



High-precision ethanol measurement by mid-IR laser absorption spectroscopy for metrological applications

OLEG ASEEV,¹ BÉLA TUZSON,^{1,*} HERBERT LOOSER,¹ PHILIPP SCHEIDEGGER,¹ CHANG LIU,¹ CARINA MORSTEIN,² BERNHARD NIEDERHAUSER,² AND LUKAS EMMENEGGER¹

¹*Empa, Laboratory for Air Pollution and Environmental Technology, Überlandstrasse 129, 8600 Dübendorf, Switzerland*

²*METAS, Lindenweg 50, 3003 Bern-Wabern, Switzerland*

**bela.tuzson@empa.ch*

Abstract: We report on the development and validation of a compact laser instrument using mid-IR direct absorption spectroscopy (DAS) for high-precision measurements of ethanol in breath-like air mixtures. Leveraging the intermittent continuous wave (iCW) driving for conventional narrow-band distributed feedback (DFB) quantum cascade laser (QCL) emitting around 9.3 μm and using a 25 m path length multiple-pass absorption cell at reduced pressure, a precision of 9 ppb (amount fraction, nmol mol^{-1}) at 60 s integration time is achieved even in the presence of 5% of H_2O and CO_2 . Thus, the instrument is well suitable for metrological studies to investigate observed, but yet unquantified, discrepancies between different breath alcohol reference-generation methods. The approach can be generalized and applied for other organic molecules in a wide range of applications.

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1. Introduction

In many countries, alcohol breath analyzers are approved as evidential measurement devices to prosecute driving under the influence of alcohol [1]. Handheld analyzers used by the authorities must undergo type approval, conformity assessment, and annual verification. Currently, the metrological requirements for analyzer performance are based on the International Organization of Legal Metrology (OIML) specifications [2]. For calibration, there are two kinds of measurement standards in use [3]: i) dry ethanol-air mixtures in pressurized gas cylinders that are certified and made directly traceable to primary gravimetrically prepared standards [4], and ii) dynamic systems for ethanol-air-water vapor mixture generation based on Henry's Law, where air is passed through a water-ethanol solution at a given temperature [5].

Dry standards are controversial because they lack water vapor, which is a critical parameter in breath-alcohol measurements. Therefore, dynamic calibration standards, produced by the saturation method in so-called wet bath simulators, are usually preferred. Calibration gases produced in this way depend only on the temperature and the alcohol concentration of the liquid phase. The gas phase concentration is generally calculated using the Dubowski equation [5]. Critical points in the use of the wet bath simulator are the liquid temperature stability, the lack of traceability evidence on the outlet gas, and the uncertainty of the Henry coefficients used for the formulation of the Dubowski equation [6–9]. In fact, traceability and accuracy are ensured only by assuming a conventional value, fixed in OIML R 126 Recommendation for these coefficients [2]. Whilst this approach is generally accepted, it is metrologically highly unsatisfactory.

Recently, alternative methods were proposed based on diffusion and injection for generating a test gas for breath alcohol measurements to possibly replace the saturation

method using the wet bath simulator [7,10]. Their advantages over the saturation method are the faster response time and better operation stability. Following the injection principle, a traceable generator for wet breath-alcohol was built at METAS (Switzerland) [11]. Preliminary results indicate a disagreement between the saturation and dynamic-gravimetric methods of up to 2% based on measurements using a flame-ionization-detector (FID) as comparator. From the point of view of road safety or medical care, a 2% disagreement in reference systems for the measurement of breath alcohol may appear as a minor issue. However, if we consider legal metrology requirements for evidential breath analyzers, i.e. the maximum permissible error of 5%, as defined by the OIML Recommendation, a 2% relative disagreement is highly significant during type approval and initial verification. It is very laborious and costly for instrument manufacturers to adapt for non-concordant reference systems in different countries. Furthermore, for individuals, a 2% difference in measurement results may have crucial impacts in the context of fines or driving license withdrawals with severe consequences especially for professional drivers. Therefore, it is vital to further constrain the observed disagreement. Currently, none of the commercially available measurement systems has the required precision and selectivity for such metrological investigations. Thus, breath alcohol analysis, the worldwide most frequent forensic test, lacks convincing means in terms of SI traceability; a situation that one should consider urgent.

