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Towards an Optical Gas Standard for Traceable Calibration-Free and Direct NO₂ Concentration Measurements

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Abstract: We report a direct tunable diode laser absorption spectroscopy (dTDLAS) instrument developed for NO₂ concentration measurements without chemical pre-conversion, operated as an Optical Gas Standard (OGS). An OGS is a dTDLAS instrument that can deliver gas species amount fractions (concentrations), without any previous or routine calibration, which are directly traceable to the international system of units (SI). Here, we report NO₂ amount fraction quantification in the range of 100–1000 µmol/mol to demonstrate the current capability of the instrument as an OGS for car exhaust gas application. Nitrogen dioxide amount fraction results delivered by the instrument are in good agreement with certified values of reference gas mixtures, validating the capability of the dTDLAS-OGS for calibration-free NO₂ measurements. As opposed to the standard reference method (SRM) based on chemiluminescence detection (CLD) where NO₂ is indirectly measured after conversion to NO, titration with O₃ and the detection of the resulting fluorescence, a dTDLAS-OGS instrument has the benefit of directly measuring NO₂ without distorting or delaying conversion processes. Therefore, it complements the SRM and can perform fast and traceable measurements, and side-by-side calibrations of other NO₂ gas analyzers operating in the field. The relative standard uncertainty of the NO₂ results reported in this paper is 5.1% ($k = 1$, which is dominated (98%) by the NO₂ line strength), the repeatability of the results at 982.6 µmol/mol is 0.1%, the response time of the instrument is 0.5 s, and the detection limit is 825 nmol/mol at a time resolution of 86 s.

Keywords: gas analysis; laser absorption spectroscopy; dTDLAS; nitrogen dioxide (NO₂); metrology

1. Introduction

Nitrogen dioxide (NO₂) is a prominent air pollutant emitted from combustion processes, burning fuel, cars or power plants. Exposure to elevated levels of NO₂ in the atmosphere causes serious respiratory diseases [1]. Accurate and reliable measurement methods for amount fraction (concentration) levels below 1 ppm are needed for atmospheric NO₂ air quality control [2] and to monitor NO₂ emitted directly from the exhausts of cars (1–2500 µmol/mol, note: µmol/mol is often called ppm) as required for the type approval emission limits quality control test (i.e., the EURO 5/6 emission standard states the range of NO₂ emission levels, which need to be measured during type approval, to be in the 1–30 µmol/mol for cars with a functional exhaust catalyst, and 30–1000 µmol/mol for cars with a malfunctioning exhaust catalyst). The standard reference method (SRM) for measuring NO₂ is based on chemiluminescence detection (CLD), as documented in the European standard EN 14211:2012 [3], where NO₂ is only measured *indirectly* (i.e., NO₂ in a sample is calculated from the difference of NOx and NO after the conversion (catalytic or photolytic) of NO₂ to NO. The NO then reacts with the ozone (O₃) to produce electronically excited NO*₂ which decays to NO₂ and emits light (luminescence) that is detected by, e.g., a photomultiplier tube. The NOx concentration is determined using the

measured signals, and the NO_2 concentration by subtracting NO (detected in an independent parallel channel) from NOx [4,5]). This indirect measurement of NO_2 can lead to an overestimation of NO_2, as other NOy gas species (HNO_3, HNO_2, N_2O_5) in the sample can also be converted into NO as well. It is worth noting that NO_2 is the only air pollutant where the SRM is based on an *indirect* measurement. Due to the fact that NO_2 is only indirectly measured, very reactive and that there is a lack of accurate static calibration reference materials CRM (gases), e.g., for car exhaust gas applications, in the 1–2500 ppm range with $\leq$1% uncertainties, there is the need to implement new accurate and reliable measurement methods (reference methods for ambient air and other applications) for *direct* NO_2 measurements [2] and alternative calibration approaches (e.g., an instrument standard OGS) to complement CRMs [6].

