

# 1 Gravimetrically-Prepared Carbon Dioxide Standards in Support of Atmospheric Research

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## 16 Abstract

17  
18 We have explored a one-step method for gravimetric preparation of CO<sub>2</sub>-in-air standards in  
19 aluminum cylinders. We consider both adsorption to stainless steel surfaces used in the  
20 transfer of highly-pure CO<sub>2</sub>, and adsorption of CO<sub>2</sub> to cylinder walls. We demonstrate that CO<sub>2</sub>-  
21 in-air standards can be prepared with relatively low uncertainty (~0.04%, ~95% Confidence  
22 Level) by introducing aliquots whose masses are known to high precision, and by using well-  
23 characterized cylinders. Five gravimetric standards, prepared over the nominal range 350 to  
24 490 μmol mol<sup>-1</sup> (parts per million, ppm), showed excellent internal consistency, with residuals  
25 from a linear fit equal to 0.05 ppm. This work complements efforts to maintain the World  
26 Meteorological Organization, Global Atmosphere Watch, mole fraction scale for carbon dioxide  
27 in air, widely used for atmospheric monitoring. This gravimetric technique could be extended to  
28 other atmospheric trace gases, depending on the vapor pressure of the gas.  
29

## 30 Introduction

31  
32  
33 Numerous laboratories make routine measurements of atmospheric carbon dioxide to better  
34 understand its sources, sinks, and temporal variability. These measurements are typically  
35 calibrated using high-pressure gas standards containing CO<sub>2</sub> in air (typically natural air with

1 assigned CO<sub>2</sub> mole fractions), traceable to primary standards prepared or analyzed using  
2 absolute methods, such as manometry (Keeling et al., 1986;Zhao and Tans, 2006) and  
3 gravimetry (Machida et al., 2011;Rhoderick et al., 2016;Brewer et al., 2014), which provide  
4 traceability to the SI. The World Meteorological Organization (WMO), Global Atmosphere  
5 Watch (GAW) initially adopted the Scripps Institution of Oceanography scale (Keeling et al.,  
6 1986) and subsequently the National Oceanic and Atmospheric Administration (NOAA) scale  
7 (Zhao et al., 1997), both of which are based on repeated manometric measurements of a suite  
8 of primary standards, for WMO-affiliated monitoring networks. The WMO scale has been  
9 updated over the years as understanding has improved and measurement records of primary  
10 standards have increased (Keeling et al., 2002;Keeling et al., 1986;Zhao and Tans, 2006).

11  
12 [Determining the absolute amount of CO<sub>2</sub> in air is a challenge for both gravimetric and](#)  
13 [manometric methods, particularly since the relative uncertainties must be very small \(~0.006%](#)  
14 [1-sigma, or about a factor of 4 lower than the WMO network compatibility goal of 0.1 ppm](#)  
15 [\(WMO, 2018\)\), in order to assess changes \(drift\) in cylinders over many years.](#) Long-term  
16 monitoring of atmospheric CO<sub>2</sub> requires a stable reference, sufficient to identify small  
17 atmospheric gradients (of order 0.1 μmol mol<sup>-1</sup>, or 0.1 ppm, in the remote troposphere).  
18 Hereafter we will use ppm (parts per million) for μmol mol<sup>-1</sup>. Both methods can be influenced  
19 by the adsorption of CO<sub>2</sub> to surfaces. There is increasing evidence that CO<sub>2</sub> can adsorb to the  
20 internal surfaces of cylinders and desorb with decreasing pressure (Langenfelds et al.,  
21 1996;Miller et al., 2015;Leuenberger et al., 2015;Brewer et al., 2018;Schibig et al., 2018). This  
22 impacts both the gravimetrically-assigned mole fraction and the mole fraction of CO<sub>2</sub> in air  
23 withdrawn from cylinders over time. Further, since cylinder characteristics may differ among  
24 cylinder manufacturers, understanding the behavior of CO<sub>2</sub> in cylinders is critical to maintaining  
25 stable scales over time.