To address this issue, we propose laser absorption spectroscopy (LAS) as a long established, sensitive, selective, and transparent approach [12], which has also been successfully applied as absolute method in metrology [13]. With the development of mid-IR semiconductor laser sources, such as quantum cascade lasers (QCL) or interband cascade lasers (ICL), it became possible to take full advantage of the strongest, fundamental absorption features of most molecules in compact and field-deployable setups [14]. Further benefits of LAS are the inherent high temporal resolution (< 1 s), and the possibility of in situ and real time measurements without the need for sample treatment or preparation procedures. Compared to non-dispersive infrared (NDIR) technology, which is used in commercial ethanol analyzers, there are several advantages of using laser sources. The coherent radiation of a laser source allows for extended optical path lengths up to 10^4 meters, realized by employing either multipass cell or optical cavity, which increases the absorption signal and thus the sensitivity, according to Lambert-Beer's law. Additionally, the signal-to-noise ratio (SNR) is improved compared to conventional IR light sources, due to the much brighter IR radiation of the laser sources. Furthermore, the narrow bandwidth laser emission can be rapidly scanned through individual ro-vibrational lines at rates of kHz, leading to highly selective and sensitive measurements of the absorbing species, especially at reduced sample pressure [15].

While mid-IR LAS has been very successful in many applications targeting small inorganic compounds, its application becomes more challenging for larger molecules, which exhibit broader and congested absorption features requiring wide spectral coverage. Although, this paradigm generally applies, we demonstrate that the narrow spectral coverage of a distributed feedback (DFB)-QCL may deliver enough spectral information to measure gas mixtures containing organic molecules. To be applicable, it is however necessary that there is sufficient fine-structure in the absorption feature of the target compound, and that the maximum tuning range of the DFB-QCL is fully exploited, e.g. by intermittent continuous wave (iCW) operation to extend its spectral coverage, as recently proposed by Fischer et al [16]. A similar approach was used earlier by Kosterev et al [17], but only for pure ethanol and reaching a detection limit of 125 ppb, which is more than one order of magnitude higher than required for our target application.

The objective of this work was to develop and validate a metrological breath-alcohol laser spectrometer based on the direct absorption technique for metrological applications. We show that ethanol represents an excellent target compound to be examined by iCW-driven QCL absorption spectroscopy (iCW-QCLAS). The high analytical precision of the instrument

allows investigating small differences between the saturation method according to Dubowski and a SI-traceable method. Furthermore, a compact instrumentation could be used as transfer-standard in international inter-comparisons and represents an important alternative to existing approaches, involving “black-box” commercial analyzers or gas-mixtures in bottles. Moreover, the use of our approach for ethanol analysis can be generalized and applied for other organic molecules in a wide range of applications.

2. Experimental

2.1 Spectral range selection

Like all alcohols, ethanol (C_2H_5OH) has characteristic infrared bands due to O–H and C–O stretching. The very broad O–H stretching band is centered at 3400 cm^{-1} , while the C–O stretching produces a strong band in the 1065 cm^{-1} region. These two options are also intensively exploited in commercial breath analyzers based on NDIR [18]. Using the latter region significantly improves selectivity and specificity for ethanol in a breath-like gas matrix containing 5% CO_2 and saturated water vapor at 34°C . Furthermore, using reduced gas pressure for the measurements allows the instrument to be operated at room temperature without the risk of condensation. A pressure of 100 hPa was found to be a good compromise between the intensity of the absorption signal and the broadening of the spectral features. For best performance in terms of selectivity, it is, however, important to account for the other species present in the gas mixture and investigate potential spectral interferences. Figure 1(a) shows the simulated transmission spectrum of 25 ppm (amount fraction, $\mu\text{mol mol}^{-1}$) ethanol, corresponding to the lowest concentration used in standard mixtures, in the $600\text{--}4500\text{ cm}^{-1}$ region in a breath like gas matrix at room temperature, reduced pressure of 100 hPa, and for an absorption path length of 25 m. The ethanol data were taken from the Pacific Northwest National Laboratory (PNNL) IR database (<http://nwir.pnl.gov>) [19] and adjusted according to our experimental conditions. Thereby, we also converted the decadic units of absorbance normalized at 296 K into transmittance, using the following equation:

$$T(\nu, T_{296}) = 10^{-A(\nu, T_{296}) C L \frac{P}{1\text{ atm}}} \quad (1)$$

where $T(\nu, T_{296})$ is the transmittance at wavenumber ν (cm^{-1}) and room temperature (296 K), $A(\nu, T_{296})$ is the absorbance from the PNNL database ($\text{ppm}^{-1}\text{ m}^{-1}$), while C (ppm), L (m), and P (atm) are the ethanol mixing ratio, absorption path length, and the cell pressure, respectively.

