

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. $\frac{1}{4}$ 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 ~ 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, $X_{\text{CO}_2,\text{ad}}$ and $X_{\text{CO}_2,\text{dil}}$ 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 n_{air} should be split up into its components (n_{Ar} , n_{N_2} and n_{O_2}).

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 n_{air} as is because this is how we do the calculation: $n_{air} = mass_{air}/MW_{air}$

On page 7, amount is missing from the sentence “The amount of CO_2 adsorbed to the walls, expressed as a fraction of total amount of CO_2 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 n_b and n_{air} 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 405 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.

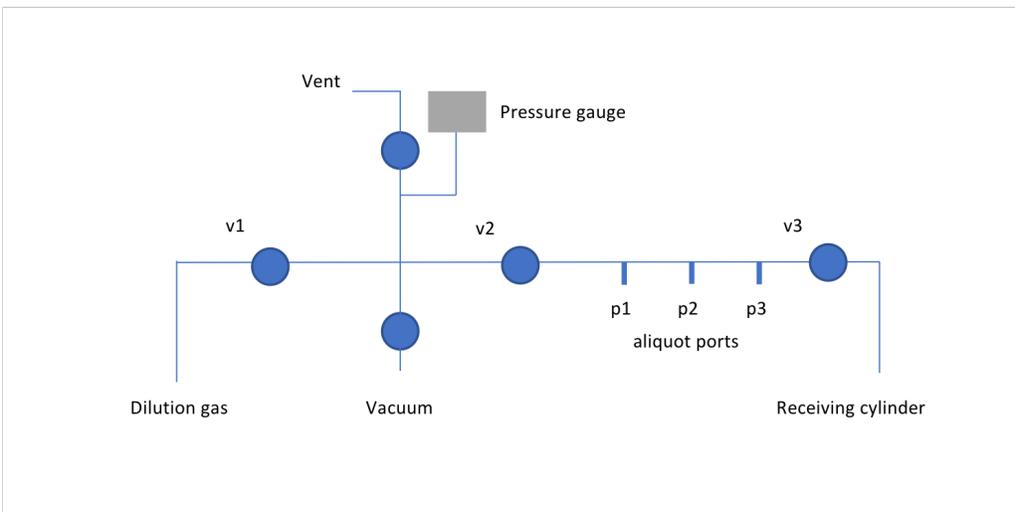


Figure 1: Schematic of the blending manifold. The sample aliquot (5-mL) was connected to one of three aliquot inlet ports (p1, p2, p3). The sample was transferred to the receiving cylinder by opening the cylinder valve, opening the valve on the 5-mL vessel, and then alternately pressurizing the section 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).

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 CO₂-in-air standards in
19 aluminum cylinders. We consider both adsorption to stainless steel surfaces used in the
20 transfer of highly-pure CO₂, and adsorption of CO₂ to cylinder walls. We demonstrate that CO₂-
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⁻¹ (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

31 **Introduction**

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 CO₂ in air (typically natural air with

1 assigned CO₂ 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).

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12 Determining the absolute amount of CO₂ 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 CO₂ requires a stable reference, sufficient to identify small
17 atmospheric gradients (of order 0.1 μmol mol⁻¹, or 0.1 ppm, in the remote troposphere).
18 Hereafter we will use ppm (parts per million) for μmol mol⁻¹. Both methods can be influenced
19 by the adsorption of CO₂ to surfaces. There is increasing evidence that CO₂ can adsorb to the
20 internal surfaces of cylinders and desorb with decreasing pressure (Langenfels 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 CO₂ in air
23 withdrawn from cylinders over time. Further, since cylinder characteristics may differ among
24 cylinder manufacturers, understanding the behavior of CO₂ in cylinders is critical to maintaining
25 stable scales over time.

