds (black–red curve), a small amount of CH₄ remains in the measurement volume at the end of the recording cycle, causing a transmittance <1. The signal reaches 1 (no CH₄) just before the next injection. In conclusion, only tiny amounts of CH₄ (~ 0.05 %) stay at the measurement position until the next injection. This holds only for slow airflows. Higher flows remove all CH₄ in less than 100 ms (green–blue curve in Fig. 9).

We showed in the previous section that a broadband transmittance value can be directly related to a CH₄ density or a λ -value of the CH₄-air mixture using calculations based on the HITRAN database and a calibration function. We limit the quantification of the λ -value to a maximum of $\lambda = 10$ (~1% CH₄-air), which corresponds to a transmittance of ~ 0.96 at ambient conditions with this optical set-up. Although the sensor is able to resolve higher transmittances this upper limit suits typical engine applications, because higher λ -values are barely of any interest. The results in the lower panel of Fig. 9 showing a different behaviour compared to the transmittance values due to the upper limit for λ and its definition. The differences between high and low flow velocity are more pronounced. At highest velocity the injection appears only as a narrow 12 ms wide peak. For slow velocities of 0.66 and 1.1 m s^{-1} , the peak width is 320 and 200 ms, respectively. The initial drop reaches down to a λ -value around $\lambda = 0.5 ~(\sim 17.4 \text{ vol }\% \text{ CH}_4)$ independent of flow velocity.

In summary, we have shown that the detection system as well as the HITRAN-based analysis model is capable of



Figure 10. Linear relation between measured and calculated transmittance from pressure cell experiments. The green line indicates perfect agreement.

quantifying CH₄ densities in gas flows under highly dynamic conditions with high accuracy and precision. The achieved accuracy in the λ -value is on average better than 0.5 %. The acquired data suggest that the detection principle might also be applicable to the inlet manifold of an engine, where conditions are more complex and quantification can be difficult.

3.2 Engine experiments

After successful application and validation of the general optical layout of a sensor probe in an idealized flow channel environment, we proceed to the application of the measurement principle at the inlet manifold of an SI engine. For this purpose, we constructed a prototype sensor probe that allows stable attachment to an SI engine.

The first step before conducting engine experiments is the calibration of the HITRAN-based look-up table, which differs from the one used in the flow channel experiments since the prototype probe assembly does not include any quartz windows. The results of the calibration measurements are shown in Fig. 10. Again, we plot measured versus calculated transmittance values and find a linear relation between calculations and measurement, consistent with our previous observation. Since in a combustion chamber typical temperatures are higher than in our pressure cell experiments, we validated that the calibration is independent of temperature (see Fig. 10 and caption). Further experiments with quantification of CH₄ densities inside the combustion chamber are subject to current research and will be considered in future publications. We apply a linear fit to obtain a calibration function in the form of Eq. (5). Here we consider only the part of the results in the transmittance range important in engine inlet manifolds. The linear fit gives a different result of $\tau_{\text{meas}} = 1.03489 \times \tau_{\text{calc}} - 0.03654$ compared to the calibra-



Figure 11. Normalized raw signal of CH_4 and CO_2+H_2O detection channels for background measurement with ambient air (**b**) and measurement with premixed gas as well as the corrected CH_4 signal (**a**). The intensity fluctuations are likely caused by engine vibrations. Due to the similarities between CH_4 and CO_2+H_2O signals in the background measurement, the latter is used as a reference for signal correction.

tion at the flow channel and caused by the absence of quartz windows. It is interesting to note here that the calibration seems to be independent of temperature. The results for 300 and 473 K overlap considering the error bars of the individual data points. Therefore, we can apply a single calibration that is valid for the complete temperature range of interest.