Strictly speaking, Eq. (1) is only correct for single ro-vibrational absorption lines. In the case of ethanol, however, we do not have any information about individual ro-vibrational lines and we treat the whole spectrum by only one pressure independent absorbance $A(\nu, T_{296})$. Nevertheless, as a first approximation this approach is suited to gain information on the expected absorption strengths and to find the optimal spectral range for the spectroscopic measurements. The spectra of CO_2 and H_2O were simulated by using the parameters from the HITRAN spectral database [20] to generate the high resolution absorption line profiles.

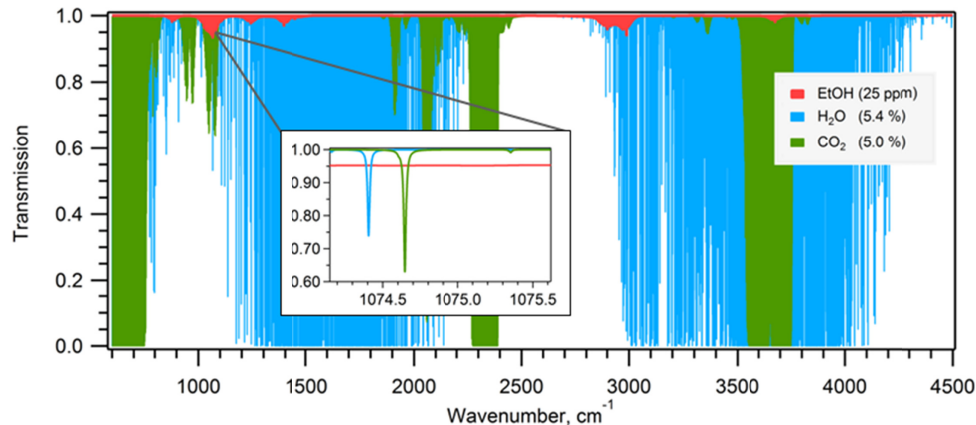


Fig. 1. Simulated mid-IR transmission spectra of 25 ppm ethanol, 5.4% water, and 5.0% CO_2 at gas pressure of 100 hPa, room temperature, and absorption path length of 25 m. The inset shows the spectral window selected for precise measurement of ethanol. The H_2O and CO_2 absorption lines are simulated based on HITRAN database, while ethanol data were taken from the PNNL database and rescaled according to Eq. (1).

In order to identify the most suitable spectral window, an automatized procedure has been implemented. Thereby, total transmission spectra of the three main compounds were simulated in a spectral window of 1.5 cm^{-1} , and then white-noise with a peak-to-peak amplitude of 10^{-3} was added, followed by deconvolution of the noisy spectra into its main components. This procedure was repeated 100 times for every 1.5 cm^{-1} window scanned within the range of $800\text{--}2300 \text{ cm}^{-1}$ with a step of 0.1 cm^{-1} . The standard deviation or uncertainty of the decomposition coefficients was used to judge the precision of the determined concentrations of the compounds at the various regions. As a result, we found the most promising range with the lowest uncertainty for the ethanol concentration determination, which is shown by the inset in Fig. 1. It contains strong lines for both CO_2 and H_2O , while the absorption feature of ethanol spans over the full spectral window. The latter hinders detecting the laser emission intensity I_0 within the tuning range of a DFB-QCL. Therefore, I_0 must be measured before sampling ethanol, which primarily requires a stable laser emission in terms of power and frequency within the time period between measurements of I_0 . Other parameters that potentially can influence the spectral stability were found not to be limiting at this time scale (see Sect. 3.1).

2.2 Instrumental design

The QC laser spectrometer developed for high precision ethanol measurements is shown in Fig. 2. The optical module is mounted on a $0.3 \times 0.6 \text{ m}^2$ breadboard, below which the electronics unit is located. The mid-IR light source is a continuous-wave DFB-QCL (Alpes Lasers SA, Switzerland) emitting around $9.3 \mu\text{m}$. The laser beam is shaped by an AR coated ZnSe lens with a focal length of 12.7 mm mounted on an XYZ translator, and it is coupled into an astigmatic multi-pass cell (MPC) (AMAC-36, Aerodyne Research Inc., USA) with a selected optical path length of 25 m. The beam exiting the cell is focused on a photovoltaic thermoelectrically cooled MCT detector (PVMI-4TE-10.6, Vigo Systems SA, Poland). The optical path and the beam shaping optical elements were optimized using raytracing simulations (FRED, Photon Engineering, USA). A solid Ge etalon with a free spectral range of 0.049 cm^{-1} attached to a motorized mount (not shown in the figure) can be flipped into the laser beam path for laser tuning rate determination. The optical module is covered by a thermo-stabilized enclosure that is actively controlled by a Peltier element to improve the stability of the system. Optionally, purging the optics with dry nitrogen to avoid ambient

water absorption is also possible. An external water chiller (ThermoCube 300, Solid State Cooling Systems, USA) is used to maintain both the laser and the optics module heatsinks at a stable temperature of 19.00 ± 0.05 °C. The sample gas temperature and pressure are monitored by a high-precision NTC-thermistor (10 k Ω , BetaTHERM Sensors, Ireland) and an absolute capacitance manometer (722B, MKS Instruments, Inc., USA), respectively.