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26
27 The gravimetric technique can employ multiple steps, in which the target gas (CO₂ 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 CO₂ to ppm levels in
2 one step (Machida et al., 2011). Matrix gases can also be added in different ways: CO₂ can be
3 mixed with individual gases (N₂, O₂, Ar) to form an air-like matrix, or CO₂ can be added to
4 natural air from which the CO₂ has been removed. Methods of targeting stable isotopes of CO₂
5 (e.g. ¹³C-CO₂) to better match natural abundances have also been explored (Brewer et al.,
6 2014).

7
8 Here we describe one-step preparation of CO₂-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 CO₂ adsorption to the cylinder walls. This work was undertaken to support NOAA
11 manometric efforts and learn more about the behavior of CO₂ in aluminum cylinders.

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 CO₂-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 CO₂ 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 CO₂ 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 CO₂ were used to calculate the initial mass of CO₂ in the cylinder. We did not
2 evacuate the cylinders further because CO₂ 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 CO₂ adsorbed to cylinder walls, and we wanted to perform
5 the gravimetric addition with a small amount of residual CO₂ in the cylinders, consistent with
6 that work. For the standards presented here, the initial CO₂ in the cylinder corresponds to <
7 0.8% of the total CO₂, and so the uncertainty associated with the mole fraction of initial CO₂,
8 derived from an independent CO₂ 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 CO₂ 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 CO₂ scale
12 (https://www.esrl.noaa.gov/gmd/ccl/ccl_uncertainties_co2.html).

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13
14 An initial aliquot of high-purity CO₂ 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 CO₂ 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 CO₂ was cryogenically
19 purified by freezing at -197 °C and pumping off non-condensable gases. We estimate the purity
20 of the CO₂ source at 99.994% and that of the cryogenically-purified CO₂ aliquots at 99.997 ±
21 0.002% (Table 2). In this smaller volume, both liquid and vapor phases of CO₂ would be present
22 at room temperature (18 °C in this case). Note that the vapor pressure of CO₂ 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 CO₂ 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 CO₂ 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

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

3

4 Each purified CO₂ 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 CO₂ to expand into the cylinder. The
16 expansion of CO₂ 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 CO₂-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 Marrin Inc; now Praxair, Los Angeles, CA). This gas was
24 analyzed for CO₂ 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 CO₂. 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 CO₂, X_{CO_2} , was calculated using equation (1), where n_a is the moles of CO₂
2 transferred from the 5-mL container, n_b is the moles of CO₂ 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 CO₂ adsorbed to
5 the cylinder walls ($X_{CO_2,ad} < 0$) expressed in ppm, and $X_{CO_2,dil}$ is the amount of CO₂ in the dilution
6 air, also expressed in ppm.

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

11 The amount of each component was determined from the mass and molecular weight. For CO₂
12 we used a molecular weight of $44.0096 \pm 0.0006 \text{ g mol}^{-1}$ (consistent with a ¹³C-CO₂ 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 (Trolrier 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 ($20.863\% \pm 0.011\% \text{ O}_2 \text{ in N}_2$). 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).

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22 The mole fraction correction for CO₂ 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 L min^{-1} and analyzed
25 continuously for CO₂ by NDIR. These studies showed remarkably consistent results: that the
26 mole fraction of CO₂ 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

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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.

15 Results and Discussion

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

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

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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 Seal process, and found CO_2 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 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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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 CO₂ into the manifold and transfer line. It
11 is possible that some residual CO₂ 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 CO₂.

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16 To support our assumption of 100% transfer efficiency, we examined both the potential for
17 adsorption of CO₂ in the manifold and transfer line, and the efficiency of transferring CO₂ from
18 the 5-mL container to a cylinder. We tested the transfer line by flowing air containing ~0.1 ppm
19 CO₂ at 0.2 L min⁻¹ through 1/8" AT-steel tubing to an NDIR analyzer. Then we injected 0.6mL of
20 10% CO₂-in-air into this air stream. After the initial slug of CO₂ was observed and the NDIR
21 signal returned to baseline, we heated the transfer line and measured the additional CO₂
22 coming off (Figure 4). Comparing the area of the CO₂ 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 CO₂ in the sample. We were able to drive off most of this CO₂ 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 CO₂-
27 free air through them, it is unlikely that a significant amount of CO₂ would remain in the
28 manifold or transfer line.