26  
27 The gravimetric technique can employ multiple steps, in which the target gas (CO<sub>2</sub> in this case)  
28 is diluted to the desired amount fraction. For example, Brewer et al. (2014) first prepared  
29 standards with mole fractions of a few percent, then made dilutions of those to the range

1 needed for ambient monitoring (~400 ppm). Others have opted to dilute CO<sub>2</sub> to ppm levels in  
2 one step (Machida et al., 2011). Matrix gases can also be added in different ways: CO<sub>2</sub> can be  
3 mixed with individual gases (N<sub>2</sub>, O<sub>2</sub>, Ar) to form an air-like matrix, or CO<sub>2</sub> can be added to  
4 natural air from which the CO<sub>2</sub> has been removed. Methods of targeting stable isotopes of CO<sub>2</sub>  
5 (e.g. <sup>13</sup>C-CO<sub>2</sub>) to better match natural abundances have also been explored (Brewer et al.,  
6 2014).

7  
8 Here we describe one-step preparation of CO<sub>2</sub>-in-air compressed gas standards in aluminum  
9 cylinders. We used information gained from recent decanting experiments (Schibig et al., 2018)  
10 to correct for CO<sub>2</sub> adsorption to the cylinder walls. This work was undertaken to support NOAA  
11 manometric efforts and learn more about the behavior of CO<sub>2</sub> in aluminum cylinders.

## 12 13 **Experimental Methods**

14  
15 Standards were prepared in 29.5-L Luxfer aluminum cylinders (~22kg empty) (Scott Marrin, Inc.  
16 Riverside, CA), with brass, packless valves (Ceodux). We chose these cylinders for two reasons.  
17 First, we wanted to perform the dilutions in one step, and therefore needed relatively large  
18 cylinders. Second, we wanted to use cylinders that were well-characterized. We have  
19 considerable experience with CO<sub>2</sub>-in-air in this type of cylinder. Specific to this work, all  
20 cylinders used were filled with natural air and decanted several times for CO<sub>2</sub> adsorption  
21 studies (Schibig et al., 2018) prior to being used for gravimetric standards described here.

22  
23 For this gravimetric work, each cylinder was evacuated to ~30 mtorr (4 Pa) and weighed on a  
24 mass comparator (Sartorius CCE40K3: 40kg capacity, 2mg readability) relative to a control  
25 cylinder of similar mass and volume. The mass comparator was calibrated using a 10 kg mass  
26 (Troemner), and linearity over the working range was confirmed by adding a 5 kg mass (Mettler  
27 Toledo) to the reference cylinder. We then added ~50 psi (0.34 MPa) natural air containing 402  
28 or 408 ppm CO<sub>2</sub> determined by analysis (WMO X2007 scale). Cylinders were then vented,  
29 partially evacuated to ~ 400 torr (53 kPa), and weighed. The mass of residual air along with the

1 mole fraction of CO<sub>2</sub> were used to calculate the initial mass of CO<sub>2</sub> in the cylinder. We did not  
2 evacuate the cylinders further because CO<sub>2</sub> adsorption studies (Schibig et al., 2018) were  
3 performed at pressures ranging from 0.1-13.8 MPa. The Schibig et al. (2018) work provided a  
4 means to determine the amount of CO<sub>2</sub> adsorbed to cylinder walls, and we wanted to perform  
5 the gravimetric addition with a small amount of residual CO<sub>2</sub> in the cylinders, consistent with  
6 that work. For the standards presented here, the initial CO<sub>2</sub> in the cylinder corresponds to <  
7 0.8% of the total CO<sub>2</sub>, and so the uncertainty associated with the mole fraction of initial CO<sub>2</sub>,  
8 derived from an independent CO<sub>2</sub> calibration (Zhao and Tans, 2006), makes a negligible  
9 contribution to the total uncertainty (Table 1). The majority of the uncertainty in the mass of  
10 CO<sub>2</sub> originally in the cylinder results from uncertainty in the mass determination of the residual  
11 air. Nevertheless, we include a standard uncertainty of 0.025% on the WMO X2007 CO<sub>2</sub> scale  
12 ([https://www.esrl.noaa.gov/gmd/ccl/ccl\\_uncertainties\\_co2.html](https://www.esrl.noaa.gov/gmd/ccl/ccl_uncertainties_co2.html)).