Laser spectroscopic techniques provide an option to develop opportunities for accurate and reliable measurement methods for direct NO_2 measurements [2]. Laser absorption spectroscopy has been demonstrated for direct measurements of the concentration of a variety of molecules in different applications such as atmospheric monitoring, combustion diagnostics and breath analysis [7–21], and therefore can serve as a good candidate to develop a reference method for direct NO_2 measurements. There have been several studies to perform direct NO_2 measurements and also addressing the shortcomings in the SRM-based measurements [2,22–26]. For atmospheric NO_2 measurements, spectroscopic techniques such as tunable diode laser absorption spectroscopy (TDLAS), quantum cascade laser absorption spectroscopy (QCLAS), cavity ringdown spectroscopy (CRDS), photoacoustic spectroscopy (PAS) and cavity attenuated phase shift spectroscopy (CAPS) have been reported with sub ppb detection limits [22,24,27–29]. Differential optical absorption spectroscopy (DOAS), TDLAS, PAS and CRDS have been successfully demonstrated for the detection of NO_2 emitted from automobile and aircraft engines, with detection limits in ppm down to the ppb range [23,30–33]. To date, for these spectroscopic NO_2 measurements, information on the metrological traceability and uncertainty assessment following, e.g., the guide to the expression of uncertainty in measurement (GUM) [34] is rarely reported. Metrological traceability of results (i.e., traceability of the results to the SI) and uncertainty assessments according to the GUM [34] of the NO_2 results derived using spectroscopic measurement methods are critical for quality control measurements [2] and type approval purposes [35].

Direct tunable diode laser absorption spectroscopy (dTDLAS) combined with the TILSAM (traceable infrared laser-spectrometric amount fraction measurement) method [36], has been demonstrated in a variety of applications addressing metrology data quality (SI-traceability and GUM compliant uncertainty assessments). dTDLAS is a variant of TDLAS that combines TDLAS with a special data evaluation procedure to derive concentration results that are directly traceable to the SI [7,37]. As reported on our previous work, a dTDLAS instrument is referred to as an optical gas standard (OGS) [7–10,37]. An OGS is similar to the ozone standard reference photometer (SRP) [38]. Employing dTDLAS, fast measurement frequencies (from sub-Hz to Hz) and response times (e.g., milliseconds to seconds) required in field measurements can be reached [39–42]. Focusing here on a new development for direct NO_2 (reactive gas) measurements in car exhaust gases, our previous works in [7–10,37] focused on dTDLAS instrument developments for the measurement of H_2O, CO and CO_2 and H_2O as well as reaching fast measurement frequencies [39–42].

In this paper, we report the details of a new dTDLAS spectrometer [43] specifically designed and developed for accurate direct NO_2 measurements. The focus of this work was to report the development stages of the NO_2 dTDLAS instrument towards an OGS (an instrument standard for direct NO_2 measurements), the testing and validation steps performed, the potentials and the current limitations of the instrument. The capabilities for direct NO_2 measurements (looking at all measured quantities desired for the results) are demonstrated via NO_2 concentration measurements. A comparison of calibration-free dTDLAS NO_2 concentration results (range: 100–1000 μmol/mol, within the car exhaust NO_2 concentration range) versus certified reference gas mixtures is done as a validation

step. We further show that the instrument is capable of direct NO_2 measurements in car exhaust gas matrix. In order to compete with, and compliment CRMs and supplement the SRM for NO_2 measurements, with other gas matrices such as the car exhaust gas matrix in focus, the traceability of the spectroscopic results to the SI is addressed and an uncertainty assessment following GUM principles is made for the NO_2 results.