The electronics compartment includes a power supply unit, an embedded computer, a temperature controller for the optical module temperature stabilization, the laser driver electronics, and an FPGA-based system-on-chip hardware-control and data acquisition module with a sampling rate of 125 MS/s and 14 bit resolution [21]. The custom-built laser driver is based on the concept of intermittent continuous wave (iCW) scanning. As demonstrated recently, this driver eliminates the need for any external electronics (e.g., function generator or DAQ) for current modulation, while maintaining a high modulation capability (up to 20 kHz), and considerably lowers the demands on power supply performance. This is due to the fact that using the iCW driving it is possible to completely decouple the driver from the external power supply during laser operation. The laser current is solely provided by the charge stored in capacitors and also results in heat dissipation of less than 1 W for driving QC lasers. In addition, the current noise characteristic of this laser driver was found to be better than 1 nA/Hz^{1/2}. Furthermore, the driver is fully configurable in terms of pulse width, duty-cycle and current amplitude via a GUI. The laser driver current is triggered every 270 μ s at 50% duty cycle, resulting in a full spectral scan at a rate of 3.7 kHz. Under these conditions, the tuning range of the laser covers about 1.7 cm⁻¹. Consecutive individual spectra are averaged on the FPGA and then transferred at 1 Hz to the host-PC for spectral analysis using a custom-written LabVIEW program. The absorption spectrum is fitted in real-time by an absorbance model that is the sum of the individual absorbance templates of the different molecular species. Further details to this approach are given in the next Section.

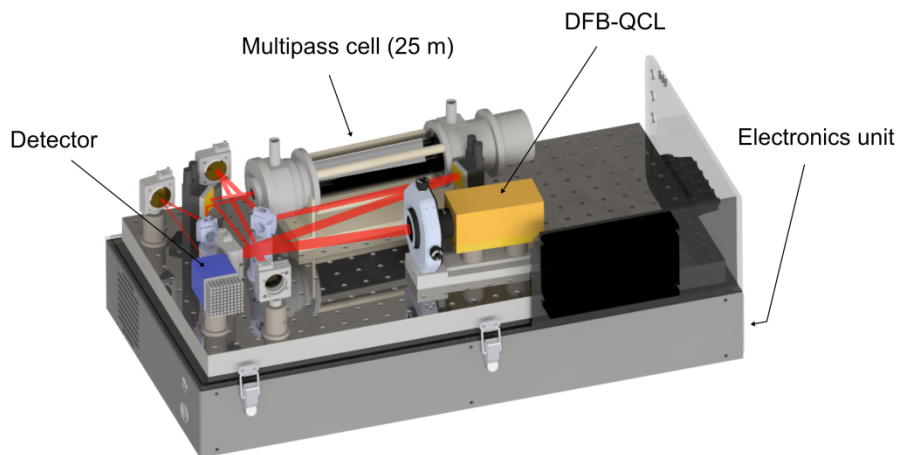


Fig. 2. 3D CAD drawing of the QCLAS for the ethanol measurement (without the cover); the red line represents the path of the IR laser beam. The enclosure beneath the optical bread-board contains the entire electronics hardware. The dimensions of the instrument with the cover are $33 \times 30 \times 63$ cm³.

3. Results and discussion

3.1 High resolution ethanol spectrum

As the instrument operates at reduced sample pressure and has a high spectral resolution, the PNNL spectral data for ethanol cannot be used for fitting purposes. Therefore, we need to generate our own reference spectra from experimental data. This procedure consists of four

steps as depicted in Fig. 3. First, the laser intensity over the tuning range, representing the zero absorption baseline I_0 , is measured by purging the MPC by either dry nitrogen or synthetic air. Then, the etalon transmission spectrum is recorded to convert the time-axis into a linearized wavenumber scale, while a narrow ro-vibrational transition from CO_2 or H_2O is used to achieve absolute wavelength calibration. Finally, ethanol diluted in synthetic air from a certified bottle is used to measure the absorption signal. Being a sticky molecule, it takes a few minutes for the ethanol concentration to reach equilibrium in the cell. Nevertheless, the laser intensity was found sufficiently stable over several tens of minutes to exclude potential drifts that may influence the shape of the spectrum. Furthermore, all measurement steps are performed under the same cell pressure and temperature condition to maintain optimal reproducibility.