13  
14 An initial aliquot of high-purity CO<sub>2</sub> was added to an evacuated 50-mL stainless steel container  
15 with a single metal bellows valve (Swagelok, model SS-4H) (pressure rated to 1000 psi, or 6.90  
16 MPa, at 37 °C). After CO<sub>2</sub> was loaded into the 50-mL container at the desired pressure, it was  
17 cryogenically transferred to a 5-mL stainless steel container, also with a metal bellows valve  
18 (total mass ~150g) that had been evacuated and weighed previously. The CO<sub>2</sub> was cryogenically  
19 purified by freezing at -197 °C and pumping off non-condensable gases. We estimate the purity  
20 of the CO<sub>2</sub> source at 99.994% and that of the cryogenically-purified CO<sub>2</sub> aliquots at 99.997 ±  
21 0.002% (Table 2). In this smaller volume, both liquid and vapor phases of CO<sub>2</sub> would be present  
22 at room temperature (18 °C in this case). Note that the vapor pressure of CO<sub>2</sub> at 18 °C is ~795  
23 psi (5.48 MPa), and that our 5-mL container and valve was rated to 1000 psi (6.89 MPa). We  
24 employed this secondary transfer to a smaller container so that we could weigh ~1.5g CO<sub>2</sub> on a  
25 balance with 0.01mg readability (Mettler Toledo AT201, 200g capacity). The 50-mL container  
26 used in the first step is too large to be weighed on the AT-201. This is an important aspect of  
27 this work. Without this secondary step, our uncertainties would have been about a factor of 10  
28 larger. The mass of CO<sub>2</sub> in each 5-mL aliquot was determined by weighing the 5-mL container  
29 relative to a control object of similar mass and density (sequence ABABA....). The AT-201 was

1 calibrated using internal weights, and span-checked by adding a 2.0000g mass to the 5-mL  
2 container.

3  
4 Each purified CO<sub>2</sub> aliquot was transferred from the 5-mL container to a partially-evacuated  
5 cylinder on a stainless steel vacuum manifold using a pressurization/expansion method (Figure  
6 1) (Dlugokencky et al., 2005). The cylinder was connected to the vacuum manifold using a 1/8"  
7 OD AT-steel transfer line. AT-steel, also known as "activity tested steel" (Grace Discovery  
8 Science, Columbia, MD) is treated using vapor deposition to improve surface inertness. In initial  
9 tests we found that AT-steel performed better than other types of stainless steel, but in  
10 subsequent tests both 1/8" O.D. stainless steel and 1/8" O.D. AT-steel performed similarly (see  
11 Results and Discussion).

12  
13 To transfer the aliquot to the cylinder, the manifold and transfer line were pre-heated to ~60 °C  
14 and evacuated to 5 mtorr (0.7 Pa). In quick succession, the cylinder valve was opened and the  
15 valve on the 5-mL container was opened allowing CO<sub>2</sub> to expand into the cylinder. The  
16 expansion of CO<sub>2</sub> resulted in significant cooling of the 5-mL container, so we heated the 5-mL  
17 container, manifold, and transfer lines to ~60 °C while alternately pressurizing the 5-mL  
18 container to ~200 psi (1.38 MPa) with CO<sub>2</sub>-free air (dilution gas) and expanding into the  
19 cylinder. After about 20 pressurization/expansion cycles, the valve on the 5-mL container was  
20 closed and the cylinder pressurized with dilution gas. The 5-mL container was removed from  
21 the manifold at a cylinder pressure of ~ 500 psi (3.45 MPa), and the cylinder was then further  
22 pressurized to 1000 psi (6.90 MPa) with dilution gas. Dilution gas consisted of scrubbed natural  
23 air (Cryogenic Ultra-pure grade, Scott Mairin Inc; now Praxair, Los Angeles, CA). This gas was  
24 analyzed for CO<sub>2</sub> by non-dispersive infrared analysis (NDIR; Licor Li-7000). Samples of dilution  
25 gas were compared to a reference of dry nitrogen (99.999%) scrubbed using Ascarite II (Sigma  
26 Aldrich). All cylinders of dilution gas contained 0.01 ± 0.01 ppm CO<sub>2</sub>. After cylinders cooled to  
27 room temperature, they were weighed on the mass comparator relative to the control cylinder.  
28

