Reply to RC1

Jeongsoon Lee (Corresponding author)
leejs@kriss.re.kr

The authors appreciate Dr. Kim's kind consideration of this manuscript. Please find our replies to the referee comments below.

General Comments

1. I note that two tanks that had close-to-ambient ratios of $N_2/O_2/Ar$, namely EB0006391 and ME0434, showed excellent agreement with values derived from CRDS prior to any correction (-0.01 and 0.09 μmol/mol, respectively, in Table 4), and the TPBC corrected values actually get worse. In addition, while the TPBC corrections overall seem to make a positive impact, the correction errors still remain quite larger than the 0.01% instrument precision error that the authors suggest should be the ultimate goal. Do the authors have any comments on what other error sources could remain that would explain these results (some of which seems to already be present at the end of the discussion section)?

- The CRDS employed in this study was calibrated against the gravimetric standard suite, the matrix compositions of which are very close to that of the atmosphere. Therefore, good agreements can be expected between the CRDS responses and the CO_2 mole fractions of EB0006391 and ME0434. Although, as pointed out, a worse agreement was found with the TPBC corrected values, this is within an acceptable margin considering the CO_2 mole fraction uncertainties of the employed cylinders, which are up to 0.1 % (Table 2). The authors conjecture that other error sources arose from imperfection in the regression analysis, mole fraction uncertainties of background gas compositions, uncertainties of pressure broadening coefficients, and instrumental drift. Accurate determination of the uncertainty budget requires further study, which is beyond the scope of this work. However, the authors will add the following sentence at the end of the discussion section.
- "It is worth noting that the quality of the TPBC correction can be improved further by using quality standards with lower composition uncertainties, including $^{13}CO_2$ isotopologues and precisely measured broadening coefficients that are deduced from advanced line-shape functions such as Galatry and Rautian profiles."
- With regard to the isotope ratio, please see the reply for specific comment 1.

2. Can the authors think of any scenarios outside of creating standard tanks from scratch that the TPBC correction would be necessary or beneficial?

- Dynamic mixing methods can be adapted to explore the nature of pressure broadening. The authors' impression with regard to improving the TPBC correction quality is that precise measurement of the corresponding absorption lines fitted by advanced line-shape functions such as Galatry and Rautian is needed.

Specific Comments

1. As the authors will know, the WS-CRDS technique measures only the main $^{12}CO_2$ isotopologue. I think any effect from this can effectively be canceled out if all of the gas mixtures used in this study (listed in both Table 2 and 3) used CO_2 from the same source cylinder. I wonder if this is indeed the case, and whether the authors should briefly address this point somewhere in the manuscript.

- The volumetric standards were prepared with "dry air" and high-purity N_2 (>99.999%). The 12/13 ratio of CO_2 raw gas for the gravimetric standards was similar to the atmospheric level of approximately -11‰. This suggests similar isotope ratios would occur across the prepared cylinders. For verification (calibration) of the prepared gravimetric (volumetric) standards, the CO_2 mole fractions in them were verified by GC-FID, which measured the total carbon isotopes. Therefore, the isotope effects were hardly discernable in this study. However, it might be the case that the isotope ratios of CO_2 in "dry air" can vary or deviate from those in the CO_2 raw gas to cause some extent of discrepancy in the CRDS response. The authors will add the following sentences at the end of section 2.1 as follow.
- "The $^{12}C/^{13}C$ ratio of CO_2 raw gas for the gravimetric standards was similar to the atmospheric level of approximately -11‰, which suggests similar isotope ratios would occur across the prepared cylinders as determined by gravimetry and volumetry. Nevertheless, isotope effects biasing the CRDS response seemed to be hardly discernable in this study because verification (calibration) of the CO_2 mole fractions in the prepared gravimetric (volumetric) standards was carried out by GC-FID, which measured the total carbon isotopes."

2. P3-L13: Was any correction to the concentrations applied based on the verification test on the GC, and if so how much? The authors state the verification test results were excellent (0.05 and 0.1 % 2σ), but it would be interesting to see if those that looked worse in the verification test also showed larger deviation in the TPBC corrections. Perhaps this could be added in a supplementary section?

- Only "survivors" from the verification measurements for the gravimetric standards were used in this study. That is, outliers over the uncertainty of the verification measurement, identifying human error during the gas handling, were removed from the testing list. It should be noted that the weighing uncertainty is much less than that of the verification measurement. Additionally, the CO_2 mole fraction uncertainty of the gravimetric mixtures included uncertainties associated with the weighing process, raw gas purities, and verification tests.

3. P3-L20: I think a more detailed description is needed for the static volumetric standard gas section. For example, line 22 mentions "dry air", is this some CO_2-free zero air that was used as the "complementary gas" (using the terminology in ISO 6144), or does it just refer to what was already in the tank prior to the "high-purity N_2" injection? Line 24 says the concentrations of the manometric cylinders were "confirmed" against the gravimetric standards: I would like clarification on whether the independent manometric values were confirmed by measurements against the gravimetric standards (on GC-FID?), and if so how the manometric vs gravimetric values compared, or if the values in the manometric tanks were "determined" from measurements against the gravimetric tanks. If the values were only confirmed, it would be nice to see how the values compared, perhaps in a supplementary section.

- The "dry air" referred to dehumidified air with CO_2, which was already in the cylinder prior to the high-purity N_2 injection. It was assumed that the high-purity N_2 (> 99.999%) did not contain O_2, Ar, and CO_2 impurities; hence, it was possible to predict the mole fractions of the four components. Because of the daily variation of CO_2, the CO_2 mole fraction was given by the calibrated values against the gravimetric standards. The term "manometric" was used to express the control of the mixing ratio using the volumetric ratio in this study; it will be toned down by replacing it with "volumetric mixing." The following sentences will be added in the corresponding section of the text.
- "Ambient air was collected with a pressurizing pump through a chemical moisture trap containing $Mg(ClO_4)_2$ in order to yield the complementary gas, namely dry air. The amount of N_2 was then varied by diluting the dry air with high-purity N_2 (> 99.999%), which eventually led to a variation in the mole fractions of the major components, N_2, O_2, Ar, and CO_2. In this way, the mole fractions of the background gas composition can be easily predicted by using the measured pressure ratio of the filled gas. In the case of the CO_2 mole fraction, three volumetric cylinders (EBXXXXXXX) were calibrated against the gravimetric standards (Table 2), because the mixing ratio of atmospheric CO_2 varies each day. Eventually, the compositions of EB0006391 and ME0434 closely reflected the atmospheric ratio of the major components."

4. P4-L18: The numbers for the y-scale shown in Figure 4 (roughly -10 ~ 5.5?) do not seem to match those in column 4 of Table 7 (-0.47 ~ 0.60), but instead those in Table 4. Authors should check that this is only a graphing error and do not affect the conclusions of the paper. Tables 4 and 7: I understand the logic of the authors' choice of separating the two tables to match the flow of the manuscript, however I do find myself frequently comparing the N_2-only vs TPBC corrected results. As such I would suggest that they be combined into one table, to represent an overview of the findings reported in this work, but I will leave that for the authors to decide.

- We apologize for the confusion. In Figure 7, $D_{STD-CRDS}$, as defined in P4-L34, denotes the deviation between the CO_2 mole fraction of the standard and the corresponding CRDS response. However, in Table 7, the same value, $D_{STD-CRDS}$, was not given contrast to Table 4 (fifth column). As suggested, Table 4 and Table 7 will be combined to enhance the readability.

Technical Corrections

1. P1-L29: “not plausible” suggests that this can’t be done in the future, which may be true, but we should still remain hopeful that substantial progress in the modeling front can still be made. Perhaps change to “not yet feasible” instead?

- This will be corrected as suggested.

2. P3-L20: I would suggest that the authors start a new paragraph for the section on the volumetrically prepared tanks.

- The preparation section will be separated and modified as suggested.

3. P3-L22: Is the “high-purity N_2” used in the dilution different from the “ultra-high-purity nitrogen” mentioned in line 15? If they are the same, then I would advise using the same naming scheme for both.

- They are the same. “Ultra-high-purity nitrogen” will be replaced with “high-purity N_2.”