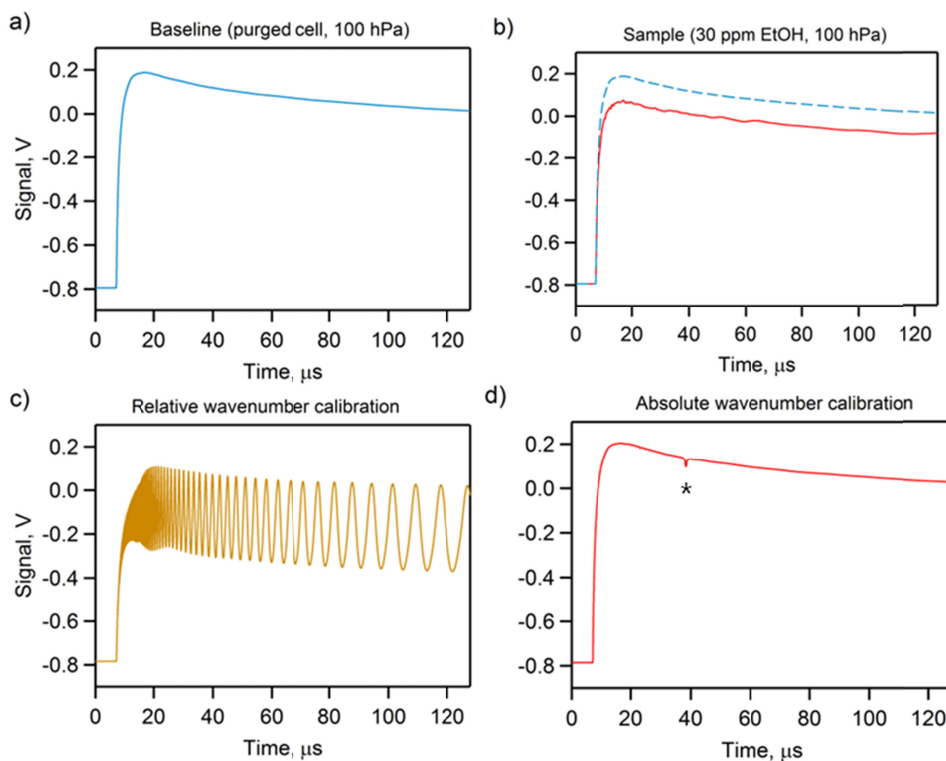


Fig. 3. Generation of high-resolution ethanol reference spectra. The required steps and their corresponding raw signals on the detector are: a) zero absorption baseline, b) transmission signal of the ethanol, c) etalon fringes for the relative laser tuning determination, and d) a ro-vibrational transition of water, indicated by (*), for the absolute wavenumber calibration.

This spectral template is then taken by the fitting procedure that uses the non-linear least-squares Levenberg-Marquardt algorithm (LMA) to minimize the sum of the squared errors between the data points and the template spectrum. This analytical approach is applicable for any arbitrary mixture, assuming a linear combination of reference spectra of the individual absorbing species.

Figure 4 shows the measured transmission spectrum of 100 ppm ethanol in synthetic air (20.5% O_2 mixed with 79.5% N_2 , Messer Schweiz AG, Switzerland) at a pressure of 100 hPa fitted by the reference spectrum. The top graph shows the residual of the fit to the measured data after half an hour of starting the measurement. The template used for the fit was generated one week before the measurement, demonstrating an excellent reproducibility of the system.

