Research Article

Purity Analysis of Gases Used in the Preparation of Reference Gas Standards Using a Versatile OPO-Based CRDS Spectrometer

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Preparation of accurate reference gas standards at low amount fractions such as for greenhouse gases requires highly sensitive instrumentation to determine the purity of the gases used in the preparation. For this purpose, a versatile CRDS spectrometer has been constructed at VSL based on high-power, continuous wave OPOs covering a very wide wavelength range of 2.3–5.1 μm. Due to the use of passivated materials, the spectrometer is also suitable for the measurement of reactive impurities. Details of the spectrometer are presented together with several examples of purity analysis.

1. Introduction

In the last 15 years, cavity ring-down spectroscopy (CRDS) has revolutionized several areas of gas analysis including trace moisture analysis (semiconductor industry), accurate measurements of greenhouse gases (Global Atmosphere Watch Programme of the World Meteorological Organization WMO), and isotope analysis. Commercial instruments are based on low-cost near-infrared DFB laser diodes and 2- or 3-mirror cavities achieving low nmol/mol (part per billion) sensitivity for small molecules (up to ∼5 atoms) at a measurement interval down to 1 second. Most instruments can detect a single analyte, yet some models can detect up to 4 analytes. Instruments are dedicated to the measurement in a specific matrix gas which is normally infrared-transparent like nitrogen, air, or hydrogen (latter for fuel cell hydrogen purity analysis). In recent years, a few instruments have been developed for other reactive and/or infrared-absorbing matrices such as NH_3, HCl, or Cl_2 mainly for dedicated applications in the semiconductor industry (see, e.g., [1]).

The high sensitivity and good long-term stability of CRDS make it an excellent tool for application in gas metrology. This has been recognized at an early stage by National Metrology Institutes (NMIs), in particular, NIST who started to develop CRDS spectrometers in the mid-nineties [2] and VSL who purchased the first commercial CRDS spectrometer in 2001 [3]. Currently, nearly all NMIs active in the preparation of reference gas standards operate CRDS instrumentation for purity analysis of the gases used to prepare reference gas standards and for the analysis of reference gas standards.

Due to the use of lasers with a narrow tuning-range commercial CRDS instruments are suitable for dedicated applications. To have a more flexible instrument suitable for a wider range of analytes and matrices, VSL in cooperation with the Radboud University in Nijmegen developed a CRDS instrument based on a tunable (2.7–3.5 μm) continuous wave optical parametric oscillator (OPO) [4]. This instrument has recently been upgraded. The wavelength range of the OPO has been significantly extended and now covers a very wide wavelength range (2.3–5.1 μm) enabling measurements of additional gases like CO or giving access to stronger absorption bands for gases like nitrous oxide (N_2O) and carbon dioxide (CO_2). The measurement cell has been modified to achieve a faster response when measuring low amount fractions of reactive compounds.

Within this paper, the upgraded spectrometer will be presented. Application of the system in gas metrology is shown by presenting examples of purity analysis of gases used for the preparation of accurate reference gas standards for
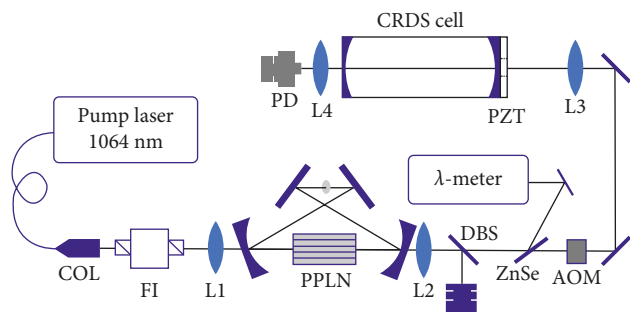
FIGURE 1: Schematic of the singly resonant cw OPO and CRDS spectrometer. The output of the seed fibre laser is amplified up to maximum 10.5 W and coupled into the OPO cavity. Part of the idler is directed to a wavelength meter, and the rest is directed via an acoustical optical modulator (AOM) to the cavity ring-down measurement cell.

greenhouse gases. Finally, an example of the measurement of the reactive impure nitric acid (HNO_3) formed after preparation of NO_2 gas standards is shown.

