Response to Reviewer 1

We thank the reviewer for comments and helpful suggestions. Specific comments are addressed below, shown in "italics".

The second paragraph of the introduction refers to a requirement for a relative standard uncertainty of \( \sim 0.01 \% \) to assess the drift in CO\(_2\) amount fraction in cylinders over many years. How is this uncertainty target determined? This assessment is based on the WMO network compatibility goal for 0.1 ppm.

Response: To resolve a drift of 0.1 ppm over several years, new standards would have to be reproducible at approx. \( 1/4 \) this level, or 0.006%. We have updated this sentence as follows.

“Determining the absolute amount of CO\(_2\) in air is a challenge for both gravimetric and manometric methods, particularly since the relative uncertainties must be very small (\( \sim 0.006\% \) 1-sigma, or about a factor of 4 lower than the WMO network compatibility goal of 0.1 ppm), in order to assess changes (drift) in cylinders over many years.”

The experimental methods section describes the transfer of an aliquot of CO\(_2\) to a cylinder from a 5 ml stainless steel container. Considerable experimental effort is employed (heating and repressurising the transfer vessel) to ensure that the CO\(_2\) is transferred with negligible losses. Would it be possible to simplify the experimental procedure by weighing the transfer vessel before and after to determine the mass transferred?

Response: We briefly experimented using the method you suggest, and found that without the additional flushing we were unable to achieve sufficient transfer using our manifold. Those standards appeared to be \( \sim 0.6 \) ppm too low. Perhaps this technique could be perfected in order to achieve higher transfer efficiencies, but we decided to use the multiple flush method instead, since we have more experience with that technique.

Equation (1) defines the transfer efficiency (f), although a value is not provided. In the results and discussion section, a statement is made that the transfer efficiency is assumed to be 100 \%. Further text is required to accompany equation (1).

Response: We added “\( f=1.00 \)” to the paragraph following eq. (1).

The paragraph which precedes equation (1) and the first sentence after refers to the unit when the quantity is implied (e.g. “number of moles” and “moles of”). In each case this should be replaced with the quantity “amount”.

Response: updated as suggested

In equation (1), in order to accurately determine the amount fraction of the mixture, X\(_{CO_2,ad}\) and X\(_{CO_2,dil}\) should be changed to amount of CO\(_2\) adsorbed and amount of CO\(_2\) in the dilution.
gas and be added to the numerator and denominator in the first term of the equation (rather than added as separate terms). Also nair should be split up into its components (nAr, nN2 and nO2).

Response: Since these terms are small (order 0.01 to 0.02 ppm), we feel that expressing them as mole fraction corrections is adequate. We prefer to keep nair as is because this is how we do the calculation: 

\[ n_{\text{air}} = \frac{\text{mass}_{\text{air}}}{\text{MW}_{\text{air}}} \]

On page 7, amount is missing from the sentence “The amount of CO2 adsorbed to the walls, expressed as a fraction of total amount of CO2 in the cylinder”.

Response: updated as suggested
Response to Reviewer 2

We thank the reviewer for comments and helpful suggestions. Specific comments are addressed below, shown in "italics".

Specific comments: Page 3, line 14: It would be better to mention the weight of the 29.5-L Luxfer cylinder.

Response: OK, we added this to the text: “(~22kg empty)”

Page 3, line 23: What are the weighing capacity and the readability?

Response: We updated the following text in this sentence: “… mass comparator (Sartorius CCE40K3, 40 kg capacity, 2 mg readability) ….

Page 4, line 17-18: This purification procedure can remove non-condensable gases but cannot remove water vapor. Is it possible to add additional cold trap at -100°C between the 50-mL and 5-mL containers to reduce the water vapor?

Response: It would be possible to install a water trap, but since the water vapor purity correction was relatively small, we chose to account for H2O in the purity coefficient.

Page 6, line 1-2: In Table 1, the suffixes ‘_a’ and ‘_b’ mean ‘initially present in cylinder’ and ‘aliquot in 5-mL container’, respectively, while the subscriptions ‘a’ and ‘b’ in the text mean the exact opposite. It’s very confusing.

Response: Thank you for pointing this out. We have made the correction in the table.

Page 6, line 2-3: It would be better to clarify that n_{air} comes from natural air initially present in the cylinder and the dilution gas.

Response: We have made this clarification.

... n_{air} is the total moles of air (sum of natural air initially present and dilution air), \( p \) is the purity ...

Page 6, line 15: I think the molecular weight of 28.9621 is not for the dilution gas but for natural air including ambient level of CO₂. From the composition of the dilution gas listed in line 17-18 (He should be included in the dilution gas) we obtain the molecular weight of 28.9560. Moreover, I think that the molecular weights of the natural air initially added to the cylinder and the dilution gas were needed to calculate the moles of the initially added natural air and the moles of the added dilution gas because these molecular weights are not necessarily same. However, the authors used single molecular weight of 28.9621 for the air with ambient level of CO₂ to compute nb and nair because the differences in the molecular weight among these airs doesn’t practically cause significant differences. I think the authors should clarify how to compute the moles of the gases used in this study.
Response: Thank you for catching this. There was an error in our MW_{air} calculation. We mixed up the molecular masses of Ne and Xe. The revised molecular weight is 28.9602 g/mol. We use a single molecular weight for both quantities of air because we consider CO_{2} and air separately. Since we account for the mass of CO_{2} separately, the initial natural air (with CO_{2} excluded) has essentially the same MW as the dilution air.

Page 7, line 12: What is the BOC Spectra Seal process?

Response: BOC Spectra Seal is a proprietary process mentioned by name in Brewer et al. (2018).

Page 13, Table 1: I think it would be better to add the column of the total uncertainty for XCO_{2}.