2. Experimental

Figure 1 depicts a schematic of the dTDLAS spectrometer for direct NO_2 measurements [43]. The instrument employs an interband cascade DFB laser (Nanoplus) emitting at 3.4 μm, a 77 cm silconert© coated stainless-steel single pass gas cell and a photovoltaic mid-infrared detector (Vigo system, detector diameter: 1 mm²). The sampling lines as well as the gas cell are coated to minimize the potential adsorption effects of NO_2 in the gas sample. For spectroscopic measurements, NO_2 gas samples flow (typical flow rate: 1.5 L/min) through the gas cell controlled by a mass flow controller (MFC, Bronkhorst) at the gas input and a valve at the output (connected to a pump) of the sampling lines as shown in Figure 1. The laser wavelength is swept at a frequency of 139.8 Hz (similar to [7–10], and the collimated laser light is passed through the gas cell on to the detector. The signal from the detector, pre-amplified with a transimpedance amplifier (Femto DLPCA 200), is acquired using a data acquisition card (DAC, 18 bits, 625 KS/s NI PCI-6289) and is subsequently saved on a personal computer (PC) with a state-of-the-art operating system.
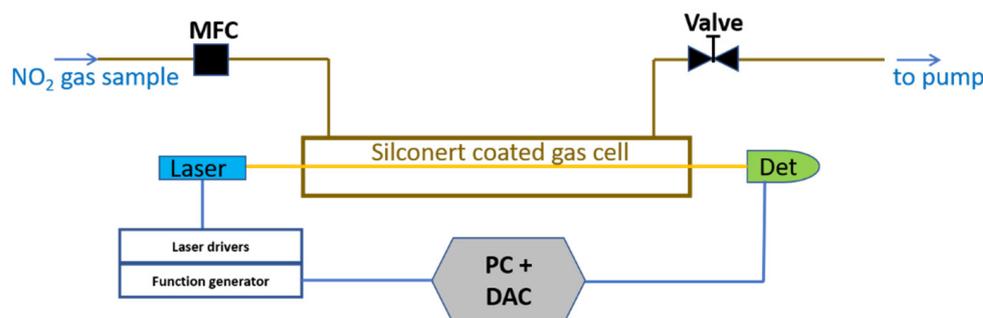
Figure 1. Schematic of the dTDLAS instrument for direct NO_2 measurements (Det: detector).

Figure 2a depicts typical signals (with NO_2 absorption lines visible around 2919.6 cm⁻¹) measured at 0.2 Hz (the measurement frequency for single scan measurements is 18 Hz, i.e., ~0.056 s time resolution which is longer than the acquisition time of approximately 0.00352 s (2200 points on the up ramp at 625KS/s) due to the extra time needed to save the data using our acquisition software and corresponds to a time resolution of about ~5.6 s, i.e., ~0.2 Hz measurement frequency for 100 averaged single scans) for a gas mixture with an NO_2 amount fraction of 979 μmol/mol in the air. It could be noted here that the measurement frequency is different from the laser modulation frequency of 139 Hz. The absorbance data (Figure 2b derived using the data in Figure 2a, 100 averaged scans, 739 points in the fit window) are fitted by a set of 8 Voigt profiles [44] in order to derive the line areas (areas underneath the absorption lines), i.e., together with the NO_2 line at 2919.59 cm⁻¹, 7 other neighboring NO_2 lines (see right y axis and the lines in red: line strength [45] plot in Figure 2b) are fitted in the spectral window selected for data analysis. The fitting was performed with the line positions, the line areas and the Lorentzian line widths kept free. The Doppler line widths were calculated at the measured gas temperature.
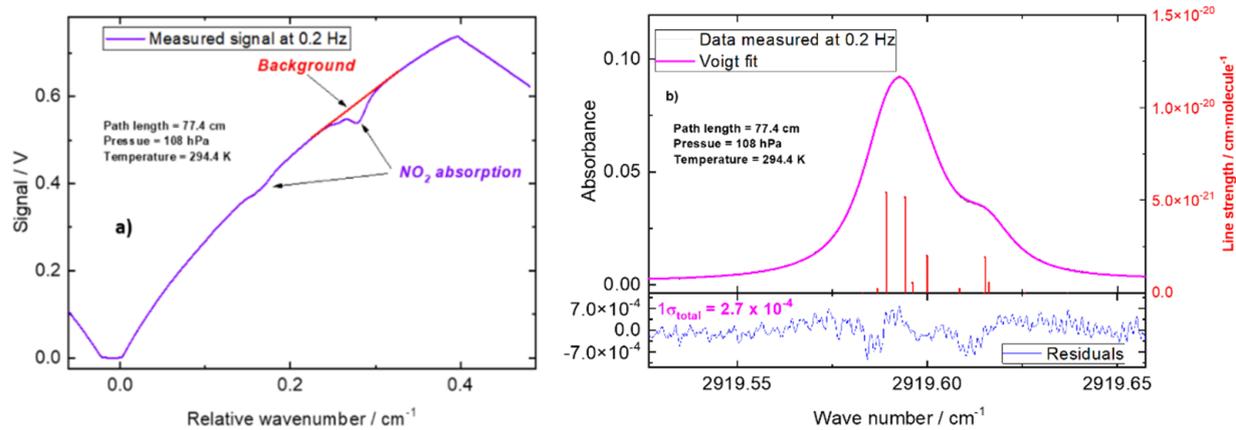
Figure 2. (**a**) Typical waves at 108 hPa signals measured using the spectrometer in Figure 1; (**b**) absorbance data derived from the data in Figure 2a. With the eight NO_2 lines shown (in red) in the line strength plot (right *y* axis), eight Voigt profiles are fitted to the data in order to derive the line areas.