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1 We tested the transfer efficiency from the 5-mL container by cryogenically moving aliquots of
2 CO₂ from one 5-mL container to another on a vacuum line (using liquid N₂), 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 ± 0.1% was achieved. Without heating, the same test
5 revealed only 99% efficiency. We expect that repeated pressurization/expansion with CO₂-free
6 air, in addition to heating, would improve the transfer efficiency of the CO₂ 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.

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11 [As mentioned earlier, we estimated the amount of CO₂ 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 CO₂ 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 CO₂ 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 CO₂](#)
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 CO₂ 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 \(not shown\).](#)

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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 \(0.3 L min⁻¹\) and high-flow \(5.0 L min⁻¹\) decanting experiments. They found that](#)
5 [changes in CO₂ 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 [CO₂ 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 CO₂ in each](#)
11 [mother cylinder increased 0.06 ± 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 CO₂ 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 ~~~0.05%~~ lower than a scale
18 based on these gravimetric standards. However, this difference is not outside the range of
19 uncertainties (~0.05% for WMO X2007 and ~0.033 % for this work, ~95% Confidence Level, or
20 coverage factor k=2). While the ¹³C-CO₂ 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 ¹³C-CO₂ 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**
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1 Five gravimetric CO₂-in-air standards, prepared at the ppm level in one dilution step, show
2 excellent internal consistency. Prepared mole fractions were adjusted for CO₂ 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 CO₂ adsorption characteristics, and by introducing condensed-phase aliquots
6 of CO₂ into small vessels that can be weighed with sufficient repeatability, CO₂-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 CO₂.

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9 10 **Acknowledgments**

11 This work was supported, in part, by NOAA's Atmospheric Chemistry, Carbon Cycle, and Climate
12 program (AC4). M.S. was supported by an Early Postdoc Mobility fellowship from the Swiss
13 National Science Foundation (SNSF) while working at NOAA in Boulder, CO.

14 **Supporting Information**

15
16 Table_1_landscape.docx

17 18 **References**

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

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

Cylinder	Adjustments				Amount Fraction		
	n _{air}	μ _n n _{air}	X _{CO2,ad}	μ _X X _{CO2,ad}	X _{CO2,dil}	μ _X X _{CO2,dil}	X _{CO2}
	mol	mol	ppm	ppm	ppm	ppm	ppm
CB11873	86.8651	0.0144	-0.015	0.01	0.01	0.01	357.545
CB11906	87.7891	0.0146	-0.015	0.01	0.01	0.01	397.497
CB11941	85.2982	0.0142	-0.017	0.01	0.01	0.01	405.337
CB11976	84.4328	0.0140	-0.020	0.01	0.01	0.01	449.301
CB12009	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)
 CO₂ a = mass of CO₂ aliquot in 5-ml container, added to cylinder
 CO₂ b = initial mass of CO₂ 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_{CO2} = total amount of CO₂ (moles) (0.99997 purity correction applied)
 n_{air} = total amount of air (moles)
 X_{CO2,ad} = correction applied to account for adsorption to cylinder walls
 X_{CO2,dil} = correction applied to account for CO₂ in the dilution gas
 X_{CO2} = mole fraction of CO₂

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2 **Table 2:** CO₂ purity assessment.