Response: We agree. In the submitted manuscript we were unable to fit all desired columns into the table, and provided an extended Table 1 in landscape format as a Supplement. In the final published version we will work with AMT to reformat Table 1 to include additional columns.
Response to Reviewer 3

We thank the reviewer for comments and helpful suggestions. Specific comments are addressed below, shown in "italics".

Page 5, line 26: A blank in the dilution gas of 0.01 ppm is quoted. This is a very low value that appears quite challenging to be quantified also in the light of the noise visible in the data presented in Figure 3 b. How is the limit of detection of the measurement method determined?

Response: We used nitrogen scrubbed with Ascarite II to purge both the reference and sample cells of the NDIR for ~12 hours. We used this as a "zero" value. We then sampled dilution gas through the sample cell. The resulting signal changed by only 0.01 ppm +/- 0.01 ppm. While we do not have a good estimate of the linearity of the NDIR in this range, the amount of CO₂ in the dilution gas appears to be sufficiently low that an uncertainty of +/- 100% is adequate for the calculation present here.

Page 7, lines 6ff: In the last part of the "Experimental Methods" section (starting page 6, line 21) the authors begin to describe their experiments to quantify CO₂ adsorption on cylinder walls where the reader is referred to experimental details of the Schibig et al 2018 paper. This is followed by a discussion (page 7, line 6 to page 8, line 9) comparing these adsorption tests with experimental findings from literature and additional decanting experiments done as part of the work submitted here. I suggest that this discussion is moved to the Results and Discussion section. In this discussion on the experimental determination of adsorbed CO₂ it is stated that all of these experiments agree in similar qualitative alterations of the CO₂ content throughout venting gas cylinders but that the individual experiments do not agree to a very high degree in quantitative terms. The authors conclude that this is due to experimental approaches that introduce confounding temperature fractionation that add to the observed increase of CO₂ over time. This is conclusive but it is not convincing to me that the authors completely exclude the possibility that there might be a small temperature fractionation influence affecting the low flow adsorption experiments done within the Schibig et al 2018 work that they rely on in the submitted manuscript. They state that during these low flow tests no significant temperature gradients were measured on the cylinder surfaces. However, in Figure 7 of that publication the adiabatic cooling effect is clearly visible in lower pressure regulator temperatures relative to the cylinder top (0.3-0.4 K) indicating the potential of a contribution from temperature fractionation. The adsorption terms are not large (0.016 ppm) and if temperature fractionation was playing a role would be even smaller. Yet, this is one of the adjustment terms and it is specified with a very low uncertainty in Tables 1 and 3. This uncertainty quote reflects the standard deviation of the calculated adsorbed CO₂ as it results from the fit functions of the data of repeated low flow decanting experiments derived from the Langmuir's adsorption/desorption model. If other effects than the Langmuir adsorption may come into play the uncertainty of the adsorption adjustment term in Table 1 will not be adequately represented by this standard deviation.

Response: We agree that the uncertainty we assigned to the adsorption correction term, derived from the standard deviation of 4-5 low-flow tests, is probably too low and not representative of the true uncertainty. We have modified the uncertainty to a conservative estimate of 0.01 ppm. We do not believe that thermal gradients in the regulator, observed by Schibig et al (2018) as you point out, would introduce fractionation of gas in the cylinder. There could be thermal fractionation occurring in the regulator, but this would be overcome by bulk flow, and seems very unlikely to impact the
mixing ratio in the cylinder itself. Further, we will consider moving the text relating to the adsorption from "Experimental Methods" to "Discussion".

Page 8, line 24: A linear fit is applied to the data and the residuals of these data are presented. On the CCL webpage a statement can be found that their NDIR system is not linear. The residuals of the fit presented in Figure 2 and Table 5 would probably improve if a quadratic fit was applied. The authors provide a clear explanation for assuming a small bias in the 4 05 ppm standard and the consistency achieved already for a linear fit proves the success of their work. Still they might add a comment on the certainty they have to assume a linear response.

Response: A laser-based spectrometric method was used for analysis of the gravimetric standards. This system should be linear. The NDIR was only used to analyze the dilution gas and for the transfer line tests.

One minor last suggestion: Page 5, line 6: the reference to Dlugokencky et al. 2005 does not show the manifold used, a further reference to Novelli et al 2001 is made in there. If the authors could show the manifold in another figure in here would be of help to the reader.

Response: We have added the figure below as suggested.

![Schematic of the blending manifold](image)

Figure 1: Schematic of the blending manifold. The sample aliquot (5-ml) was connected to one of three aliquot inlet ports (p1, p2, p3). The sample was transferred to the receiving cylinder by opening the cylinder valve, opening the valve on the 5-ml vessel, and then alternately pressurizing the section between valves v2 and v3, and opening v3 to send the gas to the cylinder. The sample manifold is constructed of ¼” o.d. stainless steel tubing with welded or Swagelok VCR connections. Valves are stainless steel, diaphragm-sealed (Swagelok model DSV51).
Gravimetrically-Prepared Carbon Dioxide Standards in Support of Atmospheric Research

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Abstract

We have explored a one-step method for gravimetric preparation of CO2-in-air standards in
aluminum cylinders. We consider both adsorption to stainless steel surfaces used in the
transfer of highly-pure CO2, and adsorption of CO2 to cylinder walls. We demonstrate that CO2-
in-air standards can be prepared with relatively low uncertainty (~0.04%, ~95% Confidence
Level) by introducing aliquots whose masses are known to high precision, and by using well-
characterized cylinders. Five gravimetric standards, prepared over the nominal range 350 to
490 µmol mol⁻¹ (parts per million, ppm), showed excellent internal consistency, with residuals
from a linear fit equal to 0.05 ppm. This work complements efforts to maintain the World
Meteorological Organization, Global Atmosphere Watch, mole fraction scale for carbon dioxide
in air, widely used for atmospheric monitoring. This gravimetric technique could be extended to
other atmospheric trace gases, depending on the vapor pressure of the gas.