The bottom panel of Figure 2b shows the residuals from the multiline Voigt fit with $1\sigma_{total} = 2.7 \times 10^{-4}$. Using the $1\sigma_{total}$ value and the peak absorbance value of 0.092, a signal-to-noise ratio of 341 was calculated for the data in Figure 2b. Due to the signal-to-noise ratio (SNR) around and below 100 and the complex multi-line structure of the NO_2 line used, higher order line shape profiles like Galatry or Hartmann–Tran profiles [46–48] were not found to be suitable and advised to fit the data in this work. Using the line area of the NO_2 line at 2919.59 cm^{-1}, derived for the data in Figure 2b, the NO_2 amount fraction (concentration) x_{NO2} can be derived using Equation (1) (which is derived from the Beer lambert law) [7]:

$$x_{NO_2} = \frac{k_B \cdot T}{S_T \cdot L \cdot p_{total}} \int_{-\infty}^{\infty} A(\widetilde{v}) d\widetilde{v} = \frac{k_B \cdot T}{S_T \cdot L \cdot p_{total}} \cdot A_{line} \tag{1}$$

where the quantity k_B is the Boltzmann constant, S_T is the line strength of the probed molecular transition at gas temperature T, L is the optical path length of the light beam transmitted through the absorbing medium, p_{total} the total gas pressure, $A(\widetilde{v})$ the spectral absorbance and A_{line} the line area. The amount fraction (concentration) results x_{NO2} is directly traceable to the SI if all the quantities in the right-hand side of Eqn. 1 are traceable to the SI as well [7–9,37]. To this end, x_{NO_2} results are derived without the calibration of the instruments with a reference gas mixture. As introduced, an instrument that can deliver amount fraction results that are directly traceable to the SI shall be referred to as an optical gas standard (OGS).

From the data in Figure 2b, a line area value of 0.0010999414 cm^{-1} is derived for the NO_2 line 2919.59 cm^{-1}, and a dTDLAS amount fraction value of (982.0 ± 49.1) μmol/mol calculated according to Eqn. 1 is combined with the TILSAM method [36]. This measured NO_2 amount fraction is in good agreement with the certified value of (979 ± 20) μmol/mol reported for the probed gas mixture, demonstrating the capability of the instrument for an absolute ("calibration-free") direct NO_2 amount fraction measurements.

Table 1 holds an uncertainty budget for dTDLAS NO_2 results. As shown in Table 1, the combined uncertainty of the NO_2 results is 5.1% (*k* = 1). The quantity *k* is a coverage factor [34]. The uncertainty of the amount fraction results of 5.1% is dominated by the uncertainty of the measured line area (1%) and the literature line strength value (5% [45]) as indicated by the higher index values (% individual contribution) in Table 1. The uncertainties of the other significant input quantities (p_{total}, T, k_B, L) are all less than 0.2%.