4. P3-L24: “comprised” -> “is comprised of”

- Dr. Kim might be referring to P3-L34 here. It will be corrected as suggested.

5. P3-L25: Perhaps mention which of the tanks reflect ratios close to ambient? I assume EB0006391 and ME0434?

- The following sentence will be added: “Eventually, the compositions of EB0006391 and ME0434 closely reflected the atmospheric ratio of N_2, O_2, Ar, and CO_2.”

6. P3-L40: “through a built-in diaphragm pump”: Technically, I believe the pump pulls a vacuum after the cavity cell, whereas the authors’ description gives the impression that air may go through the diaphragm pump into the cavity cell. Suggest editing this sentence to avoid ambiguity.

- Apologies for the ambiguity. The corresponding sentence will be corrected to “the optical cavity backed by a built-in diaphragm pump."

7. P3-L41: "inner" -> Did the authors mean "outer"?

- This will be revised as suggested.

8. P4-L8: "gravimetric standards" -> add "described in Table 3" after. How were these standards prepared in terms of N2, O2, and Ar? I assume at ambient ratios? This may be an important point, as the authors use the calibrations from these tanks as "truth".

- The corresponding sentence will be corrected to "gravimetric standards, in which the N_2, O_2, and Ar ratio is close to that in the atmosphere ratio, with CO_2 concentrations..."

9. p5-L13: Include reference for "HITRAN2004"?

- The reference was included in the references section.

10. P5-L16: "that" -> "those"

- This will be corrected as suggested.

11. Table 6: I do not follow the author's foot note "1 and 2 denote values obtained in each study" for this table. I assume the numbers in this table were derived using the PBC's in Table 5 with the known N2, O2, and Ar ratios? But, aren't the HITRAN numbers calculated the same way, or am I mistaken? The footnote almost seems more appropriate for Table 5, where the PBC values in the table were taken from each study, but then are the HITRAN numbers different in this regard? Please clarify.

- Thank you for the comment. The footnote will be deleted. To enhance readability, the following sentence will be added as a footnote.
- "Pressure broadenings were estimated without Ar due to the absence of a broadening coefficient in the corresponding studies."

Reply to RC2

Jeongsoon Lee (Corresponding author)
leejs@kriss.re.kr

The authors appreciate Dr. Loh's kind consideration of this manuscript. Please find our replies to the referee comments below.

General Comments

1. The authors present a set of total pressure broadening coefficients (TPBCs) that substantially improve agreement between CRDS determined CO_2 mixing ratios and the mixing ratios assigned to each tank during gravimetric or manometric preparation. However, the use of TPBCs does not reduce the discrepancy to within the World Meteorological Organization's CO_2 inter-laboratory compatibility goal of +/- 0.1 umol/mol (in the Northern Hemisphere, and 0.05 umol/mol in the Southern Hemisphere). As such, I would urge the authors to consider appending something similar to the following to the end of their abstract.

   P1, L20: "... instrument calibration, or better still, use standards prepared with ambient air."

   Additionally, I would like the authors to consider adding a sentence or two to this effect in their discussion section.

   - Thank you for the suggestion. Authors will add sentence as follow.
   - P1, L20: "…. Instrument calibration or use standards prepared in same background composition of ambient air.

   - The authors conjecture that major error sources arose from the mole fraction uncertainties of major components, e.g. N_2, O_2, Ar and CO_2, and uncertainty of pressure broadening coefficients. According to this opinion, the authors will add sentences at the end of discussion section as follow.
   - "It is worth noting that the quality of the TPBC correction can be improved further by using quality standards with lower composition uncertainties, including $^{13}CO_2$ isotopologues and precisely measured broadening coefficients that are deduced from advanced line-shape functions such as Galatry and Rautian profiles."
   - With regard to the isotopes ratio, please see the reply for general comment 2.

2. A further comment is that the authors do not mention the isotopic composition of the CO_2 used to prepare their synthetic standards. While I assume all eight standards were prepared

with the same batch of CO_2 (and thus having the same CO_2 isotopic composition), this is worth mentioning (and handling) explicitly (preferably with the $\delta^{13}CCO_2$ of the pure CO_2 used). As CRDS is a single line spectroscopic technique, it is inherently isotopologue specific. Therefore, using a pure CO_2 source with a significantly different isotopic composition from the background atmosphere will induce a systematic bias in CRDS determinations of mixing ratio unless this effect is accounted for. The authors already cite Lee et al. (2006), which deals with this question (though for NDIR rather than CRDS (for which the problem is at its most extreme)), so I assume they are familiar with the issue.

- The authors understand this comment is very similar to first specific comment of RC1. The 12/13 ratio of CO_2 raw gas for gravimetric standards was similar to the atmospheric level approximately -11‰. The volumetric standards with prepared with the dry air and high purity N_2 (>99.999%). This suggests similar isotope ratios would occur across the prepared cylinders. For verification (calibration) of prepared gravimetric (volumetric) standards, the CO_2 mole fractions in them were verified by GC-FID, which measured total carbon isotopes. Therefore, the isotope effect were hardly discernable in this study. However, it might be the case that the isotope ratios of CO_2 in the "dry air" can vary or deviate from the CO_2 raw gas to cause some extent of discrepancy in the CRDS response. The authors will add sentences at the end of the section 2.1 as follow.
- The $^{12}C/^{13}C$ ratio of CO_2 raw gas for the gravimetric standards was similar to the atmospheric level of approximately -11‰, which suggests similar isotope ratios would occur across the prepared cylinders as determined by gravimetry and volumetry. Nevertheless, isotope effects biasing the CRDS response seemed to be hardly discernable in this study because verification (calibration) of the CO_2 mole fractions in the prepared gravimetric (volumetric) standards was carried out by GC-FID, which measured the total carbon isotopes."

Specific Comments

5. P1 L28, consider inserting 'all' between quantify and its, and remove "considerably"

- It will be corrected as suggested.

6. P3 L20, gases to become 'gas'

- It will be corrected as pointed out

Validation of spectroscopic gas analyzer accuracy using gravimetric standard gas mixtures: Impact of background gas composition on CO_2 quantitation by cavity ring-down spectroscopy

Jeong Sik Lim, Miyeon Park, Jinbok Lee, Jeongsoon Lee

Center for Gas Analysis, Metrology for Quality of Life, Korea Research Institute of Standards and Science (KRISS), Gajeong-ro 267, Yuseong-gu, Daejeon 34113, Republic of Korea

Correspondence to: Jeongsoon Lee (leejs@kriss.re.kr)

Abstract. Effect of background gas composition on the measurement of CO_2 levels was investigated by wavelength-scanned cavity ring-down spectrometry (WS-CRDS) employing a spectral line centered at the R(1) of the $(3\ 0^0\ 1)_{III} \leftarrow (0\ 0\ 0)$ band. For this purpose, eight cylinders with various gas compositions were gravimetrically and volumetrically prepared within $2\sigma = 0.1\ \%$, and these gas mixtures were introduced into the WS-CRDS analyzer calibrated against standards of ambient air composition. Depending on the gas composition, deviations between CRDS-determined and gravimetrically (or volumetrically) assigned CO_2 concentrations ranged from -9.77 to 5.36 µmol/mol, e.g., excess N_2 exhibited a negative deviation, whereas excess Ar showed a positive one. The total pressure broadening coefficients (TBPCs) obtained from the composition of N_2, O_2 and Ar thoroughly corrected the deviations up to -0.5–0.6 µmol/mol, while these values were -0.43–1.43 µmol/mol considering PBCs induced by only N_2. The use of TBPCs enhanced deviations to be corrected to ~0.15 %. Furthermore, the above correction linearly shifted CRDS responses for a wide extent of TPBCs ranging from 0.065 to 0.081 $cm^{-1}\ atm^{-1}$. Thus, accurate measurements using optical intensity-based techniques such as WS-CRDS require TBPC-based instrument calibration or use standards prepared in same background composition of ambient air.