Introduction

Numerous laboratories make routine measurements of atmospheric carbon dioxide to better
understand its sources, sinks, and temporal variability. These measurements are typically
calibrated using high-pressure gas standards containing CO₂ in air (typically natural air with
assigned CO₂ mole fractions), traceable to primary standards prepared or analyzed using absolute methods, such as manometry (Keeling et al., 1986; Zhao and Tans, 2006) and gravimetry (Machida et al., 2011; Rhoderick et al., 2016; Brewer et al., 2014), which provide traceability to the SI. The World Meteorological Organization (WMO), Global Atmosphere Watch (GAW) initially adopted the Scripps Institution of Oceanography scale (Keeling et al., 1986) and subsequently the National Oceanic and Atmospheric Administration (NOAA) scale (Zhao et al., 1997), both of which are based on repeated manometric measurements of a suite of primary standards, for WMO-affiliated monitoring networks. The WMO scale has been updated over the years as understanding has improved and measurement records of primary standards have increased (Keeling et al., 2002; Keeling et al., 1986; Zhao and Tans, 2006).

Determining the absolute amount of CO₂ in air is a challenge for both gravimetric and manometric methods, particularly since the relative uncertainties must be very small (~0.006% 1-sigma, or about a factor of 4 lower than the WMO network compatibility goal of 0.1 ppm (WMO, 2018)), in order to assess changes (drift) in cylinders over many years. Long-term monitoring of atmospheric CO₂ requires a stable reference, sufficient to identify small atmospheric gradients (of order 0.1 µmol mol⁻¹, or 0.1 ppm, in the remote troposphere). Hereafter we will use ppm (parts per million) for µmol mol⁻¹. Both methods can be influenced by the adsorption of CO₂ to surfaces. There is increasing evidence that CO₂ can adsorb to the internal surfaces of cylinders and desorb with decreasing pressure (Langenfelds et al., 1996; Miller et al., 2015; Leuenberger et al., 2015; Brewer et al., 2018; Schibig et al., 2018). This impacts both the gravimetrically-assigned mole fraction and the mole fraction of CO₂ in air withdrawn from cylinders over time. Further, since cylinder characteristics may differ among cylinder manufacturers, understanding the behavior of CO₂ in cylinders is critical to maintaining stable scales over time.

The gravimetric technique can employ multiple steps, in which the target gas (CO₂ in this case) is diluted to the desired amount fraction. For example, Brewer et al. (2014) first prepared standards with mole fractions of a few percent, then made dilutions of those to the range
needed for ambient monitoring (~400 ppm). Others have opted to dilute CO\textsubscript{2} to ppm levels in one step (Machida et al., 2011). Matrix gases can also be added in different ways: CO\textsubscript{2} can be mixed with individual gases (N\textsubscript{2}, O\textsubscript{2}, Ar) to form an air-like matrix, or CO\textsubscript{2} can be added to natural air from which the CO\textsubscript{2} has been removed. Methods of targeting stable isotopes of CO\textsubscript{2} (e.g. 13\textsuperscript{C}-CO\textsubscript{2}) to better match natural abundances have also been explored (Brewer et al., 2014).

Here we describe one-step preparation of CO\textsubscript{2}-in-air compressed gas standards in aluminum cylinders. We used information gained from recent decanting experiments (Schibig et al., 2018) to correct for CO\textsubscript{2} adsorption to the cylinder walls. This work was undertaken to support NOAA manometric efforts and learn more about the behavior of CO\textsubscript{2} in aluminum cylinders.

**Experimental Methods**

Standards were prepared in 29.5-L Luxfer aluminum cylinders (~22kg empty) (Scott Marrin, Inc. Riverside, CA), with brass, packless valves (Ceodux). We chose these cylinders for two reasons. First, we wanted to perform the dilutions in one step, and therefore needed relatively large cylinders. Second, we wanted to use cylinders that were well-characterized. We have considerable experience with CO\textsubscript{2}-in-air in this type of cylinder. Specific to this work, all cylinders used were filled with natural air and decanted several times for CO\textsubscript{2} adsorption studies (Schibig et al., 2018) prior to being used for gravimetric standards described here.

For this gravimetric work, each cylinder was evacuated to ~30 mtorr (4 Pa) and weighed on a mass comparator (Sartorius CCE40K3: 40kg capacity, 2mg readability) relative to a control cylinder of similar mass and volume. The mass comparator was calibrated using a 10 kg mass (Troemner), and linearity over the working range was confirmed by adding a 5 kg mass (Mettler Toledo) to the reference cylinder. We then added ~50 psi (0.34 MPa) natural air containing 402 or 408 ppm CO\textsubscript{2} determined by analysis (WMO X2007 scale). Cylinders were then vented, partially evacuated to ~400 torr (53 kPa), and weighed. The mass of residual air along with the
mole fraction of CO$_2$ were used to calculate the initial mass of CO$_2$ in the cylinder. We did not evacuate the cylinders further because CO$_2$ adsorption studies (Schibig et al., 2018) were performed at pressures ranging from 0.1-13.8 MPa. The Schibig et al. (2018) work provided a means to determine the amount of CO$_2$ adsorbed to cylinder walls, and we wanted to perform the gravimetric addition with a small amount of residual CO$_2$ in the cylinders, consistent with that work. For the standards presented here, the initial CO$_2$ in the cylinder corresponds to < 0.8% of the total CO$_2$, and so the uncertainty associated with the mole fraction of initial CO$_2$, derived from an independent CO$_2$ calibration (Zhao and Tans, 2006), makes a negligible contribution to the total uncertainty (Table 1). The majority of the uncertainty in the mass of CO$_2$ originally in the cylinder results from uncertainty in the mass determination of the residual air. Nevertheless, we include a standard uncertainty of 0.025% on the WMO X2007 CO$_2$ scale (https://www.esrl.noaa.gov/gmd/ccl/ccl_uncertainties_co2.html).