Table 1. Uncertainty budget of the NO_2 amount fraction results.

| Parameter	Value	Relative Standard Uncertainty ($k = 1$)/%	Index (% Individual Contribution)
Pressure	108.5 hPa	0.20	0.10
Temperature	294.3 K	0.10	≤0.05
Path length	77.4 cm	0.13	≤0.05
Line strength (HITRAN value [40])	$5.425 \cdot 10^{-21}$ cm/molecule	5.00	96.00
Line area	0.0010999414 cm^{-1}	1.00	3.80
NO_2 concentration (x_{NO_2}) result	982 µmol/mol	5.10 (combined uncertainty)	

In order to determine the repeatability of the measurements delivered by the instrument, Figure 3a shows repeated measurements of NO_2 amount fractions performed with the 979 µmol/mol NO_2 in synthetic air gas mixture. The mean value of the results in Figure 3a is 982.6 µmol/mol, the reproducibility (1σ, standard deviation) is 8.7 µmol/mol (0.9%) and the repeatability (standard deviation of the mean) is 0.5 µmol/mol (0. 1%). The excellent repeatability of 0.1% demonstrates the capability of a dTDLAS instrument for NO_2 OGS applications. The inset in Figure 3a shows a histogram of the measurements, depicting a normal distribution of the results with a full width at half maximum (FWHM) of 9.2 µmol/mol (corresponding to an SNR of 107 for the amount fraction results at 979 µmol/mol). Figure 3b depicts a plot of the Allan deviation [49] of the NO_2 amount fraction results (here, the measurements are done at 2 Hz, i.e., at 0.5 s with 10 averaged scans) as a function of time. From the Allan plot in Figure 3b, an optimal precision of 825 nmol/mol (detection limit) is evaluated (conservatively, as there is no minimum visible) for the instrument at a time resolution of 86 s.
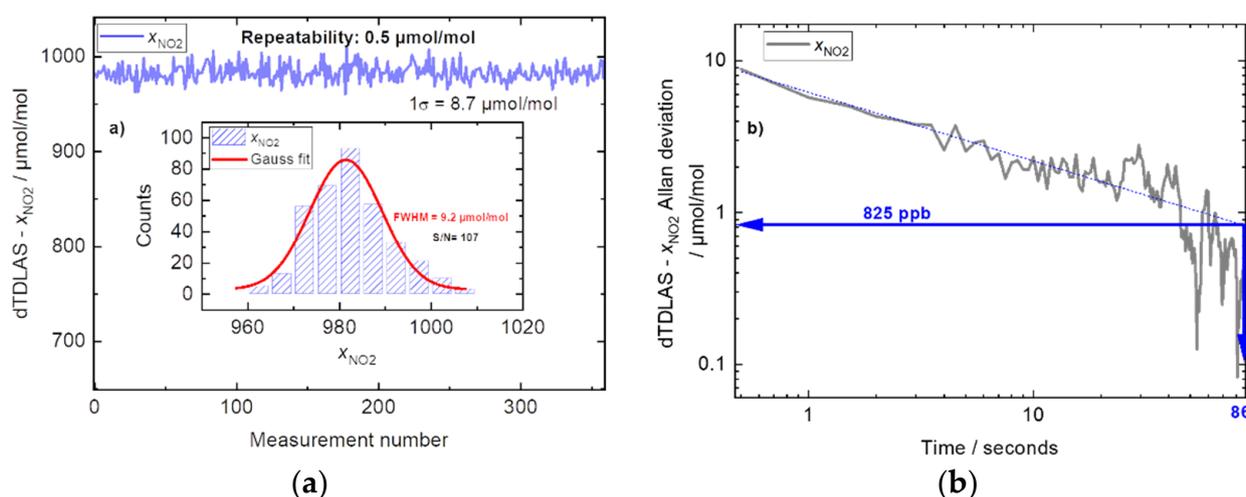
Figure 3. (**a**) Repeated NO_2 measurements: plot of NO_2 OGS amount fraction results vs. measurement number; (**b**) Allan deviation: plot of the x_{NO_2} Allan deviation as a function of time.