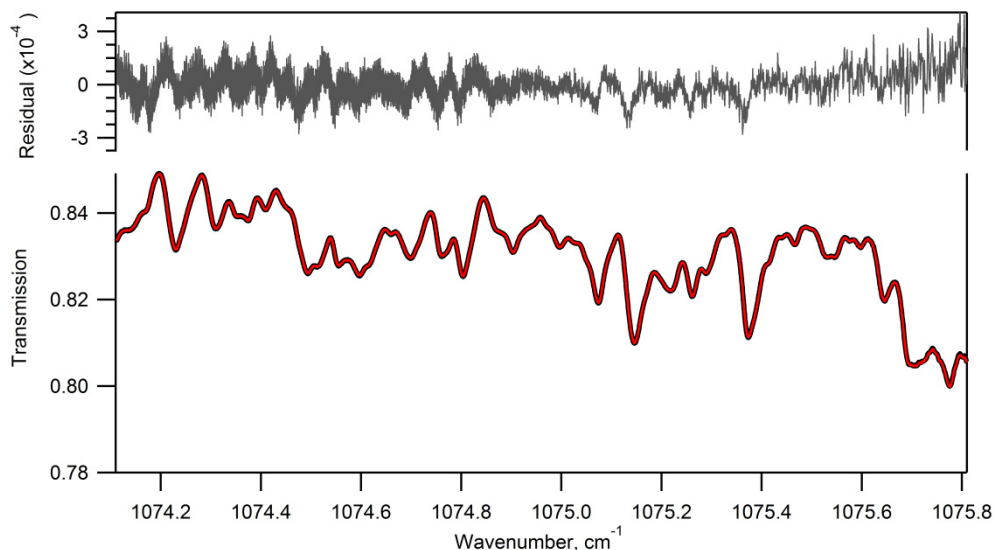


Fig. 4. High-resolution transmission spectrum (black) of 100 ppm ethanol in synthetic air recorded by a DFB-QCL at 100 hPa pressure at room temperature and for 25 m absorption path together with the fitted template (red). The residual shows a very good agreement between measured data and fitting template.

3.2 Performance of the instrument

3.2.1 Precision and stability

To evaluate the long-term performance of the instrument, a constant ethanol concentration of 30 ppm was continuously measured over one hour. The gas sample was prepared by dynamically diluting an ethanol reference gas (225 ppm ethanol, PanGas AG, Switzerland) with synthetic air using mass flow controllers (MFCs Red-y smart series, Vögtlin Instruments GmbH, Switzerland) at a total flow of 800 ml/min. This mixture was continuously flowing through the multipass cell. Figure 5 shows the time series of the measured concentration after equilibration and the associated Allan-Werle deviation plot [22]. The root-mean-square error at 1 s is about 14 ppb and it reaches its minimum of 9 ppb at around 60 s integration time. This corresponds to an absorption noise level of 1.4×10^{-5} that is equivalent with an absorbance noise at unit path length of $5.6 \times 10^{-9} \text{ cm}^{-1}$. The same precision was obtained when up to 5% CO₂ was gradually added to the gas stream. In terms of spectroscopy, similar behavior is expected also for water. However, in practice the analytical precision was limited by the technical difficulty of generating a stable humid air flow (see Section 3.2.3).

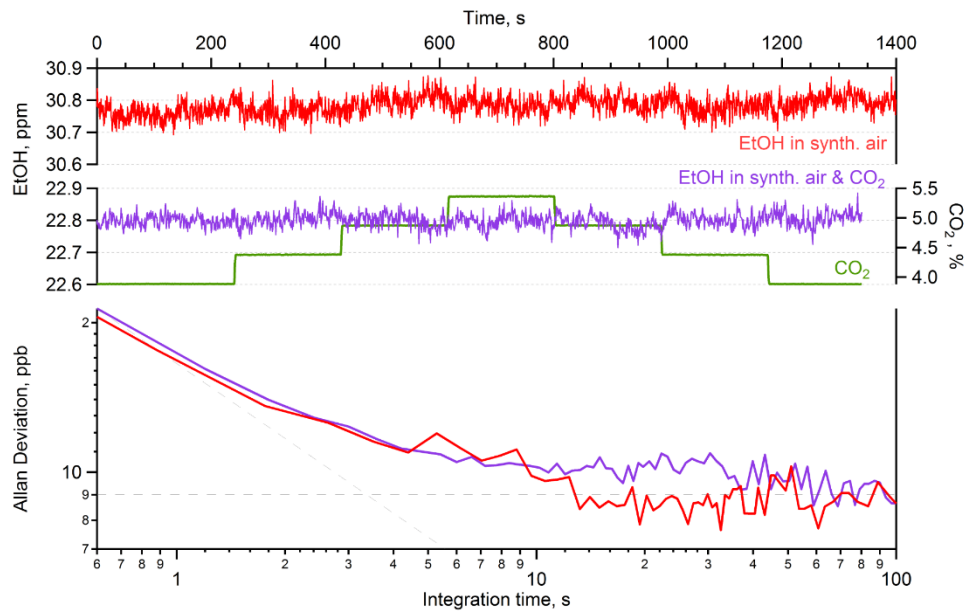


Fig. 5. Time series of ethanol concentration measurement with (purple) and without (red) addition of CO₂ at varying concentration (green) and associated Allan deviation plots.