1 Introduction

Emission of carbon dioxide (CO_2), the most important greenhouse gas, has been reported to increase, resulting in global climate change (Messerschmidt et al., 2011; Solomon et al., 2007). According to the IPCC Fourth Assessment Report (Solomon et al., 2007), CO_2 is the major contributor to global warming, having a 62.9 % share of the total radiative force caused by long-lived greenhouse gases. Although it is not yet feasible to quantify all its sources and sinks within small uncertainties (Conway et al., 1988; Schulze et al., 2009), all countries have agreed to consistently control CO_2 emissions, necessitating accurate measurements of atmospheric CO_2 mole fractions. Gas chromatography (GC) coupled with flame ionization detection (FID) (van der Laan et al., 2009), non-dispersive infrared spectroscopy (NDIR) at 4.26 µm (Lee et al., 2006; Min et al., 2009; Crawley, 2008; Tohjima et al., 2009), Fourier transform infrared (FTIR) spectroscopy (Griffith et al., 2012), tunable diode laser absorption spectroscopy (TDLAS) (Durry et al., 2010), wavelength-scanned cavity ring-down spectroscopy (WS-CRDS) (Crosson, 2008), and other cavity-enhanced absorption spectroscopies (O'Shea et al., 2013) are well-known techniques for quantifying atmospheric CO_2. Despite exhibiting the advantage of high measurement precision, GC-FID suffers from long acquisition time due to delayed CO_2 retention in the separation column (typically a few tens of minutes). NDIR shows better performance than GC-FID in real-time measurements due to using filtered spectral fingerprints of CO_2 instead of relying on analyte separation. However, frequent calibrations are required to correct NDIR response drifts. Recently, WS-CRDS has attracted attention because of its high precision and low drift. In contrast to intensity-based techniques such as NDIR and TDLAS, CRDS is immune to laser shot noise and detector electric noise due to employing the ring-down count method. Furthermore, the increased path length offered by the resonant optical cavity provides excellent sensitivity, i.e., signal-to-noise ratio, and high precision. Since a CO_2 inter-laboratory compatibility of ± 0.1 μmol/mol in the Northern Hemisphere was set as a goal by the World Meteorological Organization (WMO), WS-CRDS is viewed as a competitive technique for measuring atmospheric greenhouse gas levels (Rella et al., 2013).

Accurate measurements of atmospheric CO_2 levels by WS-CRDS require the removal of water vapor, which causes spectral interference, and an empirical cubic polynomial model for correcting the water background has been developed (Rella et al., 2013). Nevertheless, CO_2 mole fraction measurements can be adversely affected by spectral line broadening if calibration gas mixtures whose background composition is different from the natural N_2:O_2:Ar ratio in the atmosphere are used (Nara et al., 2012). In this study, standard gas mixtures containing ambient levels of CO_2 in synthetic air (N_2 + O_2 + Ar) were gravimetrically prepared for utilization as calibration standards and measuring targets for investigating the impact of background gas composition on WS-CRDS responses, owing to the excellent uncertainty of gravimetric gas mixtures. Furthermore, an empirical equation for correcting the "matrix effect" was derived in terms of total pressure broadening. The good agreement achieved between CO_2 mole fractions of the calibration standards and synthetic samples of arbitrary composition validated the measurement accuracy of matrix-effect-corrected WS-CRDS.

2 Materials and methods

2.1 Preparation of standard gas mixtures

Gas mixtures were prepared using gravimetric and volumetric methods, based on ISO 6142 (International Standard, 2001) and ISO 6144 (International Standard, 2003), respectively. The gravimetric method featured filling pure CO_2 (MG industries, USA) and N_2 (Deokyang Energen, South Korea) gases into a clean aluminum cylinder. Subsequently, pure O_2 (Praxair Co., South Korea) and Ar (Deokyang Energen, South Korea) gases were added to the obtained CO_2/N_2 mixture to obtain an ambient level of CO_2 in a matrix of synthetic air. The amounts of filled gases were determined based on their weight, which was obtained by weighing the aluminum cylinder before and after filling. The weights used for calibrating the weighing balance (Mettler Toledo, XP 26003L, USA) were calibrated against the national kilogram standard to ensure measurement traceability. For high weighing precision, an automatic weighing machine patented by KRISS was used to control the loading position on the weighing pan of the top loading balance, resulting in a typical weighing uncertainty of less than 0.005 %. A circular turntable was used to support tare and sample cylinders. During weighing, the drift of the weighing balance and the buoyancy effect exerted by the cylinders were effectively corrected or cancelled out by using the following bracketing sequence: tare – cylinder A – tare – cylinder B – tare – cylinder C. The preparation of standard gas mixtures based on this technique has been reported in detail elsewhere (Wessel, 2008). The CO_2 mole fraction in the resulting mixture can be computed as follows:

$$y_j = \frac{\sum_{\mathrm{A}=1}^{P}\left(\frac{x_{j,\mathrm{A}} \cdot m_{\mathrm{A}}}{\sum_{i=1}^{n} x_{i,\mathrm{A}} \cdot M_{\mathrm{i}}}\right)}{\sum_{\mathrm{A}=1}^{P}\left(\frac{m_{\mathrm{A}}}{\sum_{i=1}^{n} x_{i,\mathrm{A}} \cdot M_{i}}\right)} \tag{1}$$

Here, y_j is the mole fraction of component j in the gas mixture, P is the total number of parent gases, n is the total number of components in the final mixture, m_{A} is the measured mass of parent gas A, M_i is the molar mass of component i, and $x_{i,\mathrm{A}}$ or $x_{j,\mathrm{A}}$ is the mole fraction of component i or j in parent gas A. Therefore, quantification of impurities present in pure parent gases is needed to determine the composition of each parent gas. Hence, impurities in N_2, O_2, Ar, and CO_2 were analyzed by gas chromatography employing various detection methods, e.g., thermal conductivity detection (TCD), pulsed discharge detection (PDD), flame ionization detection (FID), and atomic emission detection (AED), with detector assignments for all impurities given in Table 1. Purity, namely the mole fraction of the dominant component in “pure” parent gas (x_{pure}) was determined as follows:

$$x_{\mathrm{pure}} = 1 - \sum_{i=1}^{N} x_i \qquad (2)$$

where N is the number of impurities likely to be present in the final mixture. For selecting target impurities, the source and its purification process were considered. If the expected impurity was not detected, its mole fraction was set to half of the limit of detection (LOD/2), and the associated standard uncertainty was defined as the assigned mole fraction divided by √3, e.g., LOD/(2·√3), as expected for a uniform probability density function ranging from 0 to LOD [International Standard, 2001]. In particular, it was very important to accurately analyze the mole fractions of target components (N_2, O_2, Ar, and CO_2) in the respective raw gases, since the weighed target component amount in the obtained mixture could be biased by the presence of the same component in other raw gases as an impurity. For instance, the mole fractions of CO_2 in pure N_2, O_2, and Ar gases were determined as 0.002, 0.195, and < 0.002 μmol/mol, respectively. Thus, the amounts of CO_2 in pure N_2 and Ar gases were negligible and did not impact final mixtures with CO_2 fractions above 300 μmol/mol. However, the large amount of CO_2 in pure O_2 led to a bias of 0.04 μmol/mol, which was comparable to the uncertainty level of the final mixture. Table 1 summarizes the reference values and associated uncertainties of major impurities in raw gases.

For CO_2, a verification test was representatively performed to determine the potential systematic error of the gravimetric procedure described above, relying on comparing the detection sensitivity of CO_2 in different gas mixtures using GC-FID coupled with an MS-5A (molecular sieve 5A, 4 m) separation column. The column oven was kept at 30 °C, and high-purity N_2 (99.999 %, Deokyang Energen) was used as a carrier gas. Sample gas flows were carefully controlled to ensure that the same amount of gas was introduced into the sample loop regardless of its composition; for this purpose, mass flow controllers (MFCs) were calibrated using a flow meter (Digital flow calibrator (cat#20123), Restek Inc., USA). Therefore, the CO_2 mole fraction uncertainty of prepared mixtures included uncertainties associated with the weighing process, raw gases purities, and verification tests, resulting in a gravimetric preparation uncertainty of less than 0.1 μmol/mol (1σ).