Repeated measurements were performed at different amount fraction levels (switching from about 100 to 1000 µmol/mol as shown on Figure 4a) to study the behavior, response and linearity of the instrument. The gas mixture used for the measurements at the lowest amount fraction level of 100 µmol/mol was a primary gas mixture (SI traceable, prepared using gravimetry by a national metrology institute). At 300 µmol/mol we used a commercial gas mixture (secondary: SI-traceable, with a Deutscher Kalibrierdienst-DKD certificate [50]) and that at 1000 µmol/mol was a commercial gas mixture from the same manufacturer (internally assigned, with no SI-traceability information provided). The

standard uncertainty reported for the NO_2 amount fractions in these gas mixtures are all 1% (k = 1), corresponding to expanded uncertainties of 2% (k = 2).
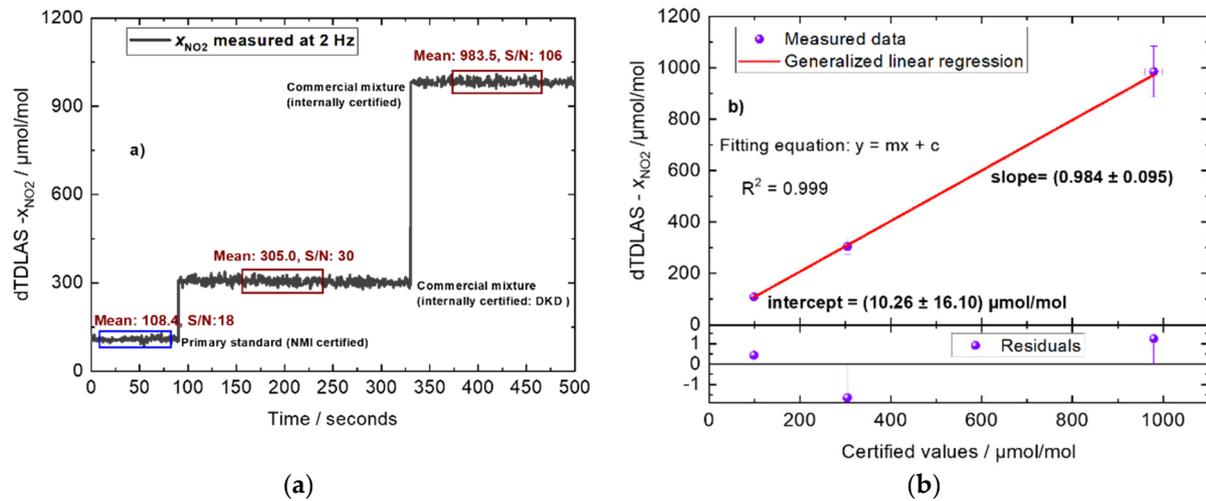
Figure 4. (**a**) Plot of the NO_2 OGS amount fraction results at different levels as a function of time (at Δt = 86 s, 1σ for 108.4, 305.0 and 983.5 are 6.2, 9.9 and 9.6, respectively); (**b**) dTDLAS NO_2 amount fraction x_{NO2} results as a function-certified values of gas mixtures.

As presented, the sampling lines and the gas cell were all coated by Silconert, resulting in a fast response time of 0.5 s for the NO_2 measurements in Figure 4a. It could be noted here that this response time of 0.5 s does not also include the cylinder switching time and the time of manually opening valves to introduce the NO_2 gas sample into the gas cell. The repeatability (calculated as the standard deviation of the mean) at the lowest NO_2 results at the 100 μmol/mol level is 0.5 μmol/mol (0.5% relative). At the respective amount fraction levels, 1σ (standard deviation) values were evaluated, demonstrating the short-term reproducibility (<10 μmol/mol at 1σ) for the NO_2 OGS results. Using the respective 1σ values, an SNR from 18 at 100 μmol/mol to 106 at 1000 μmol/mol levels, at a time resolution of 86 s, were evaluated for the measurements in Figure 4a.