3.2.2 Linearity

The instrument response to changing ethanol concentration is shown in Fig. 6. The ethanol concentration was changed within the range of 25–225 ppm at steps of 25 ppm by diluting 225 ppm ethanol with synthetic air. The highest concentration in the range corresponds to about 0.8 ‰ blood alcohol content (BAC, in g/kg) [23]. Every subsequent concentration step was measured over 30 s but after 2 min of equilibration time. All measurements were performed by using the same ethanol template recorded for 225 ppm. By fitting a linear regression model, a very tight correlation is obtained, as indicated by the associated residual plot (see Fig. 6).

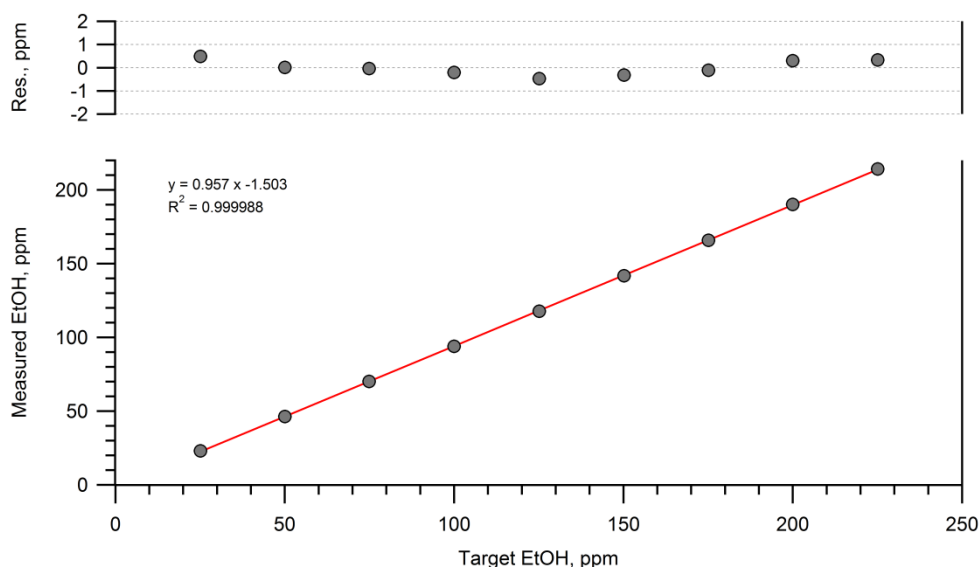


Fig. 6. Measured ethanol concentration as a function of sampled ethanol concentration in the range of interest.

3.2.3 Cross-sensitivities

Laser spectroscopy is well known as a highly selective technique, but measuring accurately a few ppm of ethanol in a gas matrix containing several percent of H_2O remains, however, very challenging, especially if the concentration of these species varies in a large range, e.g. from wet to dry conditions. In order to characterize and quantify potential interfering effects, the instrument was transferred to METAS and a dedicated gas handling setup based on MFCs was realized, which allowed for controlled mixing of the various compounds at the relevant concentrations. The MFCs were calibrated with the primary volumetric flow standard at METAS. The uncertainty for the flows is estimated to be 0.7 to 1% rel.

Furthermore, a calibration gas generator (HovaCAL digital 311, Germany) was used to explore the influence of varying H_2O concentration on the ethanol concentration retrieval. Thereby, a carrier gas (synthetic air) containing 22.5 ppm of ethanol was stepwise humidified by adding gravimetrically determined amounts of water vapor such that the H_2O concentration covered the range between 0 and 7%. Figure 7(a) shows the time series of the measured H_2O and ethanol concentrations. The elevated noise level on the ethanol retrieval is mainly due to the flow fluctuations in the humid gas supplied by the HovaCAL. During the water dilution experiments it was observed that the water absorption linewidth changes with concentration due to the self-broadening effect. This effect is strong enough to induce a systematic bias on the fit and thus, it influences the retrieved ethanol concentration. To account for this bias in the fitting routine, a series of water templates for typically seven different concentrations was assembled and fed into the fit function. In each iteration step the fit function then calculates an interpolated template to account for the contribution of the water to the detected transmission spectrum. This approach is similar to the procedure we described earlier [24]. Figure 7(b) depicts the correlation of the generated water concentration and the spectroscopically retrieved mixing ratio measurements. The averaged ethanol concentration within the steps corrected to dry conditions as a function of water concentration is shown in Fig. 7(c). We found a linear cross-correlation of 90 ± 44 ppb/% within the water concentration range from 0 to 7%. Considering the analytical precision of the laser spectrometer on ethanol, it is obvious that already 0.1% variation of the water vapor content of the sample gas would dominate the uncertainty of the EtOH measurements. According to

the OIML R 126 Recommendation, the relative humidity of the test gas that is injected continuously into a breath alcohol analyzer shall be specified to $95\% \pm 5\%$ at $34\text{ }^{\circ}\text{C}$. Thus, it allows variability in the water vapor content that would definitely have an impact on the spectroscopically determined ethanol concentration. Nevertheless, the ability to measure precisely and simultaneously the H_2O concentration of the gas matrix and the linear dependency between the two compounds allows accounting for the related interferences in real-time. This gives a reliable solution to report absolute ethanol concentrations independently of the humidity level of the sample gas. This also offers a unique opportunity to link dry- and wet calibration standards as well.