1 The mole fraction of CO<sub>2</sub>,  $X_{CO_2}$ , was calculated using equation (1), where  $n_a$  is the moles of CO<sub>2</sub>  
2 transferred from the 5-mL container,  $n_b$  is the moles of CO<sub>2</sub> initially present in the cylinder,  $n_{air}$   
3 is the total moles of air (sum of natural air initially present and dilution air),  $p$  is the purity  
4 coefficient,  $f$  is the transfer efficiency,  $X_{CO_2,ad}$  is a correction for the amount of CO<sub>2</sub> adsorbed to  
5 the cylinder walls ( $X_{CO_2,ad} < 0$ ) expressed in ppm, and  $X_{CO_2,dil}$  is the amount of CO<sub>2</sub> in the dilution  
6 air, also expressed in ppm.

7  
8

$$X_{CO_2} = \frac{pf n_a + n_b}{pf n_a + n_b + n_{air}} + X_{CO_2,ad} + X_{CO_2,dil} \quad (1)$$

10

11 The amount of each component was determined from the mass and molecular weight. For CO<sub>2</sub>  
12 we used a molecular weight of  $44.0096 \pm 0.0006 \text{ g mol}^{-1}$  (consistent with a <sup>13</sup>C-CO<sub>2</sub> content of -  
13 29 per mil on the VPDB scale, determined using off-axis integrated cavity output spectroscopy  
14 (Los Gatos Research) traceable to the University of Colorado (INSTAAR) Stable Isotope  
15 Laboratory realization of VPDB (Trolier et al., 1996; Tans et al., 2017). For the dilution gas, we  
16 used a molecular weight of  $28.9602 \pm 0.0042 \text{ g mol}^{-1}$ . The oxygen content of the dilution gas  
17 was measured using a paramagnetic method (Beckman, E2) traceable to NIST SRM 2659A  
18 ( $20.863\% \pm 0.011\% \text{ O}_2$  in N<sub>2</sub>). Argon was taken as 0.933% (Sutour et al., 2007), and the noble  
19 gases Xe, Ne, and Kr were taken as 0.09, 18.0 and 1.14 ppm, respectively. Nitrogen was  
20 assumed to comprise the remaining fraction. We assumed 100% transfer efficiency ( $f=1.0$ ) with  
21 an uncertainty of 0.01% (rectangular distribution) (see Results and Discussion).

22 The mole fraction correction for CO<sub>2</sub> adsorbed to the cylinder walls ( $X_{CO_2,ad}$ ) was determined  
23 from multiple decanting experiments (Schibig et al., 2018). Briefly, in those experiments,  
24 cylinders were filled with dry natural air (~400 ppm), and drained at  $0.3 \text{ L min}^{-1}$  and analyzed  
25 continuously for CO<sub>2</sub> by NDIR. These studies showed remarkably consistent results: that the  
26 mole fraction of CO<sub>2</sub> exiting the cylinder increased as the cylinder pressure decreased, and that  
27 the data can be described with a Langmuir isotherm (Figure 2). By fitting the data with a

1 Langmuir isotherm as derived by Leuenberger et al. (2015), and integrating the area between  
2 the Langmuir fit and the initial  $X_{CO_2}$ , we determined the amount of  $CO_2$  that desorbs from the  
3 walls as the cylinder is vented slowly to near-ambient pressure (Fig. 2). The amount of  $CO_2$   
4 adsorbed to the walls, expressed as a fraction of the total amount of  $CO_2$  in the cylinder, was  
5 typically about 0.004% (Table 3). Although the low-flow data show very good reproducibility  
6 (Table 3), we assumed a standard uncertainty of 0.01 ppm.