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

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

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9 **Table 3:** Summary of CO₂ adsorption experiments. For each cylinder, the test was repeated N
10 times. Adsorbed CO₂ is expressed as a fraction of the total CO₂ 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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Moved down [2]: Table 4: Results of mother/daughter testing on 29.5-L aluminum cylinders. Note: Final pressures do not sum correctly due to thermal differences. ¶
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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 $2.4644 \cdot 10^{-3}$ and $8.7851 \cdot 10^{-4}$. Uncertainties (unc.) are shown as ~68% Confidence Level. Results are not sensitive to how the response was normalized.

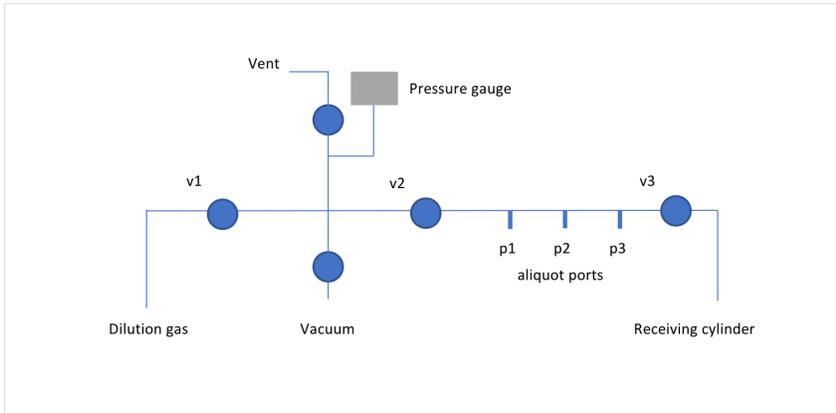
cylinder	prepared ppm	unc. ppm	response	unc.	best-fit ppm	residual ppm
CB11873	357.545	0.059	0.881915	0.000028	357.512	-0.033
CB11906	397.497	0.062	0.980465	0.000025	397.502	0.005
CB11941	405.337	0.073	1.000000	0.000025	405.429	0.092
CB11976	449.301	0.075	1.108007	0.000025	449.257	-0.044
CB12009	491.763	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 difference** calculated as Daughter (after transfer) minus Mother (after transfer).

Cylinder		~ Pressure (MPa)		CO ₂ (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

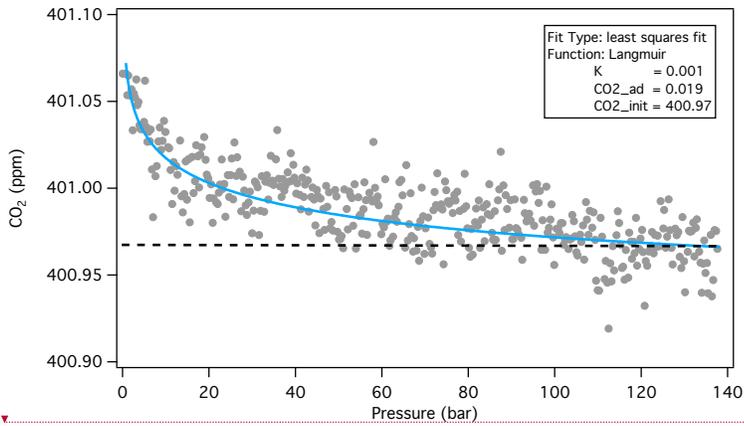
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 2 Figure 1: Schematic of the blending manifold. The sample aliquot (5-mL) was connected to one
 3 of three aliquot inlet ports (p1, p2, p3). The sample was transferred to the receiving cylinder by
 4 opening the cylinder valve (with v2 closed), opening the valve on the 5-mL vessel, and then
 5 alternately pressurizing the section between valves v2 and v3, and opening v3 to send the gas
 6 to the cylinder. The sample manifold is constructed of ¼" o.d. stainless steel tubing with welded
 7 or Swagelok VCR connections. Valves are stainless steel, diaphragm-sealed (Swagelok model
 8 DSV51).
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Figure 2: Typical result from Schibig et al. (2018) CO₂ decanting experiments showing an increase in X_{CO_2} with decreasing cylinder pressure. The fraction of CO₂ adsorbed was found by comparing the area under the Langmuir isotherm (blue line) with the area under the Langmuir isotherm but above the initial CO₂ mole fraction (dashed line). The adsorbed CO₂ 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).