An initial aliquot of high-purity CO$_2$ was added to an evacuated 50-mL stainless steel container with a single metal bellows valve (Swagelok, model SS-4H) (pressure rated to 1000 psi, or 6.90 MPa, at 37 °C). After CO$_2$ was loaded into the 50-mL container at the desired pressure, it was cryogenically transferred to a 5-mL stainless steel container, also with a metal bellows valve (total mass ~150g) that had been evacuated and weighed previously. The CO$_2$ was cryogenically purified by freezing at -197 °C and pumping off non-condensible gases. We estimate the purity of the CO$_2$ source at 99.994% and that of the cryogenically-purified CO$_2$ aliquots at 99.997 ± 0.002% (Table 2). In this smaller volume, both liquid and vapor phases of CO$_2$ would be present at room temperature (18 °C in this case). Note that the vapor pressure of CO$_2$ at 18 °C is ~795 psi (5.48 MPa), and that our 5-mL container and valve was rated to 1000 psi (6.89 MPa). We employed this secondary transfer to a smaller container so that we could weigh ~1.5g CO$_2$ on a balance with 0.01mg readability (Mettler Toledo AT201, 200g capacity). The 50-mL container used in the first step is too large to be weighed on the AT-201. This is an important aspect of this work. Without this secondary step, our uncertainties would have been about a factor of 10 larger. The mass of CO$_2$ in each 5-mL aliquot was determined by weighing the 5-mL container relative to a control object of similar mass and density (sequence ABABA....). The AT-201 was
calibrated using internal weights, and span-checked by adding a 2.0000g mass to the 5-mL container.

Each purified CO$_2$ aliquot was transferred from the 5-mL container to a partially-evacuated cylinder on a stainless steel vacuum manifold using a pressurization/expansion method (Figure 1) (Dlugokencky et al., 2005). The cylinder was connected to the vacuum manifold using a 1/8” OD AT-steel transfer line. AT-steel, also known as "activity tested steel" (Grace Discovery Science, Columbia, MD) is treated using vapor deposition to improve surface inertness. In initial tests we found that AT-steel performed better than other types of stainless steel, but in subsequent tests both 1/8” O.D. stainless steel and 1/8” O.D. AT-steel performed similarly (see Results and Discussion).

To transfer the aliquot to the cylinder, the manifold and transfer line were pre-heated to ~60 °C and evacuated to 5 mtorr (0.7 Pa). In quick succession, the cylinder valve was opened and the valve on the 5-mL container was opened allowing CO$_2$ to expand into the cylinder. The expansion of CO$_2$ resulted in significant cooling of the 5-mL container, so we heated the 5-mL container, manifold, and transfer lines to ~60 °C while alternately pressurizing the 5-mL container to ~200 psi (1.38 MPa) with CO$_2$-free air (dilution gas) and expanding into the cylinder. After about 20 pressurization/expansion cycles, the valve on the 5-mL container was closed and the cylinder pressurized with dilution gas. The 5-mL container was removed from the manifold at a cylinder pressure of ~ 500 psi (3.45 MPa), and the cylinder was then further pressurized to 1000 psi (6.90 MPa) with dilution gas. Dilution gas consisted of scrubbed natural air (Cryogenic Ultra-pure grade, Scott Marrin Inc; now Praxair, Los Angeles, CA). This gas was analyzed for CO$_2$ by non-dispersive infrared analysis (NDIR; Licor Li-7000). Samples of dilution gas were compared to a reference of dry nitrogen (99.999%) scrubbed using Ascarite II (Sigma Aldrich). All cylinders of dilution gas contained 0.01 ± 0.01 ppm CO$_2$. After cylinders cooled to room temperature, they were weighed on the mass comparator relative to the control cylinder.
The mole fraction of CO$_2$, $X_{\text{CO}_2}$, was calculated using equation (1), where $n_a$ is the moles of CO$_2$ transferred from the 5-mL container, $n_b$ is the moles of CO$_2$ initially present in the cylinder, $n_{\text{air}}$ is the total moles of air (sum of natural air initially present and dilution air), $p$ is the purity coefficient, $f$ is the transfer efficiency, $X_{\text{CO}_2,\text{ad}}$ is a correction for the amount of CO$_2$ adsorbed to the cylinder walls ($X_{\text{CO}_2,\text{ad}} < 0$) expressed in ppm, and $X_{\text{CO}_2,\text{dil}}$ is the amount of CO$_2$ in the dilution air, also expressed in ppm.

$$X_{\text{CO}_2} = \frac{pf n_a + n_b}{pf n_a + n_b + n_{\text{air}}} + X_{\text{CO}_2,\text{ad}} + X_{\text{CO}_2,\text{dil}} \quad (1)$$

The amount of each component was determined from the mass and molecular weight. For CO$_2$ we used a molecular weight of 44.0096 ± 0.0006 g mol$^{-1}$ (consistent with a $^{13}$C-CO$_2$ content of -29 per mil on the VPDB scale, determined using off-axis integrated cavity output spectroscopy (Los Gatos Research) traceable to the University of Colorado (INSTAAR) Stable Isotope Laboratory realization of VPDB (Trolier et al., 1996; Tans et al., 2017). For the dilution gas, we used a molecular weight of 28.9602 ± 0.0042 g mol$^{-1}$. The oxygen content of the dilution gas was measured using a paramagnetic method (Beckman, E2) traceable to NIST SRM 2659A (20.863% ± 0.011% O$_2$ in N$_2$). Argon was taken as 0.933% (Sutour et al., 2007), and the noble gases Xe, Ne, and Kr were taken as 0.09, 18.0 and 1.14 ppm, respectively. Nitrogen was assumed to comprise the remaining fraction. We assumed 100% transfer efficiency ($f=1.0$) with an uncertainty of 0.01% (rectangular distribution) (see Results and Discussion).