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

## 16 **Results and Discussion**

18 Following preparation, standards were analyzed using laser spectroscopy (Tans et al., 2017).  
19 Each standard was analyzed twice over a period of two weeks. The response was expressed as  
20 the mole fraction of  $CO_2$ , calculated on the WMO X2007  $CO_2$  scale, relative to that of CB11941.  
21 We use this relative response because mole fraction assignments on the X2007 scale account  
22 for differences in the abundances of stable isotopes of  $CO_2$  (mainly  $^{13}C-CO_2$ ) between the  
23 gravimetric standards and secondary standards used for calibration (Tans et al., 2017). For  
24 comparison, we also calculated response based on the analyzer signal derived from a single  $CO_2$   
25 isotopologue ( $^{16}O-^{12}C-^{16}O$ , 626). Both methods give similar results with respect to consistency  
26 of the standard set.

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

1 regression line. The standard deviation of residuals is 0.05 ppm and the largest residual is 0.09  
2 ppm. Since the uncertainty associated with the molecular weight of air is the largest contributor  
3 to the total uncertainty, but is common to all standards, it is worth recalculating uncertainty  
4 without this contribution in order to assess consistency. Without  $\mu_{MW_{air}}$ , standard  
5 uncertainties for each standard are 40-60% lower than when  $\mu_{MW_{air}}$  is included. Recalculating  
6 the regression using these lower uncertainties, we find that the residuals do not change  
7 appreciably. However, the residual for cylinder CB11941 becomes 0.098 ppm. With a standard  
8 uncertainty of 0.046 ppm, CB11941 is not consistent with the rest of the standards. This may be  
9 the result of preparation. Cylinder CB11941 was the first standard prepared, and followed  
10 testing that involved injecting high concentrations of CO<sub>2</sub> into the manifold and transfer line. It  
11 is possible that some residual CO<sub>2</sub> remained in the manifold and transfer line, and was  
12 introduced into CB11941 when the manifold and transfer line were heated. The other  
13 standards were prepared following several heating cycles, and are less likely to be influenced by  
14 any residual CO<sub>2</sub>.

15  
16 To support our assumption of 100% transfer efficiency, we examined both the potential for  
17 adsorption of CO<sub>2</sub> in the manifold and transfer line, and the efficiency of transferring CO<sub>2</sub> from  
18 the 5-mL container to a cylinder. We tested the transfer line by flowing air containing ~0.1 ppm  
19 CO<sub>2</sub> at 0.2 L min<sup>-1</sup> through 1/8" AT-steel tubing to an NDIR analyzer. Then we injected 0.6mL of  
20 10% CO<sub>2</sub>-in-air into this air stream. After the initial slug of CO<sub>2</sub> was observed and the NDIR  
21 signal returned to baseline, we heated the transfer line and measured the additional CO<sub>2</sub>  
22 coming off (Figure 4). Comparing the area of the CO<sub>2</sub> released upon heating with that of the  
23 main sample injected, we found that our AT-steel transfer line (length 1m) retained about  
24 0.04% of CO<sub>2</sub> in the sample. We were able to drive off most of this CO<sub>2</sub> on the first heating  
25 cycle, with < 0.01% released on subsequent heating. Tests with stainless steel (not AT-steel)  
26 showed similar results. By heating the lines multiple times and passing a large amount of CO<sub>2</sub>-  
27 free air through them, it is unlikely that a significant amount of CO<sub>2</sub> would remain in the  
28 manifold or transfer line.

29



1 We tested the transfer efficiency from the 5-mL container by cryogenically moving aliquots of  
2 CO<sub>2</sub> from one 5-mL container to another on a vacuum line (using liquid N<sub>2</sub>), without additional  
3 flushing, and measuring changes in mass. When both the initial 5-mL container and transfer line  
4 were heated, a transfer efficiency of  $99.9 \pm 0.1\%$  was achieved. Without heating, the same test  
5 revealed only 99% efficiency. We expect that repeated pressurization/expansion with CO<sub>2</sub>-free  
6 air, in addition to heating, would improve the transfer efficiency of the CO<sub>2</sub> aliquot to near  
7 100%. The relatively good agreement among the four standards prepared after CB11941  
8 supports this assumption. It seems unlikely that this level of agreement could be achieved with  
9 poor or variable transfer efficiency.