2. Experimental Setup

Figure 1 shows a schematic overview of experimental setup based on an OPO as light source and CRDS used for the gas detection. The pump laser of the OPO consists of a narrow line-width fibre laser (NKT Photonics, output power set at 4.4 mW) which is amplified in a fibre amplifier (IPG Photonics). This combination provides a wide mode-hop-free tuning range of 100 GHz and an output power up to 10.5 W at 1064 nm. The output of the amplifier is coupled into the OPO cavity via a collimator (COL), Faraday isolator (FI), and an AR-coated focusing lens (L1). The periodically poled crystal (PPLN) from HC Photonics is contained in an oven and has AR coatings for signal, pump, and idler wavelengths. The mirrors are highly transparent for both idler and pump wavelengths and highly reflective for the signal wavelength. The backside of the mirrors is antireflective coated for both the pump and idler. Within the PPLN crystal, the pump light is converted into the signal and idler with the signal resonating in the OPO cavity.

The output of the OPO is collimated using an uncoated CaF_2 lens (L2). Signal and residual pump are separated from the idler using a dichroic beam splitter (DBS). Part of the idler beam is directed to a wavelength meter (Bristol instruments) using a ZnSe window placed near the Brewster angle.

Four different PPLN crystals and mirror sets in the OPO cavity are used to cover the entire wavelength range of 2.3–5.1 μm. Here, more details will be given on the OPOs for the short wavelength range (2.27–2.7 μm) and high wavelength range (3.9–5.1 μm).

2.1. OPO (2.27–2.7 μm). Reports in the literature on cw singly resonant OPO systems pumped at 1064 nm and operating at wavelengths below 2.5 μm are scarce [5, 6]. This is due to the challenge to achieve stable operation as the PPLN gain bandwidth becomes very broad when the idler
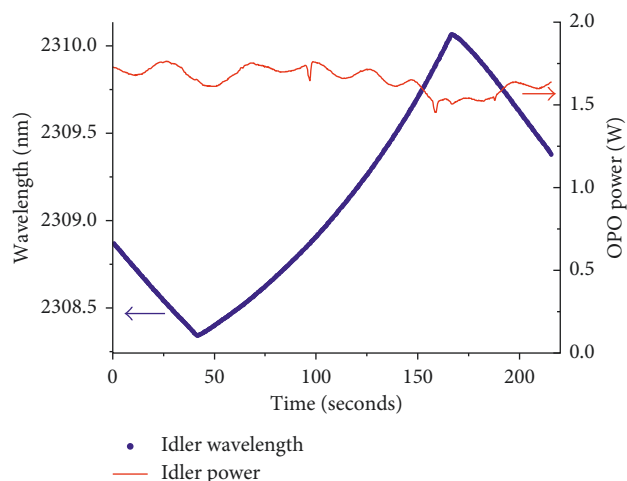

FIGURE 2: Continuous tuning of the idler wavelength (blue line) using a combination of pump-laser tuning and crystal-temperature tuning (crystal temperature is tuned over about 2°C). The idler output power is also shown (red line).

and signal are approaching the point of degeneracy (2128 nm). This wavelength range is of interest for various spectroscopic applications including the measurements of the quadrupole spectrum of molecular hydrogen [7], hydrogen fluoride detection [6], and for the study of CO and CH_4 absorption lines, which are used in satellite retrieval measurements [8].

Both water vapor and carbon dioxide strongly absorb in large part of the signal wavelength region, and therefore, the OPO cavity was flushed with a small flow of high purity nitrogen. The threshold of the OPO is 2.2 Watt, and the maximum idler output power is 3.0 Watt. The 2.2 W threshold compares favourably to the 7 W threshold stated in [5] for an OPO operating in the same wavelength region. For operation below 2.4 μm, tuning the pump laser tunes the idler continuously over only about 0.5 nm, after which the idler jumps typically 2–5 nm. Use of a 50 μm silicon etalon (866 GHz FSR) increased the continuous tuning range up to 1 nm. Insertion of this etalon leads to an increase in threshold to 4.5 W, and the output power is maximum 2.3 W. To achieve wider continuous tuning, the crystal temperature is simultaneously tuned (using Peltier elements) with the pump laser. Figure 2 shows a recording of the idler wavelength together with the idler power. Mode-hop-free tuning can be achieved over more than 1.5 nm this way.