The standard gas mixture denoted as EBXXXXXXX (Table 2) was prepared by the static volumetric method (International Standard, 2003; Waldén, 2009). Ambient air was collected with a pressurizing pump through a chemical moisture trap containing $Mg(ClO_4)_2$ in order to yield the complementary gas, namely dry air. The amount of N_2 was then varied by diluting the dry air with high-purity N_2 (> 99.999%), which eventually led to a variation in the mole fractions of the major components, N_2, O_2, Ar, and CO_2. In this way, the mole fractions of the background gas composition can be easily predicted by using the measured pressure ratio of the filled gas. In the case of the CO_2 mole fraction, three volumetric cylinders (EBXXXXXXX) were calibrated against the gravimetric standards (Table 2), because the mixing ratio of atmospheric CO_2 varies each day. Eventually, the compositions of EB0006391 and ME0434 closely reflected the atmospheric ratio of the major components. Notably, all prepared gas mixtures were maintained under very dry conditions, with the mole fraction of H_2O being less than 5 μmol/mol.

The $^{12}C/^{13}C$ ratio of CO_2 raw gas for the gravimetric standards was similar to the atmospheric level of approximately -11‰, which suggests similar isotope ratios would occur across the prepared cylinders as determined by gravimetry and volumetry. Nevertheless, isotope effects biasing the CRDS response seemed to be hardly discernable in this study because verification (calibration) of the CO_2 mole fractions in the prepared gravimetric (volumetric) standards was carried out by GC-FID, which measured the total carbon isotopes.

2.2 Cavity ring-down spectroscopy

Cavity ring-down spectroscopy (CRDS) as an ultrasensitive technique introduced by O’Keefe and Deacon in 1988 (Chen et al., 2010; Rothman et al., 2005). In principle, the leakage rate of the trapped laser source in the optical cavity can be fitted by monoexponential decay, and absorbance at wavelength λ can then be calculated from the difference of ring-down signal decay rates in the presence and absence of the target gas. Alternatively, the absorbance at λ can be determined from the ring-down time at the non-absorbing wavelength λ_0 in the presence of the target gas. In this study, a commercial wavelength-scanned cavity ring-down spectrometer (WS-CRDS, G-1301, Picarro, USA) was employed. Since the WS-CRDS system has been described elsewhere (Chen et al., 2010; Nara et al., 2012), only a brief description is provided here. The WS-CRDS analyzer, operating at a wavelength of 1.603 μm that corresponds to R(1) of the $(3\ 0^0\ 1)_{III} \leftarrow (0\ 0\ 0)$ band, is comprised of diode lasers, a high-precision wavelength monitor, a high-finesse cavity defined by three high-reflectivity mirrors (<99.995 %), a photodiode detector, and a data acquisition computer. Laser light confined in the cavity traveled along the triangular optical axis, exhibiting an effective path length of 15–20 km. Ambient air or gas from a pressure-regulated tank was supplied to the optical cavity backed by a built-in diaphragm pump, which was conditioned to a highly controlled pressure and temperature of 140 ± 0.05 Torr and 40 ± 0.01 °C, respectively.

For this study, a gas flow rate of 400 mL/min and a pig-tailed bypass-out were combined to achieve a steady gas flow undisturbed by laboratory pressure fluctuation, yielding a constant pressure in the CRDS cavity (Fig. 1). The outer diameters of stainless steel tubes connecting highly pressurized cylinders to the MFC (5850E, Brooks Inc., USA) inlet and the MFC to the spectrometer equaled 1/8 and 1/16 inch, respectively. High-purity nitrogen was used for flushing the gas lines and CRDS analyzer between switching cylinders.

The measured spectral line consisting of ~10 points was fitted by the Galatry profile to obtain quantitative information, based on the assumption that the CRDS read-out was influenced only by variations in the CO_2 concentration of tested samples, and not by variations of background gas composition (Chen et al., 2010). This assumption implies that the peak height of the fitted profile was regarded as a CRDS read-out instead of the corresponding integrated area (Nara et al., 2012). As described in Table 3, CRDS responses were calibrated against gravimetric standards, in which N_2, O_2 and Ar ratio is close to that in the atmosphere ratio, with CO_2 concentrations very similar to those of ambient air (between 360 and 410 μmol/mol). Absorbance was found to be linearly proportional to the concentration of light-absorbing gas, as indicated by the straight-line fit of CRDS responses with $R^2 \sim 0.9999$ (Fig. 2 and Table 3), supporting the validity of the attempted calibration and the hypothesis proposed in this study. In other words, deviations from expected sensitivity (i.e., CRDS response divided by the gravimetric concentration of CO_2) were due to deviations in the composition of background gas from that of ambient air, namely the extent of alien gas line broadening or narrowing.

3 Results & discussion

To investigate the effect of background gas composition on CRDS responses, gas mixtures were analyzed against ambient-air-like standards using a well-calibrated CRD spectrometer (Table 4).

Deviations of CO_2 concentrations determined by CRDS from those assigned by gravimetry (or volumetry) ranged from –2.44 to 1.39 %. CRDS responses of EB0006391 and ME0434 were in good agreement with the assigned CO_2 concentrations, showing deviations of less than 0.1 μmol/mol, whereas extreme deviations of greater than 1 % were observed for cylinders DF4560 and ME5537. In particular, the CO_2 concentration of DF4560 (CO_2 in pure N_2) showed a deviation of –9.77 μmol/mol. Therefore, it can be conjectured that N_2-induced broadening is more important than that induced by other background gases, O_2 and Ar. Since the optical cavity was kept at constant pressure and temperature, Doppler broadening was not considered. Instead, collision-induced broadening (or narrowing) was invoked in the case of variable composition. The collisional half-width, i.e., the total pressure broadening coefficient (γ_{TPB}), can be expressed as follows:

$$\gamma_{TPB} = \sum_{i=1}^{n} \gamma_i \cdot p_i \tag{3}$$

where γ_i is the pressure broadening coefficient (PBC) of component *i*, and p_i is the partial pressure of component *i*, e.g., its molar fraction multiplied by the cavity pressure of 18 kPa. The maximum peak height of the Galatry profile at a given background gas composition, $G(\gamma)$, can be assumed to be linearly proportional to the PBC for a sufficiently narrow interval of p_i, Δp_i (Varghese and Hanson, 1984). In view of the dominance of N_2-induced pressure broadening, the difference between CRDS-determined and gravimetrically (volumetrically) assigned CO_2 concentrations of the measured sample, $D_{STD\text{-}CRDS}$, can be determined as follows:

$$D_{STD-CRDS} \propto G(\gamma) \propto \gamma_{N_2} \cdot p_{N_2} \tag{4}$$

As shown in Fig. 3, a linear relationship between $D_{STD\text{-}CRDS}$ and N_2-induced line broadening was found at given partial pressures (i.e., mole fractions multiplied by cavity pressure) in the optical cavity.

The PBC of N_2 was set to 0.08064 cm^{-1} atm^{-1}, as reported by Nakamich et al. (2006). Since N_2 showed the largest PBC among those of other background components, positive (or negative) deviations between CRDS-determined and assigned CO_2 concentrations of tested cylinders, i.e., the lower (or higher) extent of pressure broadening, were observed at N_2 concentrations below (or above) the ambient value of 78 cmol/mol corresponding to ME5590 (Table 4). Thus, the CO_2 concentration could be corrected based on the following linear fit:

$$y_{corrected} = y_{CRDS} - \left(-606.63 \cdot \gamma_{N_2} \cdot p_{N_2} + 38.656\right) \tag{5}$$

where $\gamma_{N_2} \cdot p_{N_2}$ is the N_2-induced pressure broadening, y_{CRDS} is the value obtained by WS-CRDS, and $y_{corrected}$ is the CO_2 concentration corrected for N_2-induced pressure broadening. Corrected CO_2 concentrations exhibited good agreement (within 0.4 %) with the regression fit (R^2 ~ 0.9736). This correction error significantly exceeded the instrumental precision (reported as 0.01 % (1σ); Nara et al., 2012), strongly suggesting the presence of other error sources.