10

11 As mentioned earlier, we estimated the amount of CO<sub>2</sub> adsorbed to the cylinder walls  
12 (~0.004%) from the results of low-flow decanting experiments. The Schibig et al. (2018)  
13 decanting tests reveal substantially less CO<sub>2</sub> adsorbed compared to “mother/daughter” tests  
14 (Miller et al., 2015; Brewer et al., 2018), in which half the contents of one cylinder are  
15 transferred to an equal size cylinder and the adsorption determined based on the resulting  
16 mole fraction difference. From mother/daughter tests on 5.9-L cylinders from Airgas (Riverton,  
17 NJ) and 5-L cylinders from Air Products (Vilvoorde, Belgium), Miller et al. (2015) estimated that  
18 about 0.02% of the CO<sub>2</sub> was adsorbed to the walls. Brewer et al. (2018) performed similar tests  
19 on 10-L aluminum cylinders treated with the BOC Spectra Seal process, and found CO<sub>2</sub>  
20 adsorption fractions of about 0.05%.

21 In preparation for this work, we performed mother/daughter tests on both 5.9-L and 29.5-L  
22 aluminum cylinders (Scott Marrin, Riverside, CA), including cylinders CB11941 and CB11873  
23 used in this work. Cylinders CB11941 and CB11873 were filled with natural air, vented, and then  
24 evacuated to 5 psia (0.03 MPa). Air from two "mother" cylinders containing natural air was  
25 transferred into CB11941 and CB11873. We found that the CO<sub>2</sub> in daughter cylinders CB11941  
26 and CB11873 was 0.16-0.19 ppm lower than their respective mothers after transfer (Table 5),  
27 similar to the results of Miller et al. (2015) and Brewer et al. (2018). Our tests with 5.9-L  
28 cylinders also showed differences of ~0.2 ppm (not shown).

1 Mother/daughter tests suggest five to ten times more adsorption than that determined from  
2 the Schibig et al. (2018) low-flow data. The difference between mother/daughter tests and the  
3 low-flow experiments could be related to thermal fractionation. Schibig et al. (2018) performed  
4 both low-flow ( $0.3 \text{ L min}^{-1}$ ) and high-flow ( $5.0 \text{ L min}^{-1}$ ) decanting experiments. They found that  
5 changes in  $\text{CO}_2$  at the high flowrate were 2.5 times those observed at the low flowrate, and  
6 attributed the difference to thermal fractionation at the higher flow rate. During our  
7 mother/daughter tests, the mother cylinders experienced significant cooling during transfer,  
8 which could have caused fractionation as cooler air sinks in the center core of the cylinder, with  
9  $\text{CO}_2$  preferentially remaining in the mother cylinder. In fact, after transferring half of the gas  
10 from a mother cylinder to a respective daughter cylinder, the mole fraction of  $\text{CO}_2$  in each  
11 mother cylinder increased  $0.06 \pm 0.01$  ppm relative to its value determined prior to transfer  
12 (Table 5). From figure 2, which represents a typical low-flow decanting result, the increase due  
13 to desorption from the cylinder walls should be far smaller than 0.06 ppm at 50% of the original  
14 cylinder pressure.

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

26

## 27 **Conclusions**

28

1 Five gravimetric CO<sub>2</sub>-in-air standards, prepared at the ppm level in one dilution step, show  
2 excellent internal consistency. Prepared mole fractions were adjusted for CO<sub>2</sub> expected to  
3 adsorb to cylinder walls. This correction was determined from low-flow decanting studies, and  
4 is a factor of 5-10 smaller than that inferred from mother/daughter tests. With improved  
5 understanding of CO<sub>2</sub> adsorption characteristics, and by introducing condensed-phase aliquots  
6 of CO<sub>2</sub> into small vessels that can be weighed with sufficient repeatability, CO<sub>2</sub>-in-air standards  
7 can be prepared with relatively low uncertainty. This work supports parallel efforts to maintain  
8 the WMO mole fraction scale for CO<sub>2</sub>.