Normalized raw signals of the detector voltage from the engine validation experiments for background (ambient air) and actual (CH₄-N₂ mixture) measurement of CH₄ and CO₂+H₂O channels are shown in Fig. 11. The intensity fluctuations are quite similar for both channels and we do not observe any significant absorption features in the CO₂+H₂O channel. Consequently, the CO₂+H₂O channel can serve as an offline reference for correction of the I_0 signal of the broadband transmittance. The I_0 signal without CH₄ in the absorption region corresponds to the average signal of the CH₄ channel in a background measurement with ambient air. Small signal variations between two measurements, e.g. due to variations in light intensity, are taken into account by comparing the signal of the CO₂+H₂O in background and actual measurement and determining a correction factor. Accordingly, the I_0 signal of the CH₄ channel results from the average detector signal in the background measurement multiplied by the correction factor. The curves in Fig. 11 illustrate that both signals exhibit periodic fluctuations. We account for this modulation by applying a crank angle dependent correction. In detail, we divide the CH₄ signal during the measurement by the transmittance in the CO₂+H₂O channel for each crank angle. Note that the CO_2+H_2O channel can be used as a reference for signal correction, because premixed CH₄–N₂



Figure 12. Measured λ -values for gas mixtures with $\lambda = 1.0$ and $\lambda = 4.06$. The nominal value is depicted as a green line. The different colours indicate six different measurements taken under identical conditions. Here a 1° crank angle at 800 rpm ≈ 0.21 ms.

gas is used and therefore CO_2 and H_2O are absent and do not influence the signal. In the case of fired engine operation and EGR entering the inlet manifold, an additional detection channel that is neither sensitive to CH_4 nor to exhaust gas is required.

The crank angle resolved results for predefined $\lambda = 4.06$ and $\lambda = 1$ mixtures are shown in Fig. 12. The green line indicates the nominal value of the premixed gas used. For both measurement series, we find small periodic and reproducible fluctuations which likely result from engine vibrations influencing the optical system of the probe. It was not possible to completely eliminate these fluctuations through the signal correction procedure. We speculate that the fluctuations influence the coupling of light into the detection fibre that might result in wavelength dependent signal variations. A reference channel at a different wavelength cannot correct such wavelength dependent fluctuations. However, the fluctuations are rather small, with 0.3 % (0.4 %) in λ -values for $\lambda = 1.0$ (4.06) for the range $-90-360^{\circ}$ CA.

The temperature was assumed to stay constant during each engine cycle and set to the reading of the nearby thermocouple. However, the quick drop in the pressure curve resulting from the opening of the inlet valve at -320° CA (Fig. 13, upper panel) suggests that the temperature decreases as well within the estimation of an adiabatic expansion. The pressure drop results from the fact that the gas supply to the engine is not high enough during the intake stroke to maintain constant pressure in the inlet manifold. In conclusion, the drop in the measured λ -values is likely to be an artefact specific to the experimental conditions and originates from a wrong temperature input to the model. Based on our calculations, a temperature drop of ~ 20 K is already sufficient to explain the drop in the λ -value. While the determination of the CH₄



Figure 13. (a) Measured pressure for all six measurements with $\lambda = 1$. The different colours indicate six different measurements taken under identical conditions. The inlet valve opens at -320° CA and closes at -124° CA. (b) Example of a typical pressure curve for the presented injection measurements at the four-cylinder engine test station. The pressure fluctuations are much smaller compared to validation experiments.

density from the measured transmittance is only weakly dependent on temperature, a wrong temperature induces a significant error in the calculation of the total gas density, which is required for calculation of the air–fuel ratio.

To estimate the precision of the measurements, we calculated the average measured λ -value and its 95% confidence interval over all data points to be $\lambda = 3.96 \pm 0.1$ and $\lambda = 0.985 \pm 0.016$, giving a precision of ~3 and ~2%, respectively. The accuracy can be estimated by calculating the absolute value of the deviation to the nominal λ -value of the premixed gas for every data point and averaging the results. This gives an accuracy of ~2.5 and ~1.6% for the $\lambda = 4.06$ and $\lambda = 1.0$ mixture, respectively. If we exclude the region at which we observe the drop in λ -value, which likely occurs from a temperature drop characteristic of the experimental conditions, accuracy and precision improve even further. For the range from -90 to 360° CA, we achieve a precision of $\lambda = 0.994 \pm 0.015$ (4.01 \pm 0.1) and accuracy of 0.8% (1.4%) for $\lambda = 1.0$ (4.06).