2.2. OPO (3.9–5.1 μm). This OPO has been built to measure the important greenhouse gases CO, CO_2, and N_2O, which all possess strong absorption bands within this range. In the long wavelength region, the rapidly increasing attenuation coefficient of the PPLN crystal [9] makes it difficult to overcome the OPO oscillation threshold. This has limited operation of cw singly resonant OPOs typically to wavelengths up to 4.7 μm [10]. A notable exception is the work of Krieg and co-workers who obtained wavelengths up to as far as 5.4 μm [11].

The cavity was flushed with a small dry nitrogen flow (higher flows lead to wavelength instabilities) as water strongly absorbs at the signal wavelength while idler light is strongly absorbed by CO_2 for idler operation around 4.3 μm. The tuning range of the OPO extends up to 5.1 μm. While Krieg et al. could achieve mode-hop-free tuning in windows of about 15 GHz limited by the pump laser, here we obtain mode-hop-free tuning over a much wider range of 100 GHz.

2.3. CRDS Spectrometer. For gas detection, the cavity ring-down spectroscopy technique is used. The OPO output power used in the experiments is 300 mW up to 1 W. Due to the use of the acoustical optical modulator and several diaphragms, the power incident to the ring-down cell is reduced to 10–50 mW.

The 40 cm long measurement cell (internal volume of about 150 mL) is made of stainless steel and passivated with SilcoNert 2000 (SilcoTek) making it suitable for many reactive compounds like HNO_3 or HCl. Five different mirror sets (ROC = 1 m) are available to cover large part of emission range of the OPOs. Decay times up to 20 μs can be achieved yet 6–12 μs being more typical for most wavelength regions. The cavity length is modulated over one free spectral range at a frequency of 20 Hz by means of piezoelectric transducers attached to one of the mirrors.

Light emerging from the cell is focused on a Peltier-cooled (HgCdZn)Te photodetector (PVI-2TE-5, Vigo Systems S.A.). Once sufficient intracavity light intensity has built up, the idler beam is rapidly extinguished using an AOM. Spectra are recorded by measuring the ring-down time as function of the wavelength. Typically, ten scans are averaged. The minimum detection limit is wavelength dependent and is about $6 \cdot 10^{-8}$ cm^{-1} in the short term (1 second) and $5 \cdot 10^{-9}$ cm^{-1} in the long term (5 minutes) at 3150 cm^{-1}.

Both measurement of reactive gases at nmol/mol levels and purity analysis require the use of sampling lines, flow controlling devices, and cell material which are compatible with the analysed compounds. For reactive compounds, polymer tubings and a SilcoNert 2000 passivated mass flow controller (Bronkhorst High-Tech BV) are used. For measuring low amount fractions of water vapour or low CO_2, polymer tubings are not suitable due to the permeation of H_2O and CO_2 from the atmosphere through the tubing. In this case, (coated) stainless steel tubing is used. The pressure in the measurement cell was set at typically 1030 mbar using a combination of pressure controller (Bronkhorst High-Tech BV) and membrane pump. All experiments were performed at 20°C.

3. Applications in Gas Metrology

3.1. Purity Analysis. NMIs are responsible for the realization of primary standard gas mixtures (PSMs) which form the basis for disseminating traceability for the analysis of gases. PSMs are prepared by accurately weighing gases or volatile liquids into high-pressure cylinders according to ISO-6142 [12]. The ISO-19229:2015 standard [13] sets requirements for the purity analysis of materials used in the preparation of
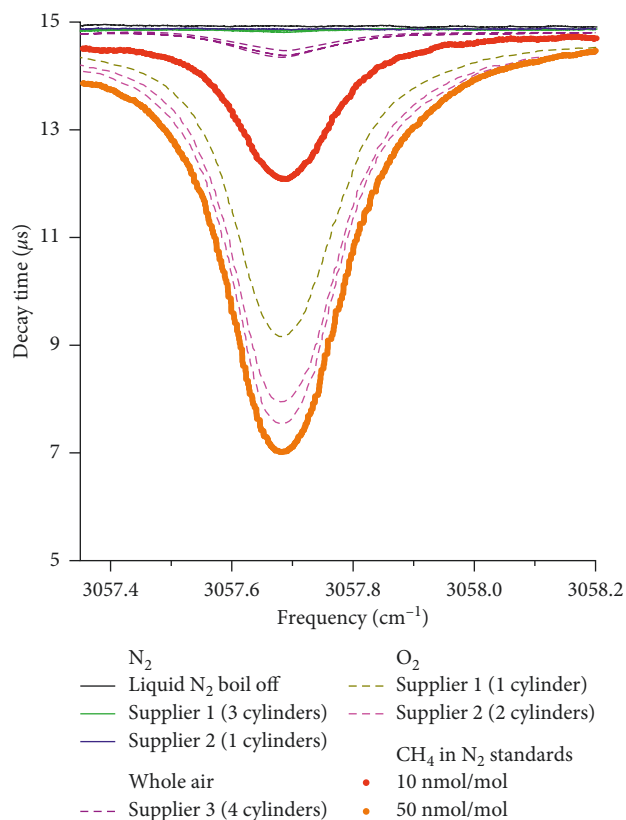