The mole fraction correction for CO$_2$ adsorbed to the cylinder walls ($X_{\text{CO}_2,\text{ad}}$) was determined from multiple decanting experiments (Schibig et al., 2018). Briefly, in those experiments, cylinders were filled with dry natural air (~400 ppm), and drained at 0.3 L min$^{-1}$ and analyzed continuously for CO$_2$ by NDIR. These studies showed remarkably consistent results: that the mole fraction of CO$_2$ exiting the cylinder increased as the cylinder pressure decreased, and that the data can be described with a Langmuir isotherm (Figure 2). By fitting the data with a
Langmuir isotherm as derived by Leuenberger et al. (2015), and integrating the area between
the Langmuir fit and the initial $X_{CO2}$, we determined the amount of $CO_2$ that desorbs from the
walls as the cylinder is vented slowly to near-ambient pressure (Fig. 2). The amount of $CO_2$
adsorbed to the walls, expressed as a fraction of the total amount of $CO_2$ in the cylinder, was
typically about 0.004% (Table 3). Although the low-flow data show very good reproducibility
(Table 3), we assumed a standard uncertainty of 0.01 ppm.

Five standards were prepared gravimetrically, with $CO_2$ mole fractions ranging from 357 to 492
ppm. Preparation uncertainties were determined by propagating uncertainties associated with
variables in equation (1) (Table 1), using software available from the National Institute of
Standards and Technology (NIST) (https://www.nist.gov/programs-projects/metrology-
software-project). The two most important factors influencing uncertainty are repeatability
associated with weighing the purified $CO_2$ aliquot (contributing ~25%) and the molecular weight
of air (contributing ~65%). For MW$_{air}$, the uncertainty is partially limited by our ability to
measure $O_2$ and calibrate the $O_2$ analyzer.

Results and Discussion

Following preparation, standards were analyzed using laser spectroscopy (Tans et al., 2017). Each standard was analyzed twice over a period of two weeks. The response was expressed as
the mole fraction of $CO_2$, calculated on the WMO X2007 $CO_2$ scale, relative to that of CB11941
$\text{X}^{\text{CB11941}}$.

We use this relative response because mole fraction assignments on the X2007 scale account
for differences in the abundances of stable isotopes of $CO_2$ (mainly $^{13}C$-$CO_2$) between the
 gravimetric standards and secondary standards used for calibration (Tans et al., 2017). For
comparison, we also calculated response based on the analyzer signal derived from a single $CO_2$
 isotopologue ($^{16}O$-$^{12}C$-$^{13}O$, 626). Both methods give similar results with respect to consistency
of the standard set.

Table 4 and Figure 3 show the best-fit results and residuals (difference between best fit and
prepared mole fraction). All standards agree (within expanded uncertainties) with the

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The adsorption correction ranged from -0.015 to -0.022
ppm (Table 1).  

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The Schibig et al. (2018) decanting tests reveal substantially
less $CO_2$ adsorbed compared to mother/daughter tests
(Miller et al., 2015; Brewer et al., 2018), in which half the
contents of one cylinder are transferred to an equal size
cylinder and the adsorption determined based on the
resulting mole fraction difference. From mother/daughter
tests on 5.9-L cylinders from Airgas (Riverton, NJ) and 5-L
 cylinders from Air Products (Vilvoorde, Belgium), Miller et
al. (2015) estimated that about 0.02% of the $CO_2$ was
adsorbed to the walls. Brewer et al. (2018) performed
similar tests on 10-L aluminum cylinders treated with the
BOC Spectra project.

In preparation for this work, we performed
mother/daughter tests on both 5.9-L and 29.5-L aluminum
 cylinders (Scott Marrin, Riverside, CA), including cylinders
CB11941 and CB11873 used in this work. Cylinders CB11941
and CB11873 were filled with natural air, vented, and then
evacuated to 5 psia (0.03 MPa). Air from two “mother”
cylinders containing natural air was transferred to
CB11941 and CB11873. We found that the $CO_2$ in daughter
cylinders CB11941 and CB11873 was 0.16-0.19 ppm lower
than their respective mothers after transfer (Table 4), similar to the results of Miller et al. (2015) and Brewer et al.
(2018). Our tests with 5.9-L cylinders showed ~0.2 ppm
differences (not shown).  

Mother/daughter tests suggest five to ten times more adsorption than that determined from the Schibig et al.
(2018) low-flow data. The difference between
mother/daughter tests and the low-flow experiments could

Moved up [1]: The adsorption correction ranged from -0.015 to -0.022 ppm (Table 1). Although the low-flow data

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regression line. The standard deviation of residuals is 0.05 ppm and the largest residual is 0.09 ppm. Since the uncertainty associated with the molecular weight of air is the largest contributor to the total uncertainty, but is common to all standards, it is worth recalculating uncertainty without this contribution in order to assess consistency. Without $\mu_{MWair}$, standard uncertainties for each standard are 40-60% lower than when $\mu_{MWair}$ is included. Recalculating the regression using these lower uncertainties, we find that the residuals do not change appreciably. However, the residual for cylinder CB11941 becomes 0.098 ppm. With a standard uncertainty of 0.046 ppm, CB11941 is not consistent with the rest of the standards. This may be the result of preparation. Cylinder CB11941 was the first standard prepared, and followed testing that involved injecting high concentrations of CO$_2$ into the manifold and transfer line. It is possible that some residual CO$_2$ remained in the manifold and transfer line, and was introduced into CB11941 when the manifold and transfer line were heated. The other standards were prepared following several heating cycles, and are less likely to be influenced by any residual CO$_2$.