Figure 4b shows a plot of the NO_2 amount fraction results as a function of the certified values reported for the probed gas mixtures. A generalized linear regression (GLR) was applied to the data in Figure 4b, resulting in a slope of 0.984 ± 0.095 (k = 2) and an intercept value of (10.25 ± 16.10) μmol/mol, respectively. The slope value of 0.984 shows the good accuracy of the dTDLAS instrument, while the small deviation from the linear fit shows good linearity. The intercept value is consistent with zero, indicating an offset free measurement. The relative residuals from the linear model in the bottom panel of Figure 4b are all within the 1% range and thus well within the expanded uncertainty of the dTDLAS results of 5.1%, k = 1), which shows good agreement (compare well; validation step) with the certified values associated with the gas mixtures.

3. Discussion

The NO_2 OGS spectrometer was tested in the concentration range from 100 to 1000 μmol/mol and was found to be in good agreement with the certified values of the reference gases, demonstrating the calibration-free OGS capability of the instrument. The detection limits of the dTDLAS instrument are 0.825 μmol/mol (at Δt = 86 s) and the relative uncertainty of the results delivered by the instrument is 5.1%, k = 1. This relative standard uncertainty was derived following GUM [34] principles. These results indicate that the instrument has the potential to measure NO_2 (that can be in the 1 to 1000 μmol/mol: detection limit of 0.825 μmol/mol) emitted from the exhaust of cars as further supported by the simulation (HITRAN [45] line data used) in Figure 5 where the interference (due to absorption by other exhaust gas molecules) on NO_2 absorption is insignificant (absorbance

in the order of 10^{-5} for H_2O, NO_2, CO_2, and CO: L = 77.4 cm, p = 100 hPa, T = 296 K). As presented, the relative repeatabilities of the NO_2 results at 1000 μmol/mol and lowest amount fraction of 100 μmol/mol are 0.1% and 0.5%, respectively. Table 2 holds a summary of the capabilities of the NO_2 OGS instrument presented in this work.
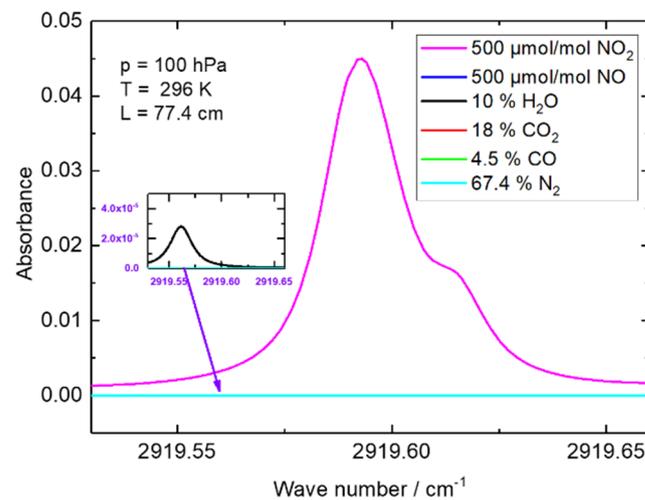
Figure 5. Simulation: NO_2 in exhaust gas matrix.

Table 2. Summary of NO_2 OGS instrument capabilities.

Quantity	Value
Current concentration range (NO_2)	100–1000 μmol/mol
Optimal precision	0.825 μmol/mol at Δt = 86 s
GUM compliant total relative uncertainty	5.1% (k = 1)
Relative repeatability at 1000 μmol/mol and at 100 μmol levels	0.1% and 0.5%
Time resolution (max = single scan to 10 scan average)	0.06 * sec to 0.5 s

* >acquisition time of 3.5 ms as extra time is needed to save the data.