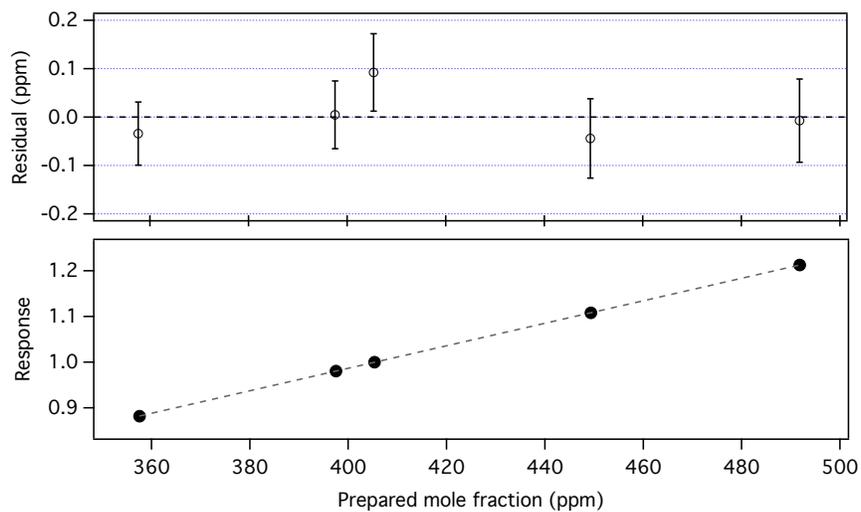
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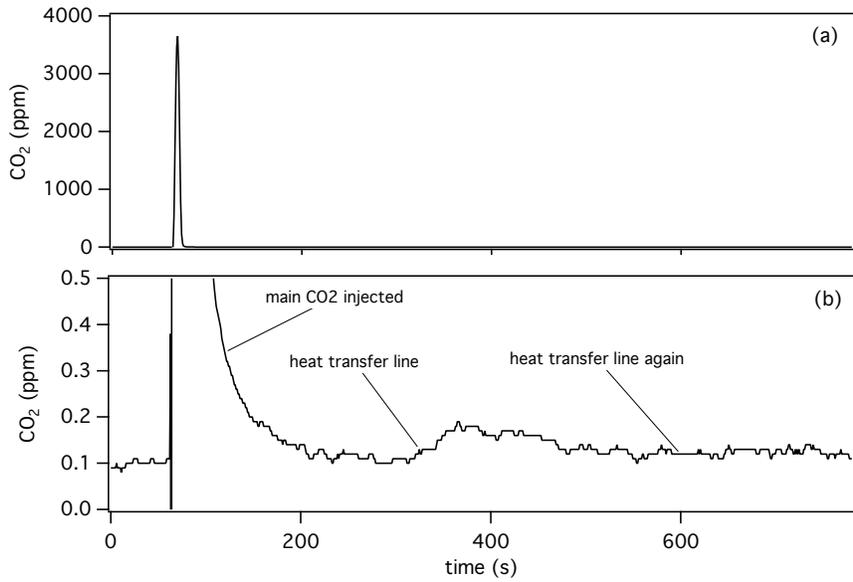


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Figure 3: Normalized response of gravimetrically-prepared standards, analyzed by laser spectroscopy (lower panel). Residuals from linear fit are shown in upper panel, along with preparation uncertainties (~68% Confidence Level, or coverage factor $k=1$).

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Figure 4: Measure of CO₂ passing through a ~1-m AT-steel transfer line. The peak in (a) results from 0.6cm³ air containing 10% CO₂ injected into CO₂-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 CO₂ driven off the tubing by heating.

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