FIGURE 3: Purity analysis for methane in the matrix gases N_2, O_2, and whole air from different suppliers. In addition, the measurement of two CH_4 reference standards (10 and 50 nmol/mol in N_2) is shown.

calibration gas mixtures and the use of these data in calculating the composition of the mixture thus prepared.

Purity analysis with results that are traceable are required when the impurity is "critical" (meets any of the 4 criteria specified in the ISO-19229:2015 standard) and significant (contributes >10% to the target uncertainty of any of the components in the gas mixture to be prepared). As an example, several NMIs are working on CH_4 gas standards at 1800 nmol/mol with a target uncertainty below 2 nmol/mol in order to meet the challenging World Meteorological Organization data quality objectives (DQOs) for underpinning trend assessment [14]. Traceable measurements of the methane impurity in the matrix gases (synthetic air consisting of nitrogen and oxygen or scrubbed whole air) is required in this case. The maximum allowed uncertainty of 2 nmol/mol also compromises various other uncertainty contributions (e.g., due to weighing of the gases); hence, the amount fraction of CH_4 in the matrix gas must be determined with an uncertainty even smaller than 2 nmol/mol. At several NMIs, the accuracy of gas standards like for methane is now limited by the ability to measure trace level impurities in the matrix gases used to produce the standards [15].

Gas manufacturers provide specifications for the purity of their pure gases for a limited set of impurities. These specifications are often conservative, in particular for nitrogen. In case the specification is based on nontraceable measurements, then the specification may not be used for
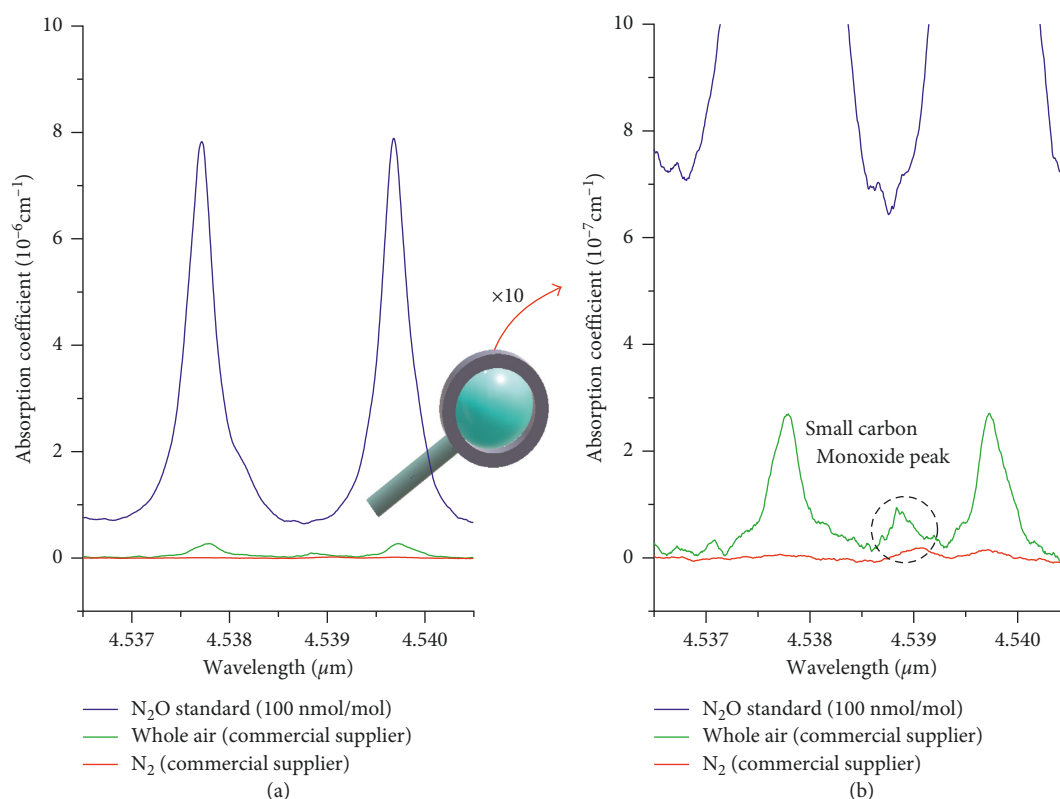
FIGURE 4: (a) Measurement of a 100 nmol/mol N_2O standard, a cylinder of whole air, and a cylinder of nitrogen. (b) 10x magnification of (a) showing more clearly the presence of N_2O in whole air.