A similar experiment was conducted to check the influence of CO_2 on EtOH. In this case, however, no cross-correlation could be observed within the measurement precision.

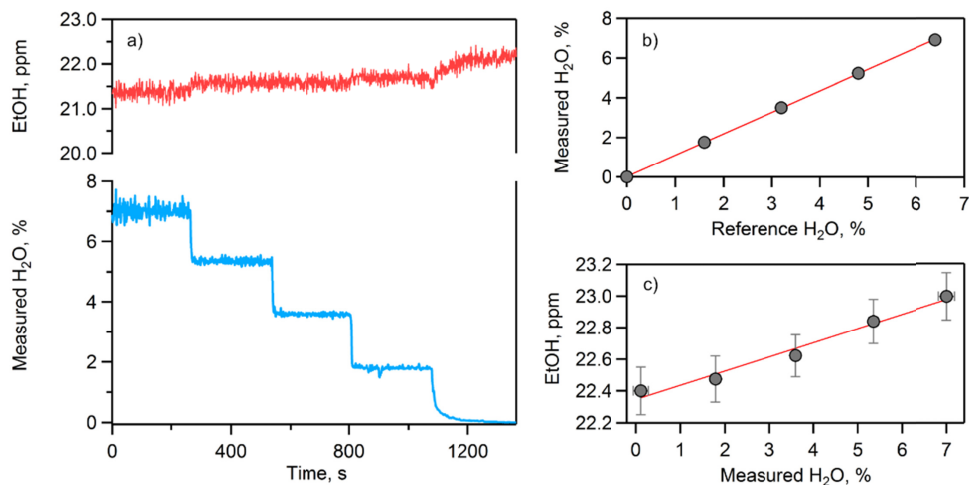


Fig. 7. a) Response of the retrieved ethanol concentration on changing water concentration in the gas mixture. b) Linearity of H_2O measurements in the absence of ethanol. c) Ethanol concentration corrected for dry conditions as a function of H_2O concentration. The error bars correspond to $\pm 1\sigma$.

4. Conclusions

A laser spectrometer for the precise measurement of ethanol in breath-like air mixtures has been developed and characterized. Despite the broad spectral features of ethanol, it has been shown that a conventional DFB-QCL is fully adequate to perform high-precision measurements. The absorption of ethanol at around $9.3\text{ }\mu\text{m}$ revealed a rich spectral structure at reduced pressure of 100 hPa. Furthermore, the intermittent continuous wave driving allowed covering a spectral range of 1.7 cm^{-1} , which significantly contributed in improving sensitivity and selectivity of the spectrometer. Thus, a measurement precision of 9 ppb of ethanol has been achieved. The instrumental response to changing ethanol concentration demonstrates an outstanding linearity over the entire operational range of 25–250 ppm. Possible cross-sensitivity to water vapor and CO_2 were also investigated. Changing the water vapor concentration in the range between 0 and 7% revealed a linear impact of $90 \pm 44\text{ ppb}/\%$ on the retrieved ethanol concentration. Analogue experiments with CO_2 showed no cross-sensitivity within the uncertainty of the measurements. Thus, the instrument allows high precision determination of the ethanol concentration in both dry and breath-like (wet) gas matrices, and it is, thus fully compatible with the OIML R 126 Recommendation regarding the test gas which must contain a volume fraction of CO_2 of $5\% \pm 0.5\%$ and a relative humidity of $95\% \pm 5\%$ at $34\text{ }^{\circ}\text{C}$. Therefore, the spectrometer is suited to reassess the distribution coefficients associated with Dubowski's formula and their uncertainty by direct

comparison of ethanol concentrations in both wet (conventional OIML) and dry (SI-traceable) gas mixtures. Finally, in more general terms, our results demonstrate that a conventional DFB-QCL can be used for precise measurements of organic compounds with broad absorption spectra if they exhibit pronounced spectral features. This is in contrast to the frequent assumption that only broad spectral coverage allows the selective measurement of gaseous organic substances and it may thus lead to a paradigm change in gas sensing, i.e. for medical applications involving breath analysis by mid-IR QCLAS.

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