To support our assumption of 100% transfer efficiency, we examined both the potential for adsorption of CO$_2$ in the manifold and transfer line, and the efficiency of transferring CO$_2$ from the 5-mL container to a cylinder. We tested the transfer line by flowing air containing ~0.1 ppm CO$_2$ at 0.2 L min$^{-1}$ through 1/8" AT-steel tubing to an NDIR analyzer. Then we injected 0.6mL of 10% CO$_2$-in-air into this air stream. After the initial slug of CO$_2$ was observed and the NDIR signal returned to baseline, we heated the transfer line and measured the additional CO$_2$ coming off (Figure 4). Comparing the area of the CO$_2$ released upon heating with that of the main sample injected, we found that our AT-steel transfer line (length 1m) retained about 0.04% of CO$_2$ in the sample. We were able to drive off most of this CO$_2$ on the first heating cycle, with < 0.01% released on subsequent heating. Tests with stainless steel (not AT-steel) showed similar results. By heating the lines multiple times and passing a large amount of CO$_2$-free air through them, it is unlikely that a significant amount of CO$_2$ would remain in the manifold or transfer line.
We tested the transfer efficiency from the 5-mL container by cryogenically moving aliquots of CO₂ from one 5-mL container to another on a vacuum line (using liquid N₂), without additional flushing, and measuring changes in mass. When both the initial 5-mL container and transfer line were heated, a transfer efficiency of 99.9 ± 0.1% was achieved. Without heating, the same test revealed only 99% efficiency. We expect that repeated pressurization/expansion with CO₂-free air, in addition to heating, would improve the transfer efficiency of the CO₂ aliquot to near 100%. The relatively good agreement among the four standards prepared after CB11941 supports this assumption. It seems unlikely that this level of agreement could be achieved with poor or variable transfer efficiency.

As mentioned earlier, we estimated the amount of CO₂ adsorbed to the cylinder walls (~0.004%) from the results of low-flow decanting experiments. The Schibig et al. (2018) decanting tests reveal substantially less CO₂ adsorbed compared to “mother/daughter” tests (Miller et al., 2015; Brewer et al., 2018), in which half the contents of one cylinder are transferred to an equal size cylinder and the adsorption determined based on the resulting mole fraction difference. From mother/daughter tests on 5.9-L cylinders from Airgas (Riverton, NJ) and 5-L cylinders from Air Products (Vilvoorde, Belgium), Miller et al. (2015) estimated that about 0.02% of the CO₂ was adsorbed to the walls. Brewer et al. (2018) performed similar tests on 10-L aluminum cylinders treated with the BOC Spectra Seal process, and found CO₂ adsorption fractions of about 0.05%.

In preparation for this work, we performed mother/daughter tests on both 5.9-L and 29.5-L aluminum cylinders (Scott Marrin, Riverside, CA), including cylinders CB11941 and CB11873 used in this work. Cylinders CB11941 and CB11873 were filled with natural air, vented, and then evacuated to 5 psia (0.03 MPa). Air from two “mother” cylinders containing natural air was transferred into CB11941 and CB11873. We found that the CO₂ in daughter cylinders CB11941 and CB11873 was 0.16–0.19 ppm lower than their respective mothers after transfer (Table 5), similar to the results of Miller et al. (2015) and Brewer et al. (2018). Our tests with 5.9-L cylinders also showed differences of ~0.2 ppm (not shown).
Mother/daughter tests suggest five to ten times more adsorption than that determined from the Schibig et al. (2018) low-flow data. The difference between mother/daughter tests and the low-flow experiments could be related to thermal fractionation. Schibig et al. (2018) performed both low-flow (0.3 L min\(^{-1}\)) and high-flow (5.0 L min\(^{-1}\)) decanting experiments. They found that changes in CO\(_2\) at the high flowrate were 2.5 times those observed at the low flowrate, and attributed the difference to thermal fractionation at the higher flow rate. During our mother/daughter tests, the mother cylinders experienced significant cooling during transfer, which could have caused fractionation as cooler air sinks in the center core of the cylinder, with CO\(_2\) preferentially remaining in the mother cylinder. In fact, after transferring half of the gas from a mother cylinder to a respective daughter cylinder, the mole fraction of CO\(_2\) in each mother cylinder increased 0.06 ± 0.01 ppm relative to its value determined prior to transfer (Table 5). From figure 2, which represents a typical low-flow decanting result, the increase due to desorption from the cylinder walls should be far smaller than 0.06 ppm at 50% of the original cylinder pressure.

Finally, we compare these standards to the WMO X2007 CO\(_2\) scale. The mean ratio of gravimetrically assigned mole fractions to values assigned on the WMO X2007 scale is 1.00045, with standard deviation 0.00017. Thus, the WMO X2007 scale is ~0.05% lower than a scale based on these gravimetric standards. However, this difference is not outside the range of uncertainties (~0.05% for WMO X2007 and ~0.033 % for this work, ~95% Confidence Level, or coverage factor k=2). While the \(^{13}\)C-CO\(_2\) content of these gravimetrically-prepared standards is lower than that of natural air (-29 per mil, compared to about -8 per mil for natural air), and these standards were compared to WMO secondary standards with \(^{13}\)C-CO\(_2\) at ambient levels during analysis, this introduces negligible bias because the analytical method compensates for different isotopic abundances (Tans et al., 2017). Further discussion on differences between the WMO X2007 scale and these gravimetric standards will be included in a subsequent publication.