The relative uncertainties of the NO_2 results of 5.1% (k = 1) are dominated (96% of the total uncertainty) by the uncertainty of the line strength value. Therefore, to further reduce the uncertainty of the results, future work will be focused on reducing the uncertainty of the line strength value. Since the dTDLAS results are in good agreement with the certified values (see Figure 4b), it can be concluded that the line strength used for the analysis is validated. The line strength value is taken from the HITRAN database [45]. This first validation of the line strength value was further assessed in a separate analysis to determine the line strength value from the data measured with the 300 μmol/mol gas mixture, resulting in a line strength value of $(5.444 \pm 0.076) \cdot 10^{-21}$ cm/molecule, k = 1, at 294.4 K for the NO_2 line 2919.59 cm^{-1}. It could be noted here that the accuracy of the measured line strength would be dependent on the accuracy of the certified gas mixture used. This line strength value $(5.444 \pm 0.076) \cdot 10^{-21}$ cm/molecule is in agreement with HITRAN's [45] value of $(5.425 \pm 0.271) \cdot 10^{-21}$ cm/molecule, k = 1, at 296 K, further validating the HITRAN value [45]. In order to test the effect of a new line strength value with a reduced uncertainty, we used the line strength value $5.444 \cdot 10^{-21}$ cm/molecule and the standard uncertainty ($0.076 \cdot 10^{-21}$ cm/molecule: 1.4% relative) to evaluate the uncertainty of the NO_2 results (similar to Table 1), yielding relative uncertainty of 1.7% (k = 1). The uncertainty of the dTDLAS results currently stands at 5.1%, and a 1.7% relative uncertainty for the NO_2 amount fraction results will fulfill the requirements of portable

emission measurement systems (PEMS) of less than 2% for NO_2. Regarding the line strength, we estimate that we can achieve an uncertainty better than 1.7% or 0.2% in future line strength measurements, similarly to in our previous works [51,52], which would lead to a corresponding improvement in the NO_2 amount fraction uncertainty. One of the critical points in achieving an OGS is ensuring direct traceability to the SI. The traceability of the NO_2 amount fraction results in this work was addressed via the traceability of the input quantities on the right-hand side of Eqn.1, such as quantities p_{total}, T, L (SI-traceable to respective PTB standards). As presented, the validated line strength S_T value was taken from the HITRAN database [45] and SI-traceability was not reported. Therefore, in addition to a reduced uncertainty in the line strength value, new SI-traceable NO_2 line strength measurements are planned in separate experiments similar to [51,52].

This work shows that an OGS for NO_2 amount fraction measurements is feasible. An OGS (providing *direct* NO_2 amount fraction results traceable to the SI) for NO_2 can complement the current standard reference method (based on CLD), where NO_2 is "only" *indirectly* measured (note: the concept of indirect measurement is not the issue here, but rather the conversion efficiency of NO_2 to NO and maintaining a minimum residence time). By providing amount fraction results that are directly traceable to the SI, an OGS can also complement (use in the place of) calibrate reference gases both in the laboratory and in the field. An OGS will add the advantage of simultaneous in situ measurement and side-by-side field NO_2 calibrations of other analyzers.

4. Conclusions

We presented a new dTDLAS NO_2 instruments are designed to be operated as an optical gas standard (OGS) and can thus perform absolute ("calibration free") NO_2 amount fraction measurements directly, i.e., without any chemical conversion which is needed in the current standard reference method CLD. Nitrogen dioxide amount fractions in the range of 100–1000 µmol/mol were delivered by the instrument and are in good agreement with certified reference values attributed to the reference gas mixtures. The relative uncertainty of the results is currently at 5.1% ($k = 1$) and is almost completely (96%) dominated by the inaccurate molecular reference data. The relative repeatability of the results at 982.6 µmol/mol is 0.1% and the instrument response time ranges from 0.5 s with a 10-scan average to 0.06 s in the single scan mode. Future work will focus on measuring a new SI-traceable NO_2 line strength value to further reduce the line strength uncertainty influence and thus the instrument accuracy. The instruments' detection limit of 0.825 µmol/mol makes it well suited for direct measurements of the NO_2 concentration in car exhaust gases. Therefore, further plans are to extend the capability of the instrument for simultaneous measurements of NO_2 and NO concentrations (in both atmospheric, i.e., less than 1 µmol/mol level, and car exhaust gas species).

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