The pressure broadening correction of ME5537 showed the highest deviation of 0.4 %. The background gas composition of ME5537 (70.98 % N_2, 18.85 % O_2, and 10.13 % Ar) implied that the Ar content should be taken into account for the correction. Since CO_2 self-broadening is negligible due to the low concentration of CO_2 compared to that of other components (N_2, O_2, and Ar) in the investigated gas mixtures, the total pressure broadening coefficient (TPBC) could be expressed as a function of alien gas PBCs and the partial pressures of the corresponding components:

$$\gamma_{TPBC} = \gamma_{N_2} p_{N_2} + \gamma_{O_2} p_{O_2} + \gamma_{Ar} p_{Ar} \tag{6}$$

Table 5 shows the reported PBCs for N_2, O_2, and Ar, and Table 6 shows TPBCs of all cylinders, with (a), (b), and (c) denoting results obtained independently by Pouchet et al. (2004), Nakamichi et al. (2006), and HITRAN2004 (Rothman et el. 2005), respectively.

Since the coefficients of Ar have not been reported by Pouchet et al. (2004) and HITRAN2004, the corresponding TPBCs include only N_2- and O_2-related pressure broadening (Table 6). Therefore, the TPBCs in (a) and (c) were underestimated in comparison to those in (b). For instance, TPBCs of 0.0636 and 0.0685 were obtained for cylinder ME5537 in the cases of (a) and (c), respectively, with the value for (b) equaling 0.07625. As shown in Table 6, the TPBC of ME5537 exhibited the largest deviation of 20 %, originating mainly from the Ar mole fraction. Figure 4 shows $D_{STD\text{-}CRDS}$ values (taken from fourth column in Table 4) as a function of calculated TPBCs (taken from Table 6).

TPBC values reported by Nakamichi et al. (2006) exhibited a linear correlation with CRDS responses within the investigated background composition interval. In practice, Huang and Yung (2004) reported that the Lorentzian width is inversely proportional to the peak value of the Voigt function for a fixed Gaussian width. The results shown in Fig. 4 reveal that $D_{STD\text{-}CRDS}$ values decreased with increasing TPBCs, in agreement with previous reports (Huang and Yung, 2004). Only the result of (b) exhibited a fairly linear behavior; however, non-linearity was observed when the broadening coefficients of O_2 or Ar were not taken into account. The following equation was derived for correcting CRDS-determined concentrations:

$$y_{corr.TPB} = y_{CRDS} - (-3382.1 \cdot \gamma_{TPBC} + 262.65) \tag{7}$$

Here, y_{CRDS} is the CRDS-measured value of the standard gas mixture, and $y_{corr.TPB}$ is the corresponding corrected CRDS response computed using the relation in (b) (Fig. 4). Table 4 summarizes the results obtained after correction using Eq. (7), showing that the correction was improved from 0.68 (N_2 PBC) to 0.33 µmol/mol (TPBC) in terms of standard deviations (1σ) of differences (corrected minus gravimetry-assigned). Furthermore, R^2 was improved to 0.99 when pressure broadening related to three main components of air (N_2, O_2, and Ar) was taken into account. For every cylinder, excellent agreement was observed after implementing the TPBC corresponding to the assigned values. In particular, even cylinders DF4560, ME5590, and ME5537, whose background gas compositions were significantly different from that of ambient air, exhibited good correlation of CO_2 concentrations determined by CRDS with those assigned by gravimetry or volumetry. It is worth noting that the quality of the TPBC correction can be improved further by using quality standards with lower back ground composition uncertainties, including $^{13}CO_2$ isotopologues and precisely measured broadening coefficients that are deduced from advanced line-shape functions such as Galatry and Rautian profiles.

4 Conclusions

In this study, we investigated the impact of background gas composition on spectroscopic quantitation of CO_2 at ambient concentration. Standard gas mixtures with various background compositions were prepared by gravimetry or volumetry for use as calibration standards and test samples. Purity analysis and gravimetric weighing showed high accuracy and precision. For purity analysis, analytical techniques such as GC-PDD, TCD, FID, AED, and dew point metering were used. Raw gas (N_2, O_2, Ar, and CO_2) purities were obtained within uncertainties of less than 0.001 % (1σ). Moreover, biasing impurities in N_2, O_2, and CO_2 were accurately crosschecked. With a weighing precision of 0.007 %, the preparation uncertainties of gravimetric and volumetric mixing were demonstrated to be lower than 0.05 and 0.1 % (2σ), respectively, after performing verification tests. The preparation uncertainty of volumetry was slightly higher than that of gravimetry, still being sufficiently satisfactory to distinguish error sources for “matrix effect” correction. Based on the composition accuracy of the prepared gas mixtures, CO_2 levels were determined by WS-CRDS for eight standard gas mixtures with different background compositions. An injection unit with a bypass-out was used to ensure a precise and moderate gas inflow from a highly pressurized cylinder to the WS-CRD spectrometer, which was calibrated against well-certified standard gas mixtures of air composition with CO_2 levels of 360–410 µmol/mol. Among the eight cylinders, the CRDS responses of EB0006391 and ME0434 were well-matched to the corresponding preparative values, whereas the values obtained for other cylinders exhibited large deviations between +5.36 and −9.77 µmol/mol. For a N_2-enriched mixture (DF4560), the CRDS-determined CO_2 concentration was 2.44 % lower than the preparative value. Since CRDS calibration was performed using standards with ambient air composition, the fact that CRDS responses tended to be negative for N_2-enriched and positive for Ar-enriched mixtures was in good agreement with the results obtained in earlier experimental (Nara et al., 2012; Zhao et al., 1997) and theoretical studies (Huang and Yung, 2004), reflecting the dependence of line broadening on alien gas composition.

Therefore, a linear shift of CRDS responses was observed for TPBCs above 0.05 cm^{-1} atm^{-1}, which covers 20 % N_2-enriched and 10 % Ar-enriched gas mixtures. TPBC-corrected CRDS responses were in good agreement with the gravimetric (or volumetric) concentration of the investigated gas mixtures within 0.15 % (± 0.6 µmol/mol). Considering the instrumental uncertainty of 0.01 % (1σ), the improved PBC uncertainties should lead to lower discrepancies of corrected CRDS responses.

The correction presented in Eq. (7) works only for the designated vibrational transition, i.e., R(1) of the $(3\ 0^0\ 1)_{III} \leftarrow (0\ 0\ 0)$ band at 1.603 μm, and referred PBCs, but a similar calibration strategy can be used for determining gas mixing ratios by other intensity-based optical measurement techniques.

Code availability: Not applicable

Data availability: Not applicable

Appendices: None

Supplement link: N/A

Team list: Jeong Sik Lim, MiYeon Park, Jinbok Lee, and Jeongsoon Lee

Author contribution: Jinbok Lee prepared the certified reference materials, J. Lim and M. Park performed measurements and analysis. Jeongsoon Lee designed experiments, and J. Lim prepared the manuscript with contributions from other co-authors.

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

Disclaimer: None.

Acknowledgements: This work was funded by the Korea Meteorological Administration Research and Development Program under Grant No. KMIPA 2015-2032. No data sharing issues exist, as all numerical information is provided in the figures produced by solving the equations in this paper. All data in this paper are properly cited and referred to in the reference list.

References

Chen, H., Winderlich, J., Gerbig, C., Hoefer, A., Rella, C. W., Crosson, E. R., Van Pelt, A. D., Steinbach, J., Kolle, O., Beck, V., Daube, B. C., Gottlieb, E. W., Chow, V. Y., Santoni, G. W., and Wofsy, S. C.: High-accuracy continuous airborne measurements of greenhouse gases (CO_2 and CH_4) using the cavity ring-down spectroscopy (CRDS) technique, Atmos. Meas. Tech., 3, 375–386, doi:10 doi:10.5194/amt-3-375-2010.5194/amt-3-375-2010, 2010.

Conway, T. J., Tans, P., Waterman, L. S., Thoning, K. W., Masarie, K. A., and Gammon, R. H.: Atmospheric carbon dioxide measurements in the remote global troposphere 1981-1984, Tellus, Ser. B., 40B(2), 81–115, doi: 10.1111/j.1600-0889.1988.tb00214.x, 1998.