The red curve of the $\lambda = 4.06$ mixture in Fig. 12 is an exception and lies a few percent under the other measurements over the complete engine cycle. This variation is due to the high transmittance values around 95% in these measurements and their sensitivity to variations of the background signal. The intensity of the light source and emission spectrum varies over time due to small temperature fluctuations of the QTH lamp. This affects the calculation of broadband transmittance values from the recorded voltage signals. Thus, the real background signal in the actual measurement can differ from the recorded background signal if there is too



Figure 14. Normalized raw signal of CH₄ and exhaust detection channel for background and injection measurements. We find periodic intensity fluctuations overlaying the detector signal likely caused by engine vibrations. The fluctuations are different for motored (**b**) and fired (**a**) engine operations. Here a 1° crank angle at 1000 rpm ≈ 0.17 ms.

much time (e.g. a few minutes) between measurements. It is not possible to compensate for the difference completely through other detection channels. We found that a very small change of 0.15 % in the averaged background signal would be enough to put the red curve in Fig. 12 level with the other curves. This sensitivity in the background signal is a specific challenge of the validation experiments with premixed gases. Note that this likely is also a reason why there are remaining fluctuations after signal correction as mentioned above. In measurements with injection of CH₄ into the inlet manifold, the I_0 signal can be directly extracted in every single engine cycle at regions without CH₄ present, e.g. between closing of the inlet valves and the start of the next injection.

We have to note here that the prototype probe suffers from internal reflections of the output window that produces an additional signal on the detectors (up to $\sim 25 \%$ of the overall signal). Through adjustment of the optics this could be reduced to $\sim 10 \%$ of the overall signal. We overcome this problem by measuring the dark signal without a reflector and subtracting it from the signal during the measurements. However, we find that there are signal variations, which influence the strength of the internal reflections, e.g. depending on the adjustment of the probe. This effect might lead to a deviation in the transmittance values for single measurements resulting in a different quantification outcome. Consequently, there is still some uncertainty of the dark signal, and this matter will be addressed in an improved second-generation prototype probe.

For the injection measurements, the modifications to the inlet manifold shown in Fig. 4 were removed, i.e. the external gas supply and cover plate separating the respective cylinder,



Figure 15. (a) Measurement results for different injection durations. (b) Measurement results for different injection starting times. Here a 1° crank angle at 1000 rpm ≈ 0.17 ms.

to enable regular engine operation. The result is a different pressure curve as shown in the lower panel of Fig. 13, because all four cylinders of the engine are now connected to each other. There are variations in pressure ($\sim 3\%$), but they are about 10 times smaller than in the validation measurements ($\sim 30\%$) and do not include a distinct drop. In conclusion, we do not expect a significant temperature drop and thus no artificial effect on the result of the data analysis.

However, we find significantly stronger modulations on the raw signals of the detection channels (Fig. 14) than before. These modulations likely result from engine vibrations and influences between all four cylinders now connected through the inlet manifold. Figure 14 shows the normalized signal of CO₂+H₂O and CH₄ channels for a measurement with injection (upper panel) and without injection (background, lower panel). Both detection channels suffer from the same harmonic variations having the same frequency but slightly different amplitudes. However, there is a phase shift between background and injection measurement indicated by the dashed blue lines. This shift is probably caused by the difference between motored and fired operation, supporting our hypothesis that the signal fluctuations result from engine vibrations. For the data analysis, we use the normalized CO₂+H₂O signal as mentioned earlier to correct the CH₄ channel signal for these fluctuations. Here, we assume that during the short time of a single measurement the amount of CO_2 and H_2O in the ambient air is constant. Thus, we can use this channel for signal correction.