9  
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14 **Supporting Information**

15  
16 Table\_1\_landscape.pdf

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

Cylinder	----- Components -----							n <sub>CO2</sub> mol
	CO <sub>2</sub> _a g	μ_CO <sub>2</sub> _a g	CO <sub>2</sub> _b g	μ_CO <sub>2</sub> _b g	Air g	μ_Air g	n <sub>CO2</sub> mol	
<b>CB11873</b>	1.36062	0.00008	6.80E-03	2.24E-05	2515.630	0.033	3.1070E-02	
<b>CB11906</b>	1.52917	0.00007	7.28E-03	1.25E-05	2542.391	0.026	3.4911E-02	
<b>CB11941</b>	1.51156	0.00015	1.07E-02	1.25E-05	2470.254	0.030	3.4589E-02	
<b>CB11976</b>	1.66307	0.00011	7.32E-03	1.18E-05	2445.190	0.014	3.7954E-02	
<b>CB12009</b>	1.71751	0.00007	7.72E-03	1.81E-05	2307.297	0.039	3.9200E-02	

  

Cylinder	----- Adjustments -----						-- Amount Fraction-- X <sub>CO2</sub> ppm
	n <sub>air</sub> mol	μ_n <sub>air</sub> mol	X <sub>CO2,ad</sub> ppm	μ_X <sub>CO2,ad</sub> ppm	X <sub>CO2,dil</sub> ppm	μ_X <sub>CO2,dil</sub> ppm	
<b>CB11873</b>	86.8651	0.0144	-0.015	0.01	0.01	0.01	357.545
<b>CB11906</b>	87.7891	0.0146	-0.015	0.01	0.01	0.01	397.497
<b>CB11941</b>	85.2982	0.0142	-0.017	0.01	0.01	0.01	405.337
<b>CB11976</b>	84.4328	0.0140	-0.020	0.01	0.01	0.01	449.301
<b>CB12009</b>	79.6713	0.0133	-0.022	0.01	0.01	0.01	491.763

Note: Entries preceded by " μ\_" represent standard uncertainties (~68% Confidence Level)

CO<sub>2</sub>\_a = mass of CO<sub>2</sub> aliquot in 5-mL container, added to cylinder

CO<sub>2</sub>\_b = initial mass of CO<sub>2</sub> in cylinder (based on analyzed mole fraction and mass of residual air)

Air = mass of air (includes 10-15g residual air initially present in cylinder)

n<sub>CO2</sub> = total amount of CO<sub>2</sub> (moles) (0.99997 purity correction applied)

n<sub>air</sub> = total amount of air (moles)

X<sub>CO2,ad</sub> = correction applied to account for adsorption to cylinder walls

X<sub>CO2,dil</sub> = correction applied to account for CO<sub>2</sub> in the dilution gas

X<sub>CO2</sub> = mole fraction of CO<sub>2</sub>

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2 **Table 2:** CO<sub>2</sub> purity assessment.

Component	Fraction	Method
CO <sub>2</sub> (source)	0.99994	
CO <sub>2</sub> (aliquot)*	0.99997	
H <sub>2</sub> O	0.00003	electrolytic
CH <sub>4</sub>	0.00002	laser spectroscopy
CO	0.00001	laser spectroscopy
N <sub>2</sub> O	2·10 <sup>-8</sup>	GC-ECD
ethyne	3·10 <sup>-9</sup>	GC-GCMS
ethene	2·10 <sup>-9</sup>	GC-GCMS
propane	2·10 <sup>-9</sup>	GC-GCMS
other hydrocarbons	< 2·10 <sup>-8</sup>	GC-GCMS
total non-condensable	0.00002	residual pressure

3 \*Since the CO<sub>2</sub> aliquots were cryogenically purified to remove non-condensable gases,  
 4 we calculate the aliquot purity based on H<sub>2</sub>O only. Non-condensibles include e.g., N<sub>2</sub>,  
 5 O<sub>2</sub>, Ar, H<sub>2</sub>, CO, and CH<sub>4</sub>.

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9 **Table 3:** Summary of CO<sub>2</sub> adsorption experiments. For each cylinder, the test was repeated N  
 10 times. Adsorbed CO<sub>2</sub> is expressed as a fraction of the total CO<sub>2</sub> in the cylinder.