Crawley, L. H.: Application of non-dispersive infrared (NDIR) spectroscopy to the measurement of atmospheric trace gases, MSc Thesis, University of Canterbury, Christchurch, New Zealand, 2008.

Crosson E. R.: A cavity ring-down analyzer for measuring atmospheric levels of methane, carbon dioxide, and water vapor, Appl. Phys. B, 92, 403–408, doi: 10.1007/s00340-008-3135-y, 2008.

Durry, G., Li, J. S., Vinogradov, I., Titov, A., Joly, L., Cousin, J., Decarpenterie, T., Amarouche, N., Liu, X., Parvitte, B., Korablev, B., Gerasimov, M., and Zéninari, V.: Near infrared diode laser spectroscopy of C_2H_2, H_2O, CO_2 and their isotopologues and the application to TDLAS, a tunable diode laser spectrometer for the Martian PHOBOS-GRUNT space mission, Appl. Phys. B, 99, 339–351, doi: 10.1007/s00340-010-3924-y, 2010.

Griffith, D. W. T., Deutscher, N. M., Caldow, C., Kettlewell, G., Riggenbach, M., and Hammer, S.: A Fourier transform infrared trace gas and isotope analyzer for atmospheric applications, Atmos. Meas. Tech., 5, 2481–2498, doi:10.5194/amt-5-2481–2012, 2012.

Huang, X. and Yung, Y. L.: A common misunderstanding about the Voigt line profile, J. Atmos. Sci., 61, 1630–1632, doi: 10.1175/1520-0469(2004)061<1630:ACMATV>2.0.CO;2, 2004.

International Standard, *ISO* 6142, 2001.

International Standard, *ISO* 6144, 2003.

Lee, J-Y., Hee-Soo, Y., Marti, K., Moon, D. M., Lee, J. B., and Kim, J. S.: Effect of carbon isotopic variations on measured CO_2 abundances in reference gas mixtures, J. Geophys. Res., 111(D5), D053302, doi: 10.1029/2005JD006551, 2006.

Messerschmidt, J., Geibel, M. C., Blumenstock, T., Chen, H., Deutscher, N. M., Engel, A., Feist, D. G., Gerbig, G., Gisi, M., Hase, F., Katrynski, K., Kolle, O., Lavric, J. V., Notholt, J., Palm, M., Ramonet, M., Rettinger, M., Schmidt, M., Sussmann, R., Toon, G., Truong, C. F., Warneke, T., Wennberg, P. O., Wunch, D., and Xueref-Remy, I.: Calibration of TCCON column-averaged CO_2: the first aircraft campaign over European TCCON sites, Atmos. Chem. Phys., 11, 10765–10777, doi: 10.5194/acp-11-10765-2011, 2011.

Min, D., Kang, N., Moon, D. M., Lee, J. B., Lee, D. S., and Kim, J. S.: Effect of variation in argon content of calibration gases on determination of atmospheric carbon dioxide, Talanta, 80, 422–427, doi:10.1016/j.talanta.2009.03.019, 2009.

Nakamichi, S., Kawaguchi, Y., Fukuda, H., Enami, S., Hashimoto, S., Kawasaki, M., Umekawa, T., Morino, I., Suto, H., and Inoue, G.: Buffer-gas pressure broadening for the $(3\ 0^0\ 1)_{III} \leftarrow (0\ 0\ 0)$ band of CO_2 measured with continuous-wave cavity ring-down spectroscopy, Phys. Chem. Chem. Phys., 8, 364–368, doi: 10.1039/b511772k, 2006.

Nara, H., Tanimoto, H., Tohjima, Y., Mukai, Y., Nojiri, Y., Katsumata, K., and Rella, C. W.: Effect of air composition (N_2, O_2, Ar, and H_2O) on CO_2 and CH_4 measurement by wavelength-scanned cavity ring-down spectroscopy: calibration and measurement strategy, Atmos. Meas. Tech., 5, 2689–2701, doi:10.5194/amt-5-2689-2012, 2012.

O'Shea, S. J., Bauguitte, S. J.-B., Gallagher, M. W., Lowry, D., and Percival, C. J.: Development of a cavity-enhanced absorption spectrometer for airborne measurements of CH_4 and CO_2, Atmos. Meas. Tech., 6, 1095–1109, doi:10.5194/amt-6-1095-2013, 2013.

Pouchet, I., Zéninari, V., Parvitte, B., and Durry, G.: Diode laser spectroscopy of CO_2 in the 1.6 µm region for the in situ sensing of the middle atmosphere, J. Quant. Spectrosc. Radiat. Transfer, 83, 619–628, doi: 10.1016/S0022-4073(03)00108-0, 2004.

Solomon, S., Qin, D., Manning, M., Chen, Z., Marquis, M., Averyt, K., Tignor M. M. B, and Miller, H. L. (Eds.): Climate Change 2007: The Physical Science Basis. Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change, Cambridge University Press, New York, N. Y., 2007.

Rella, C. W., Chen, H., Andrews, A. E., Filges, A., Gerbig, C., Hatakka, J., Karion, A., Miles, N. L., Richardson, S. J., Steinbacher, M., Sweeney, C., Wastine, B., and Zellweger, C.: High accuracy measurements of dry mole fractions of carbon dioxide and methane in humid air, Atmos. Meas. Tech., 6, 837–860, doi:10.5194/amt-6-837-2013, 2013.

Rothman, L. S., Jacquemart, D., Barbe, A., Benner, D. C., Birk, M., Brown, L. R., Carleer, M. R., Chackerian Jr. C., Chance, K., Coudert, L. H., Dana, V., Devi, V. M., Flaud, J.-M., Gamache, R. R., Goldman, A., Hartmann, J.-M., Jucks, K. W., Maki, A. G., Mandin, J.-Y., Massie, S. T., Orphal, J., Perrin, A., Rinsland, C. P., Smith, M. A. H., Tennyson, J., Tolchenov, R. N., Toth, R. A., Vander Auwera, J., Varanasi, P., and Wagner, G.: The HITRAN 2004 molecular spectroscopic database, J. Quant. Spectrosc. Radiat. Transfer, 96, 139–204, doi: 10.1016/j.jqsrt.2004.10.008, 2005.

Schulze, E. D., Luyssaert, S., Ciais, P., Freibauer, A., Janssens, I. A., Schulze, E. D., Soussana, J. F., Smith, P., Grace, J., Levin, I., Thiruchittampalam, B., Heimann, M., Dolman, A. J., Valentini, R., Bousquet, P., Peylin, P., Peters, W., Rödenbeck, C., Etiope, G., Vuichard, N., Wattenbach, M., Nabuurs, G. J., Poussi, Z., Nieschulze, J., Gash, J. H., Schulze, E. D., Soussana, J. F., Smith, P., Grace, J., Levin, I., Thiruchittampalam, B., Heimann, M., Dolman, A. J., Valentini, R., Bousquet, P., Peylin, P., Peters, W., Rödenbeck, C., Etiope, G., Vuichard, N., Wattenbach, M., Nabuurs, G. J., Poussi, Z., Nieschulze, J., and Gash, J. H.: Importance of methane and nitrous oxide for Europe's terrestrial greenhouse-gas balance, Nat. Geosci., 2, 842–850, doi:10.1038/ngeo686, 2009.

Tohjima, Y., Katsumata, K., Morino, I., Mukai, H., Machida, T., Akama, I., Amari, Y., and Tsunogai, U. Theoretical and experimental evaluation of the isotope effect of NDIR analyzer on atmospheric CO_2 measurement, J. Geophys. Res., 114(D13), D13302, doi:10.1029/2009JD011734, 2009.

van der Laan, S., Neubert, R. E. M., and Meijer, H. A. J.: A single gas chromatograph for accurate atmospheric mixing ratio measurements of CO_2, CH_4, N_2O, SF_6 and CO, Atmos. Meas. Tech., 2(2), 549–559, doi: 10.5194/amt-2-549-2009, 2009.

Varghese, P. L. and Hanson, R. K.: Collisional narrowing effects on spectral line shapes measured at high resolution, Appl. Opt., 23, 2376, doi:10.1364/AO.23.002376, 1984.