critical impurities, yet it can be used for noncritical impurities.

To date, the CRDS spectrometer has been applied at VSL to perform purity analysis in the following gases: N_2, O_2, synthetic air, whole air, CO, CH_4, NO, and SO_2. The instrument was found to be not suitable for purity analysis of pure NO_2 as the mirrors are damaged due to the formation of a layer at the mirror surface, probably due to a reaction of NO_2 with residual H_2O. Here, some examples will be presented on purity analysis performed at VSL.

3.1.1. Methane. Methane is an important greenhouse gas with an average concentration in the atmosphere of 1853 ± 2 ppb in 2016 [16]. For the preparation of CH_4 in synthetic air, the purity analysis of nitrogen and oxygen is required while for CH_4 prepared in whole air (this is outside air from which H_2O and some other compounds are removed completely/partly), the purity analysis of the whole air matrix is needed. Figure 3 shows results of a series of measurements to determine the methane amount fraction in pure gases (N_2, O_2, and whole air). Nitrogen from 2 different suppliers and nitrogen from evaporated liquid nitrogen all contain very low methane fractions (<0.2 nmol/mol). In contrast, the 3 tested oxygen cylinders (2 different suppliers) contain relatively high amount fractions (27–43 nmol/mol). The methane amount fraction in the cylinders with whole air as measured here (1.1–1.6 nmol/mol) is in line with the values in [15] where a range of

1.0 ± 0.1 nmol/mol to 2.8 ± 0.1 nmol/mol was reported for a batch of whole air cylinders from the same supplier.

3.1.2. Nitrous Oxide. Nitrous oxide (N_2O) is an important greenhouse gas with a current ambient mole fraction of 325 nmol/mol. For the monitoring of N_2O, the WMO set a very challenging DQO of 0.1 nmol/mol in order to enable the monitoring of long-term trends. This in turn sets very high demands on the N_2O gas standards used for calibrating the instrument and thus on the purity analysis of the gases used to prepare these gas standards. The CRDS spectrometer has been operated with the long wavelength OPO (3.9–5.1 μm) to analyse nitrous oxide in various high purity matrix gases (Figure 4) employed for the preparation of N_2O gas standards.

The analysis shows that the whole air (which was cryogenically purified by the manufacturer) contains a significant amount of N_2O (3.4–3.7 nmol/mol was found in the 4 cylinders of whole air that were analysed) while the N_2O in nitrogen under test is below the detection limit of 0.2 nmol/mol (4 cylinders of nitrogen were analysed). In addition, 3 oxygen cylinders were analysed and no N_2O was observed (data not shown). The detection limit needs to be further improved to reach the 0.1 nmol/mol DQO limit of the WMO using, for example, a longer measurement cell or higher reflectivity mirrors.