Cylinder	N	average %	std. dev. %
CB11873	5	0.0043%	0.0003%
CB11941	4	0.0042%	0.0003%
CB11906	5	0.0038%	0.0004%
CB11976	5	0.0044%	0.0005%
CB12009	5	0.0044%	0.0002%

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**Table 4:** Analysis of CO<sub>2</sub>-in-air standards. "Best-fit" values were determined from a linear fit (response vs. prepared CO<sub>2</sub>) using orthogonal distance regression, with fit coefficients equal to  $2.4644 \cdot 10^{-3}$  and  $8.7851 \cdot 10^{-4}$ . Uncertainties (unc.) are shown as ~68% Confidence Level. Results are not sensitive to how the response was normalized.

cylinder	prepared ppm	unc. ppm	response	unc.	best-fit ppm	residual ppm
CB11873	357.545	0.059	0.881915	0.000028	357.512	-0.033
CB11906	397.497	0.062	0.980465	0.000025	397.502	0.005
CB11941	405.337	0.073	1.000000	0.000025	405.429	0.092
CB11976	449.301	0.075	1.108007	0.000025	449.257	-0.044
CB12009	491.763	0.077	1.212741	0.000039	491.756	-0.007

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**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 differences were calculated as Daughter minus Mother (after transfer).

Cylinder		~ Pressure (MPa)		CO <sub>2</sub> (ppm)
CB11795	Mother	12.07	initial	401.928
CB11795	Mother	5.79	after transfer	401.988
CB11941	Daughter	0.03	initial	N.A.
CB11941	Daughter	5.72	after transfer	401.828
			Change in Mother	0.06
			Daughter - Mother	-0.16
CB11088	Mother	13.80	initial	408.125
CB11088	Mother	6.69	after transfer	408.188
CB11873	Daughter	0.03	initial	N.A.
CB11873	Daughter	6.55	final	407.995
			Change in Mother	0.06
			Daughter - Mother	-0.19

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1 **Figure Captions**

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3 **Figure 1:** Schematic of the blending manifold. The sample aliquot (5-mL) was connected to one  
4 of three aliquot inlet ports (p1, p2, p3). The sample was transferred to the receiving cylinder by  
5 opening the cylinder valve (with v2 closed), opening the valve on the 5-mL vessel, and then  
6 alternately pressurizing the section between valves v2 and v3, and opening v3 to send the gas  
7 to the cylinder. The sample manifold is constructed of ¼" o.d. stainless steel tubing with welded  
8 or Swagelok VCR connections. Valves are stainless steel, diaphragm-sealed (Swagelok model  
9 DSV51).

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11 **Figure 2:** Typical result from Schibig et al. (2018) CO<sub>2</sub> decanting experiments showing an  
12 increase in X<sub>CO<sub>2</sub></sub> with decreasing cylinder pressure. The fraction of CO<sub>2</sub> adsorbed was found by  
13 comparing the area under the Langmuir isotherm (blue line) with the area under the Langmuir  
14 isotherm but above the initial CO<sub>2</sub> mole fraction (dashed line). The adsorbed CO<sub>2</sub> calculated this  
15 way, expressed as a mole fraction, is similar to the parameter CO<sub>2,ad</sub> from the Langmuir model  
16 (Leuenberger et al., 2015;Schibig et al., 2018). Fit parameters, K, CO<sub>2\_ad</sub>, and CO<sub>2\_init</sub> are  
17 described in Leuenberger et al. (2015).

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19 **Figure 3:** Normalized response of gravimetrically-prepared standards, analyzed by laser  
20 spectroscopy (lower panel). Residuals from linear fit are shown in upper panel, along with  
21 preparation uncertainties (~68% Confidence Level, or coverage factor k=1).

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23 **Figure 4:** Measure of CO<sub>2</sub> passing through a ~1-m AT-steel transfer line. The peak in (a) results  
24 from 0.6cm<sup>3</sup> air containing 10% CO<sub>2</sub> injected into CO<sub>2</sub>-free air flowing at 0.2 L min<sup>-1</sup>. Panel (b) is  
25 an expanded view of panel (a), showing a second peak at ~ 400s, which results from CO<sub>2</sub> driven  
26 off the tubing by heating.

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