Conclusions
Five gravimetric CO$_2$-in-air standards, prepared at the ppm level in one dilution step, show excellent internal consistency. Prepared mole fractions were adjusted for CO$_2$ expected to adsorb to cylinder walls. This correction was determined from low-flow decanting studies, and is a factor of 5-10 smaller than that inferred from mother/daughter tests. With improved understanding of CO$_2$ adsorption characteristics, and by introducing condensed-phase aliquots of CO$_2$ into small vessels that can be weighed with sufficient repeatability, CO$_2$-in-air standards can be prepared with relatively low uncertainty. This work supports parallel efforts to maintain the WMO mole fraction scale for CO$_2$.  

Acknowledgments

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Supporting Information

Table_1_landscape.docx

References


### Table 1: Components and standard uncertainties associated with standard preparation.

<table>
<thead>
<tr>
<th>Cylinder</th>
<th>( n_{\text{Air}} )</th>
<th>( \mu_{n_{\text{Air}}} )</th>
<th>( X_{\text{CO}_2, \text{ad}} )</th>
<th>( \mu_{X_{\text{CO}_2, \text{ad}}} )</th>
<th>( X_{\text{CO}_2, \text{ad}} )</th>
<th>( \mu_{X_{\text{CO}_2, \text{ad}}} )</th>
<th>( X_{\text{CO}_2} )</th>
<th>( \mu_{X_{\text{CO}_2}} )</th>
<th>( n_{\text{CO}_2} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>CB11873</td>
<td>86.8651</td>
<td>0.0144</td>
<td>-0.015</td>
<td>0.01</td>
<td>0.01</td>
<td>0.01</td>
<td>357.545</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CB11906</td>
<td>87.7891</td>
<td>0.0146</td>
<td>-0.015</td>
<td>0.01</td>
<td>0.01</td>
<td>0.01</td>
<td>397.497</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CB11941</td>
<td>85.2993</td>
<td>0.0142</td>
<td>-0.017</td>
<td>0.01</td>
<td>0.01</td>
<td>0.01</td>
<td>405.337</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CB11976</td>
<td>84.4516</td>
<td>0.0140*</td>
<td>-0.020</td>
<td>0.01</td>
<td>0.01</td>
<td>0.01</td>
<td>405.307</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CB12009</td>
<td>79.6713</td>
<td>0.0133</td>
<td>-0.022</td>
<td>0.01</td>
<td>0.01</td>
<td>0.01</td>
<td>491.763</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Note: Entries preceded by "*" represent standard uncertainties (±68% Confidence Level)

- \( \mu_{n_{\text{Air}}} \): mass of \( \text{CO}_2 \) in a 5-mL container (corrected to standard)
- \( \mu_{X_{\text{CO}_2, \text{ad}}} \): mass of \( \text{CO}_2 \) in a 5-mL container (corrected to standard)
- \( \mu_{X_{\text{CO}_2}} \): mass of \( \text{CO}_2 \) (initially present in cylinder)
- \( \mu_{n_{\text{CO}_2}} \): mass of \( \text{CO}_2 \) (initially present in cylinder)
- \( X_{\text{CO}_2, \text{ad}} \): amount of \( \text{CO}_2 \) absorbed by cylinder walls
- \( X_{\text{CO}_2} \): amount of \( \text{CO}_2 \) in the dilution gas

\( n_{\text{Air}} \): total amount of air (moles)

\( \mu_{n_{\text{Air}}} \): standard uncertainty of \( n_{\text{Air}} \)

\( X_{\text{CO}_2, \text{ad}} \): correction applied for adsorption to cylinder walls

\( X_{\text{CO}_2} \): correction applied for \( \text{CO}_2 \) in the dilution gas

\( X_{\text{CO}_2} \): mole fraction of \( \text{CO}_2 \)
**Table 2**: CO₂ purity assessment.

<table>
<thead>
<tr>
<th>Component</th>
<th>Fraction</th>
<th>Method</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO₂ (source)</td>
<td>0.99994</td>
<td></td>
</tr>
<tr>
<td>CO₂ (aliquot)*</td>
<td>0.99997</td>
<td></td>
</tr>
<tr>
<td>H₂O</td>
<td>0.00003</td>
<td>electrolytic</td>
</tr>
<tr>
<td>CH₄</td>
<td>0.00002</td>
<td>laser spectroscopy</td>
</tr>
<tr>
<td>CO</td>
<td>0.00001</td>
<td>laser spectroscopy</td>
</tr>
<tr>
<td>N₂O</td>
<td>2·10⁻⁹</td>
<td>GC-ECD</td>
</tr>
<tr>
<td>ethyne</td>
<td>3·10⁻⁹</td>
<td>GC-GCMS</td>
</tr>
<tr>
<td>ethene</td>
<td>2·10⁻⁹</td>
<td>GC-GCMS</td>
</tr>
<tr>
<td>propane</td>
<td>2·10⁻⁹</td>
<td>GC-GCMS</td>
</tr>
<tr>
<td>other hydrocarbons</td>
<td>&lt; 2·10⁻⁸</td>
<td>GC-GCMS</td>
</tr>
<tr>
<td>total non-condensible</td>
<td>0.00002</td>
<td>residual pressure</td>
</tr>
</tbody>
</table>

*Since the CO₂ aliquots were cryogenically purified to remove non-condensible gases, we calculate the aliquot purity based on H₂O only. Non-condensibles include e.g., N₂, O₂, Ar, H₂, CO, and CH₄.*

**Table 3**: Summary of CO₂ adsorption experiments. For each cylinder, the test was repeated N times. Adsorbed CO₂ is expressed as a fraction of the total CO₂ in the cylinder.