3.1.3. Pitfalls in Purity Analysis: Permeation. For the analysis of most gases, polymer tubings are highly suitable due to
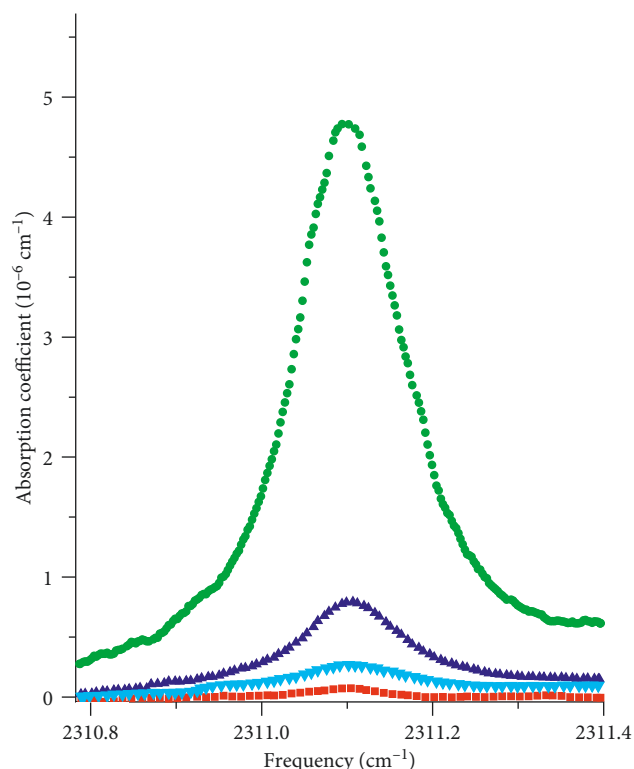
FIGURE 5: Measurement of CO_2 in high purity nitrogen using different kinds of tubings. The flow rate is 30 L/h. The observed CO_2 amount fractions are 2 nmol/mol for 2 m long stainless steel (■) tubing, 85 nmol/mol for 10 m long PTFE (●), 14 nmol/mol for the ca 1.2 m long FEP (▲), and 5 nmol/mol for the ca 0.6 m long FEP (▼).

FIGURE 6: Measurement of HNO_3 in 3 different 10 μmol/mol NO_2 standards. The PNNL spectra for HNO_3 are shown together with a water absorption spectrum from HITRAN. The highest observed HNO_3 amount fraction is 456 nmol/mol for cylinder treatment 1 with 2 μmol/mol H_2O added. The lowest observed HNO_3 amount fraction (treatment 2) is 43 nmol/mol.

their low adsorption affinity [17]. There are some notable exceptions. One example is in measurements where tubings need to be heated (e.g., in field experiments to avoid condensation of water), and polymer tubings might start releasing certain compounds [18] which can give rise to spurious results. Another notable exception is for the measurement of low amount fractions of gases which are present in high amount fractions in the atmosphere such as water and carbon dioxide. Permeation of these gases from the atmosphere to the sample gases can cause spurious readings [19]. Therefore, to determine the amount fractions of impurities like H_2O and CO_2 in pure gases, impermeable tubings such as (coated) stainless steel need to be used.

Figure 5 shows the results from measurements of CO_2 in nitrogen which has passed through a purifier from SAES (MICRO TORR, model MC190-906FV) to remove CO_2, and then the gas flows through a tubing before being analysed in the CRDS spectrometer. For impermeable tubings like stainless steel, low CO_2 amount fractions are observed (about 2 nmol/mol). For the FEP and PTFE polymer tubings, CO_2 from the laboratory air (present at around 400 μmol/mol) permeates through the tubing resulting in elevated CO_2 amount fractions. The observed amount fractions scale with the length of the tubing. For the 10 m PTFE tubing, as much as 85 nmol/mol CO_2 is observed.
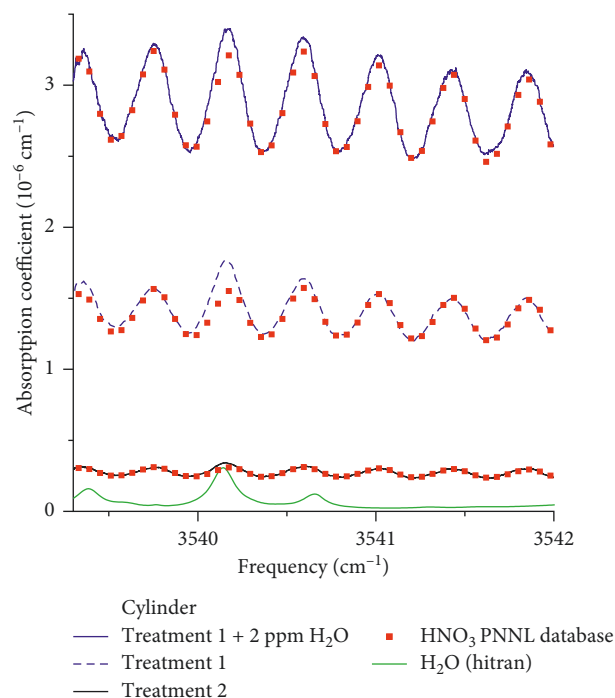
3.1.4. Nitric Acid Measurement.