Waldén, J. (Ed.): Metrology of Gaseous Air Pollutants, No. 79 (Finnish Meteorological Institute Contributions), Finnish Meteorological Institute, Finland, 2009.

Wessel R. M., van der Veen, A. M. H., Ziel, P. R., Steele, P., Langenfelds, R., van der Schoot, M., Smeulders, D., Besley, L., da Cunha, V. S., Zhou, Z., Qiao, H., Heine, H. J., Martin, B., Macé, T. P., Gupta, K., di Meane, E. A., Sega, M., Rolle, F., Maruyama, M., Kato, K., Matsumoto, N., Kim, J. S., Moon, D. M., Lee, J. B., Murillo, F. R., Nambo, C. R., Caballero, V. M. S., de Jesús Avila Salas, M., Castorena, A. P., Konopelko, L. A., Kustikov, Y. A., Kolobova, A. V., Pankratov, V. V., Efremova, O. V., Musil, S., Chromek, F., Valkova, M., Milton, M. J. T., Vargha, G., Guenther, F., Miller, W. R., Botha, A., Tshilongo, J., Mokgoro, I. S., and Leshabane, N.: International comparison CCQM-K52: Carbon dioxide in synthetic air, Metrologia, 45, 08011, Technical Supplement, 2008.

Zhao, C. L., Tans, P. P., and Thoning, K. W.: A high precision manometric system for absolute calibrations of CO_2 in dry air, J. Geophys. Res., 102(D5), 5885–5894, doi: 10.1029/96JD03764, 1997.

Table 1. Purities of raw carbon dioxide and background gases (N_2, O_2, and Ar).

Impurity Component	Mole fraction [μmol/mol]				Detectors[1]
	CO_2	N_2	O_2	Ar	
H_2	<0.1	<0.1	<0.1	<0.1	PDD[2]
O_2	<0.1	0.003 ± 0.003	-	0.003 ± 0.002	PDD
Ar	<0.1	21.6 ± 4.32	<1.0	-	TCD[3]
N_2	12.8 ± 2.56	-	3.1 ± 0.62	2.4 ± 0.48	PDD
CO	0.3 ± 0.06	<0.005	0.08 ± 0.016	<0.005	PDD and FID[4]
CH_4	2.6 ± 0.52	<0.005	<0.005	<0.005	PDD and FID
CO_2	-	0.002 ± 0.001	0.195 ± 0.039	<0.002	PDD and FID
H_2O	4.5 ± 2.25	1.6 ± 0.8	1.1 ± 0.55	0.9 ± 0.45	Dew point meter
C_2	2.8 ± 0.56	-	-	-	AED[5]
C_3–C_5	0.7 ± 0.35	-	-	-	AED
Purity (%) (k = 2)	99.9976± 0.0007	99.9976 ± 0.0009	99.9995 ± 0.0002	99.9996 ± 0.0001	

1. Tabulated detectors were coupled to the main body of the gas chromatograph (Agilent 6890A)
2. Pulsed discharge detector
3. Thermal conductivity detector
4. Flame ionization detector
5. Atomic emission detector

Table 2. Mole fractions of gas mixtures.

Cylinder #	Gas composition [cmol/mol]				Preparation method
	CO_2[1]	N_2	O_2	Ar	
DF4560	400.61 (0.05%)	99.96	-	-	gravimetry
EB0011591	351.78 (0.10%)	83.45	16.48	0.04	volumetry
EB0011528	353.08 (0.10%)	80.97	18.19	0.81	volumetry
ME5590	386.94 (0.05%)	78.33	21.63	-	gravimetry
EB0006391	406.40 (0.10%)	78.16	20.87	0.93	volumetry
ME0434	402.25 (0.05%)	78.07	21.03	0.87	gravimetry
ME5502	384.35 (0.05%)	77.57	20.53	1.86	gravimetry
ME5537	385.35 (0.05%)	70.98	18.85	10.12	gravimetry

1. Numbers denote the mole fraction (µmol/mol) of CO_2 and its relative preparation uncertainty

Table 3. Summary of CRDS calibration results.

Cylinder #	CO_2 mole fraction [μmol/mol]			Difference	
	Gravimetrically assigned value (A)	Before CRDS calibration	After CRDS calibration (B)	(B − A) [μmol/mol]	(B – A) / A × 100 [%]
ME0424	371.22	371.18	371.29	0.07	0.0193
ME0485	380.31	380.23	380.28	−0.03	−0.0088
ME5552	384.76	384.66	384.67	−0.09	−0.0222
ME0434	402.25	402.41	402.30	0.05	0.0117

Table 4. CO_2 concentrations determined by gravimetry and measured by well-calibrated CRDS, together with the correction due to N_2-induced pressure broadening (PBC(N_2)) and total broadening coefficient (TPBC). Differences between the measured (corrected) and assigned concentrations are also listed.

Cylinder #	CO_2 mole fraction [μmol/mol]				Difference			
	Gravimetrically assigned value (A)	CRDS measured value (B)	PBC (N_2) corrected (C)	TPBC corrected (D)	$D_{STD-CRDS}$ (B – A) [μmol/mol]	(B – A) / A × 100 [%]	(C – A) / A × 100 [%]	(D – A) / A × 100 [%]
DF4560	400.61	390.84	401.09	400.82	−9.77	−2.44	0.12	0.05
EB0011591	351.78	349.62	351.79	351.97	−2.16	−0.61	0.00	0.05
EB0011528	353.08	352.05	353.00	353.15	−1.03	−0.29	−0.02	0.02
ME5590	386.94	386.51	386.17	386.47	−0.43	−0.11	−0.20	−0.12
EB0006391	406.40	406.39	405.97	406.15	−0.01	0.00	−0.11	−0.06
ME0434	402.25	402.34	401.87	402.09	0.09	0.02	−0.09	−0.04
ME5502	384.35	384.80	384.09	384.17	0.45	0.12	−0.07	−0.05
ME5537	385.35	390.71	386.78	385.95	5.36	1.39	0.37	0.16

Table 5. Summary of N_2-, O_2-, and Ar-related pressure broadening coefficients in cm^{-1} atm^{-1}. All parameters were taken by using the Voigt function.

	Pouchet et al.	Nakamichi et al.	HITRAN 2004
γ_{N_2}	0.0721	0.08064	0.0778
γ_{O_2}	0.0660	0.06695	0.0702
γ_{Ar}	-	0.06312	-
γ_{air}	-	-	0.0758

5

Table 6. Pressure broadening for investigated gas mixtures based on pressure broadening coefficients from different sources.

Cylinder #	Pouchet et al.[1]	Nakamichi et al.	HITRAN 2004[1]
DF4560	0.0721	0.08061	0.0778
EB0011591	0.0710	0.07835	0.0765
EB0011528	0.0704	0.07798	0.0758
ME5590	0.0708	0.07765	0.0761
EB0006391	0.0701	0.07759	0.0755
ME0434	0.0702	0.07758	0.0755
ME5502	0.0695	0.07747	0.0748
ME5537	0.0636	0.07625	0.0685

1. Pressure broadenings were estimated without Ar due to the absence of a broadening coefficient in the corresponding studies.

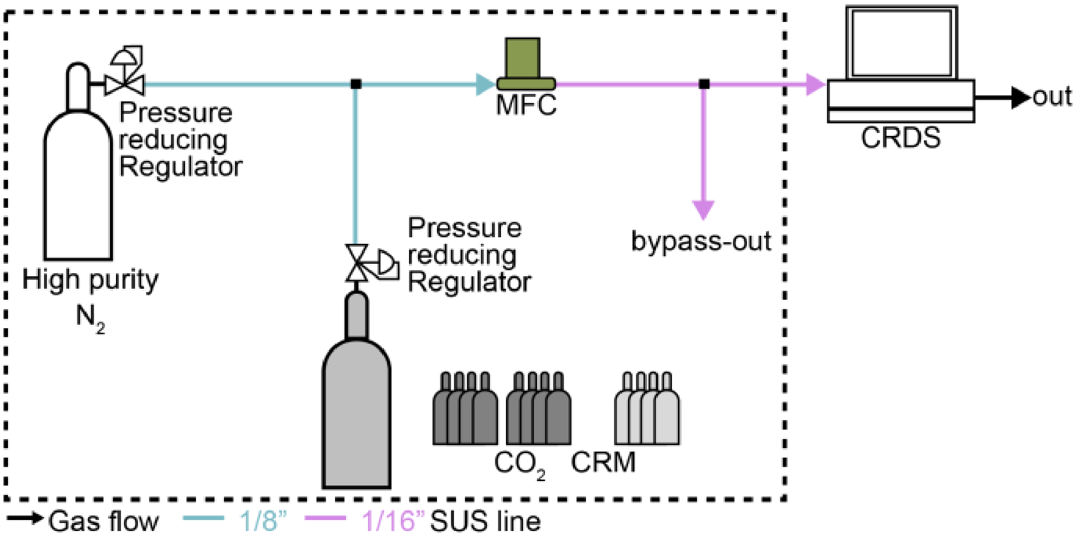

Figure 1: Schematic diagram depicting the gas supply to the WS-CRDS analyzer. The acronym SUS represents the stainless steel.