After ensuring a good repeatability of the engine operation through repetition of measurements, we performed measurements with varying engine parameters. Instead of the λ value, we show here the mole fraction, since otherwise observations in regions with small amounts of CH₄ are hardly visible. The upper panel of Fig. 15 shows the results for different injection times. The injection starts at -360° CA and a cloud of CH₄ passes through the absorption path of the probe soon afterwards (detection is located 5 cm downstream from injection). The differences between the injection times are rather small because they correspond to flammable mixtures ($\lambda = 0.96$, 1.0 and 1.1) and a smooth engine operation. Still, the differences are clearly visible in the inset of Fig. 15.

Finally, we changed the start of injection as shown in the lower panel of Fig. 15 while operating the engine under stoichiometric conditions. The different injections naturally result in different times the methane cloud passes the absorption path. For the delay of the injection start to -320° CA, which corresponds to the nominal opening of the inlet valve, a change in the shape of the cloud is also visible. This suggests some influence on the mixture formation in the inlet manifold, although the differences are rather small. This and the fact that a kind of methane cloud is visible in the measurements indicates that the mixture process in the inlet manifold in this particular example is comparatively weak.

4 Conclusion and outlook

We presented the development of an optical sensor system for time-resolved quantification of CH₄ densities in gas flows based on non-dispersive IR absorption spectroscopy. The system defines a platform for mixture formation analysis in modern CNG-fuelled SI engines and serves as a diagnostic tool for development of combustion engines. The design of the optical set-up enables diagnostic measurements at the inlet manifold of a test station engine. Time-resolved broadband transmittance measurements of CH4 inside a flow channel, which serves as a model for an inlet manifold, showed that the time resolution is high enough to examine the behaviour of a typical 7 ms injection. Simulations of expected broadband transmittance values using the HITRAN database show very good quantitative agreement with the experimental data, with a maximum relative deviation of 1.1 %. Application of an empirical calibration further improves the agreement. The procedure allows for an accurate quantification of the λ -value during injection. It is important to note that the relation of detector signal and CH₄ density depends on the environmental conditions. This is in contrast to previous applications in gasoline engines and makes CH₄ quantification more challenging. Therefore, the knowledge of pressure and temperature is crucial in order to achieve the maximum measurement accuracy.

As a further step, a prototype probe for measurements at the inlet manifold of an SI engine was tested. A modified engine inlet allowed validation measurements with premixed gas mixtures to ensure high accuracy. Using premixed gas, we confirmed that the measurement accuracy is < 3% on average regarding the deviation from the nominal value. Nevertheless, the prototype suffers from problems concerning internal reflections and vibrations. Some of them seem to depend on the engine operation conditions. Most fluctuations caused by engine vibrations can be corrected for using the signal from another detection channel as a reference. In engine applications, the constant temperature assumption is another source of error, especially if fast temperature changes caused by fast pressure changes or exhaust gases entering the inlet manifold occur. In summary, we have shown a functioning prototype of an inlet manifold probe for mixture analysis in CNG engines, which is able to determine crank angle resolved fuel-air ratios with an accuracy of < 3%. We note that despite only showing averaged results over several engine cycles, the system is capable of delivering diagnostic data on a single cycle basis. Future research will address the improvement of the prototype probe, the proper consideration of temperature effects in the data analysis as well as the detection and quantification of exhaust gases that might enter the inlet manifold from the combustion chamber or from external EGR.

We emphasize that the sensor system presented here is not limited to applications in automotive development. The basic concept is capable of measuring CH₄ densities in any flows with high accuracy, precision and time resolution. Moreover, a change in the bandpass filter enables the quantification of other IR-active molecular species like CO₂, CO, H₂O, NH₃ and NO_x, especially if they are part of the HI-TRAN database. Adjustment and validation of the quantification method would be required accordingly as well as characterization of spectral influences from optical components.

Data availability. The experiments and results shown in this publication are strongly industry-related research. We explain our experimental preparations and analysis steps in great detail in this work and are available for questions. Please understand that therefore we do not publicly provide the underlying data and Matlab code used for analysis. Given individual requests by fellow researchers, we will of course consider making parts of the data available.

Competing interests. The authors declare that they have no conflict of interest.

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