In the atmosphere, NO_2 is present at amount fractions of a few nmol/mol up to 50 nmol/mol and more in streets with a lot of traffic. Traditionally, NO_2 in the atmosphere is measured indirectly by analysers based on chemiluminescence, and these instruments are mostly calibrated with nitric oxide (NO) gas standards. Recent introduction of direct NO_2-measuring instruments such as cavity attenuated phase shift spectroscopy (CAPS) [20] has led to an increased need for NO_2 gas standards at low μmol/mol level for calibration and validation purposes. Gas standards for nitrogen dioxide (NO_2) in cylinders typically contain also nitric acid (HNO_3) as was already shown by Fried and co-workers 30 years ago [21]. HNO_3 is formed in a reaction of NO_2 with residual water assumed to be mainly originating from the walls of the filling station or cylinder wall and in lesser extent from the matrix gas (high purity nitrogen from cylinders used for the mixture preparation can contain less than 20 nmol/mol water in the gas phase [22]). At VSL, a lot of effort is put in reducing residual water during the preparation of NO_2 gas standards to suppress the formation of nitric acid [23].

When measuring HNO_3, care must be taken that a proper sampling system is used as HNO_3 readily adsorbs or reacts with many parts of the sampling system [24]. Use of polymer materials is mostly recommended, and these were also used here. In a typical analysis, it takes about 30 minutes to reach a stable signal at a flow rate of 30 L/h.

HNO_3 absorption lines of the strong fundamental ν_1-band centred around 3550 cm^{-1} are measured. For this band,

no line strength data are currently available in the HITRAN database [25], and hence, the PNNL database was used to determine the HNO_3 amount fraction in the NO_2 mixtures [26].

HNO_3 has been analysed in a set of NO_2 mixtures. Two different cylinder wall treatments were tested. To some NO_2 mixtures, water was deliberately added to determine the influence of water on the nitric acid formation.

A wavelength region was selected with high HNO_3 and negligible NO_2 absorption, and spectra were recorded for NO_2 mixtures (Figure 6) prepared in gas cylinders with different cylinder wall treatments. For cylinder treatment 1, the HNO_3 amount fraction is typically 200 nmol/mol. Addition of water (2 μmol/mol) leads, as expected, to an increased amount fraction of nitric acid. Furthermore, it is noted that only small part of the 2 μmol/mol water added has been converted to HNO_3. For cylinder treatment 2, less HNO_3 is observed (about 43 nmol/mol in the example shown). Also for six other NO_2 mixtures prepared in cylinder treatment 2, low HNO_3 amount fractions were observed (typically <100 nmol/mol, data not shown). In addition, nitrous acid (HNO_2), a compound which could also be formed in a reaction between NO_2 and water, was measured in a subset of mixtures, but its presence could not be confirmed.

Using the CRDS spectrometer, it is hence possible to select cylinder treatments which provide the lowest amount fractions of nitric acid. Work is planned to use a HNO_3 permeation tube in combination with a magnetic suspension balance to dynamically generate HNO_3 to calibrate the CRDS spectrometer instead of only relying on PNNL database.

4. Conclusions

A versatile spectrometer was presented that due to its wide tuning range can detect a wide range of gases typically down to the low nmol/mol level or even lower for strong absorbing gases. The spectrometer was successfully applied to purity analysis of gases used for the preparation of reference gas standards at VSL. In addition, an example was presented of the measurement of an impurity which is formed after mixture preparation (HNO_3 in NO_2 reference gas standards). As the requirements for the accuracy of the gas standards are getting more and more challenging, purity analysis will become more often the limiting factor. Work is under way to further improve the sensitivity of the spectrometer. Note that the application of the spectrometer is not limited to purity analysis but also includes, for example, certification of measurement standards (see [27] for an example for formaldehyde).

Data Availability

Data can be provided on request.

Conflicts of Interest

The author declares that there are no conflicts of interest regarding the publication of this paper.

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