<table>
<thead>
<tr>
<th>Cylinder</th>
<th>N</th>
<th>Average</th>
<th>Std. Dev.</th>
</tr>
</thead>
<tbody>
<tr>
<td>CB11873</td>
<td>5</td>
<td>0.0043%</td>
<td>0.0003%</td>
</tr>
<tr>
<td>CB11941</td>
<td>4</td>
<td>0.0042%</td>
<td>0.0003%</td>
</tr>
<tr>
<td>CB11906</td>
<td>5</td>
<td>0.0038%</td>
<td>0.0004%</td>
</tr>
<tr>
<td>CB11976</td>
<td>5</td>
<td>0.0044%</td>
<td>0.0005%</td>
</tr>
<tr>
<td>CB12009</td>
<td>5</td>
<td>0.0044%</td>
<td>0.0002%</td>
</tr>
</tbody>
</table>
Table 4: Analysis of CO₂-in-air standards. "Best-fit" values were determined from a linear fit (response vs. prepared CO₂) using orthogonal distance regression, with fit coefficients equal to $2.4644 \times 10^{-4}$ and $8.7851 \times 10^{-4}$. Uncertainties (unc.) are shown as ~68%. Results are not sensitive to how the response was normalized.

<table>
<thead>
<tr>
<th>Cylinder</th>
<th>Prepared ppm</th>
<th>Unc. ppm</th>
<th>Response</th>
<th>Unc. ppm</th>
<th>Best-fit ppm</th>
<th>Residual ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>CB11873</td>
<td>357.545</td>
<td>0.050</td>
<td>0.881915</td>
<td>0.000028</td>
<td>357.512</td>
<td>-0.033</td>
</tr>
<tr>
<td>CB11906</td>
<td>397.497</td>
<td>0.062</td>
<td>0.980465</td>
<td>0.000025</td>
<td>397.502</td>
<td>0.005</td>
</tr>
<tr>
<td>CB11941</td>
<td>405.337</td>
<td>0.073</td>
<td>1.000000</td>
<td>0.000025</td>
<td>405.429</td>
<td>0.092</td>
</tr>
<tr>
<td>CB11976</td>
<td>449.301</td>
<td>0.075</td>
<td>1.108007</td>
<td>0.000025</td>
<td>449.257</td>
<td>-0.044</td>
</tr>
<tr>
<td>CB12009</td>
<td>491.763</td>
<td>0.077</td>
<td>1.212741</td>
<td>0.000039</td>
<td>491.756</td>
<td>-0.007</td>
</tr>
</tbody>
</table>

Table 4: Results of mother/daughter testing on 29.5-L aluminum cylinders. Note: Final pressures do not sum correctly due to thermal differences.
Table 5: Results of Mother/Daughter testing on 29.5-L aluminum cylinders. Note: Final pressures do not sum correctly due to thermal differences. Mother/Daughter difference calculated as Daughter (after transfer) minus Mother (after transfer).

<table>
<thead>
<tr>
<th>Cylinder</th>
<th>Pressure (MPa)</th>
<th>CO₂ (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CB11795</td>
<td>Mother</td>
<td>12.07</td>
</tr>
<tr>
<td></td>
<td>Initial</td>
<td></td>
</tr>
<tr>
<td>CB11795</td>
<td>Daughter</td>
<td>5.79</td>
</tr>
<tr>
<td></td>
<td>After transfer</td>
<td></td>
</tr>
<tr>
<td>CB11941</td>
<td>Mother</td>
<td>0.03</td>
</tr>
<tr>
<td></td>
<td>Initial</td>
<td></td>
</tr>
<tr>
<td>CB11941</td>
<td>Daughter</td>
<td>5.72</td>
</tr>
<tr>
<td></td>
<td>After transfer</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Change in Mother - Daughter</th>
<th>Change in Daughter - Mother</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.06</td>
<td>-0.16</td>
</tr>
</tbody>
</table>

| CB11088   | Mother         | 13.80     | 408.125   |
|           | Initial        |           |           |
| CB11088   | Daughter       | 6.69      | 408.188   |
|           | After transfer |           |           |
| CB11873   | Mother         | 0.03      | N.A.      |
|           | Initial        |           |           |
| CB11873   | Daughter       | 6.55      | 407.995   |
|           | Final          |           |           |

<table>
<thead>
<tr>
<th>Change in Mother - Daughter</th>
<th>Change in Daughter - Mother</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.06</td>
<td>-0.19</td>
</tr>
</tbody>
</table>
Figure 1: Schematic of the blending manifold. The sample aliquot (5-mL) was connected to one of three aliquot inlet ports (p1, p2, p3). The sample was transferred to the receiving cylinder by opening the cylinder valve (with v2 closed), opening the valve on the 5-mL vessel, and then alternately pressurizing the section between valves v2 and v3, and opening v3 to send the gas to the cylinder. The sample manifold is constructed of ¼” o.d. stainless steel tubing with welded or Swagelok VCR connections. Valves are stainless steel, diaphragm-sealed (Swagelok model DSV51).
Figure 2: Typical result from Schibig et al. (2018) CO$_2$ decanting experiments showing an increase in $X_{CO_2}$ with decreasing cylinder pressure. The fraction of CO$_2$ adsorbed was found by comparing the area under the Langmuir isotherm (blue line) with the area under the Langmuir isotherm but above the initial CO$_2$ mole fraction (dashed line). The adsorbed CO$_2$ calculated this way, expressed as a mole fraction, is similar to the parameter CO$_2_{ad}$ from the Langmuir model (Leuenberger et al., 2015; Schibig et al., 2018).
Figure 3: Normalized response of gravimetrically-prepared standards, analyzed by laser spectroscopy (lower panel). Residuals from linear fit are shown in upper panel, along with preparation uncertainties (~68% Confidence Level, or coverage factor k=1).
Figure 4: Measure of CO$_2$ passing through a ~1-m AT-steel transfer line. The peak in (a) results from 0.6cm$^3$ air containing 10% CO$_2$ injected into CO$_2$-free air flowing at 0.2 L min$^{-1}$. Panel (b) is an expanded view of panel (a), showing a second peak at ~400s, which results from CO$_2$ driven off the tubing by heating.