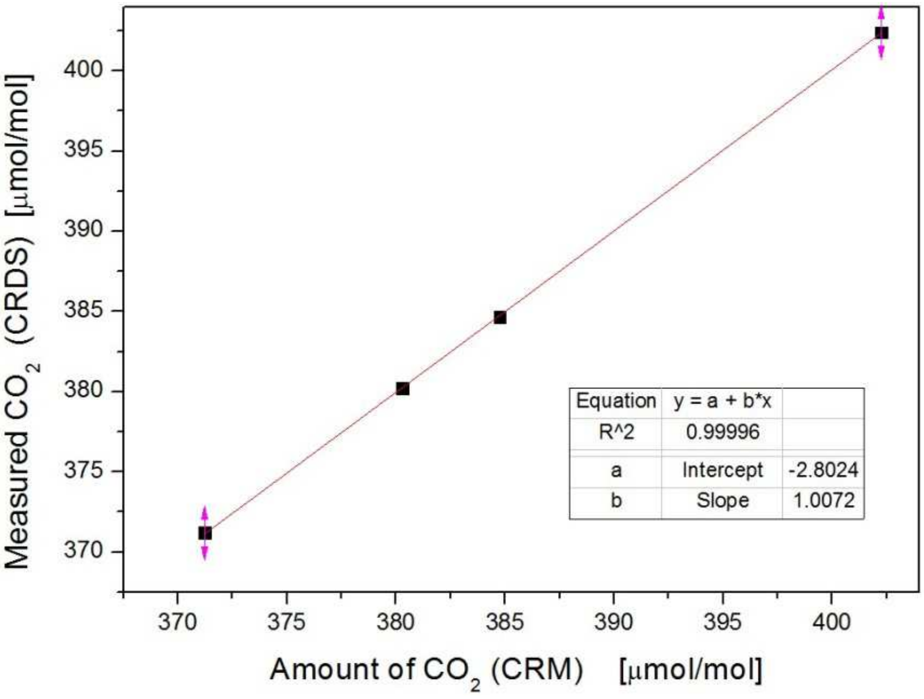

Figure 2: Result of WS-CRDS calibration using gravimetric standards (ambient air background composition, see main text for details). Good agreement between gravimetric and CRDS-determined CO_2 concentrations was observed.

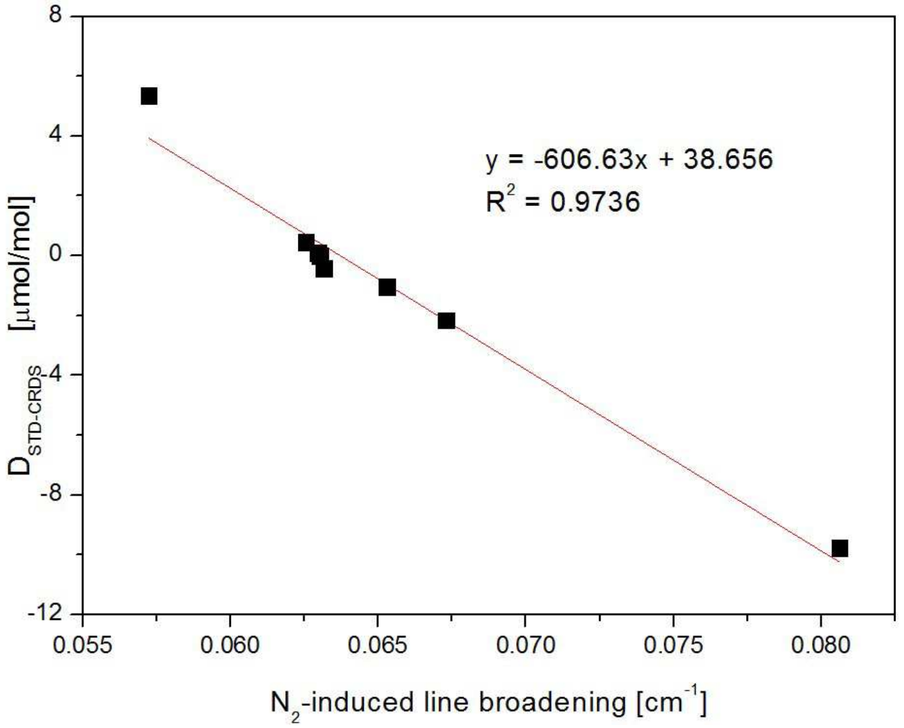

Figure 3: N_2-induced line broadening (*x*-axis) vs. difference between CRDS-measured and assigned CO_2 levels of standard gas mixtures (*y*-axis).

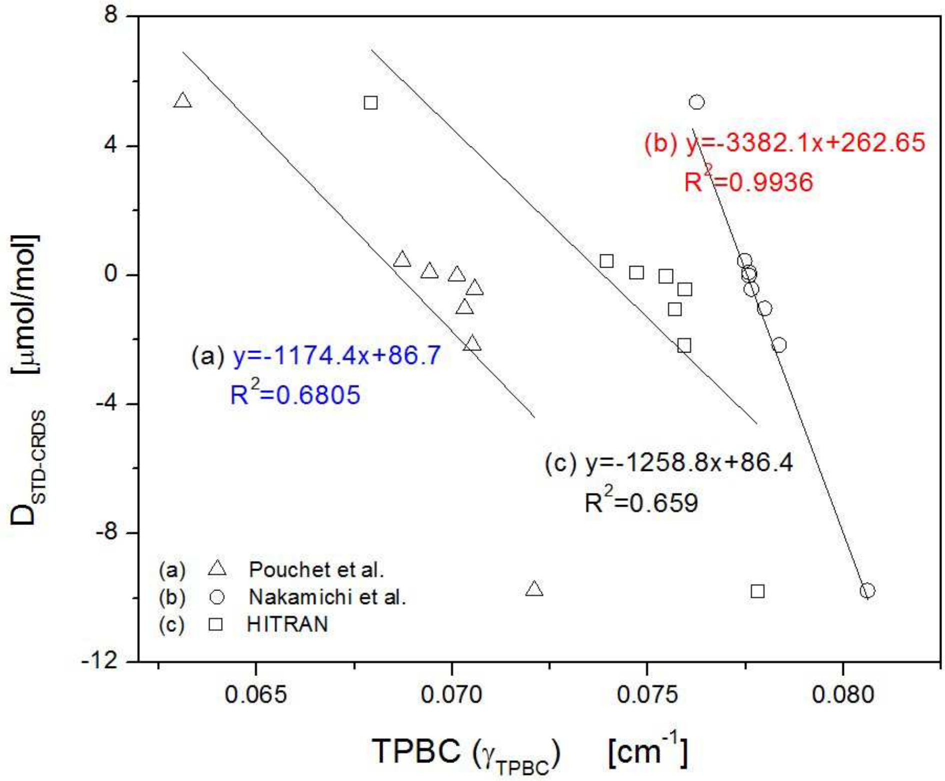

Figure 4: Total pressure broadening coefficient vs. difference between CRDS-measured and assigned CO_2 levels of standard gas mixtures. Due to the lack of γ_{Ar}, correlations (a) and (c) exhibit poor fits.