Atmos. Meas. Tech. Discuss., https://doi.org/10.5194/amt-2018-273
Manuscript under review for journal Atmos. Meas. Tech.
Discussion started: 3 September 2018

Atmospheric Measurement Techniques
Discussions

Gravimetrically-Prepared Carbon Dioxide Standards in Support of Atmospheric Research

[1]Bradley D. Hall*, [1,2]Andrew M. Crotwell, [1,2]Benjamin R. Miller,
[3]Michael Schibig, and [1]James W. Elkins

[1]National Oceanic and Atmospheric Administration, Global Monitoring Division, 325 Broadway, Boulder, Colorado 80305, USA
[2]University of Colorado, Cooperative Institute for Research in Environmental Science, Boulder, Colorado 80309, USA
[3]Climate and Environmental Physics, Physics Institute and Oeschger Centre for Climate Change Research, University of Bern, Switzerland

*corresponding author: Bradley.Hall@noaa.gov

Abstract

We have explored a one-step method for gravimetric preparation of CO_2-in-air standards in aluminum cylinders. We consider both adsorption to stainless steel surfaces used in the transfer of highly-pure CO_2, and adsorption of CO_2 to cylinder walls. We demonstrate that CO_2-in-air standards can be prepared with relatively low uncertainty (~0.04%, ~95% Confidence Level) by introducing aliquots whose masses are know 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 compliments efforts to maintain the World Meteorological Organization, Global Atmosphere Watch, mole fraction scale for carbon dioxide, 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 CO_2 in air (typically natural air with assigned CO_2 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-GAW 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 CO_2 in air is a challenge for both gravimetric and manometric methods, particularly since the relative uncertainties must be very small (~0.01% 1-sigma) in order to assess changes (drift) in cylinders over many years. Long-term monitoring of atmospheric CO_2 requires a stable reference, sufficient to identify small atmospheric gradients (of order 0.1 $\mu mol\ mol^{-1}$, or 0.1 ppm, in the remote troposphere). Hereafter we will use ppm (parts per million) for $\mu mol\ mol^{-1}$. Both methods can be influenced by the adsorption of CO_2 to surfaces. There is increasing evidence that CO_2 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 CO_2 in air withdrawn from cylinders over time. Further, since cylinder characteristics may differ among cylinder manufacturers, understanding the behavior of CO_2 in cylinders is critical to maintaining stable scales over time.

The gravimetric technique can employ multiple steps, in which the target gas (CO_2 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_2 to ppm levels in one step (Machida et al., 2011). Matrix gases can also be added in different ways: CO_2 can be mixed with individual gases (N_2, O_2, Ar) to form an air-like matrix, or CO_2 can be added to natural air from which the CO_2 has been removed. Methods of targeting stable isotopes of CO_2 (e.g. ^{13}C-CO_2) to better match natural abundances have also been explored (Brewer et al., 2014).

Here we describe one-step preparation of CO_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_2 adsorption to the cylinder walls. This work was undertaken to support NOAA manometric efforts and learn more about the behavior of CO_2 in aluminum cylinders.

Experimental Methods

Standards were prepared in 29.5-L Luxfer aluminum cylinders (Scott Marrin, Inc. Riverside, CA), with brass, packless valves (Ceoduex). 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_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_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) 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_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 NOAA 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 ºC 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 (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. 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_{CO2}, 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_{air} is the total moles of air, p is the purity coefficient, f is the transfer efficiency, $X_{CO2,ad}$ is a correction for the amount of CO_2 adsorbed to the cylinder walls ($X_{CO2,ad} < 0$) expressed in ppm, and $X_{CO2,dil}$ is the amount of CO_2 in the dilution air, also expressed in ppm.

$$X_{CO2} = \frac{pfn_a + n_b}{pfn_a + n_b + n_{air}} + X_{Co2,ad} + X_{CO2,dil} \qquad (1)$$

The number of moles 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 28.9621 ± 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. We assumed 100% transfer efficiency with an uncertainty of 0.01% (rectangular distribution) (see Results and Discussion).

The mole fraction correction for CO_2 adsorbed to the cylinder walls ($X_{CO2,ad}$) 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 1). 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 1). The amount of CO_2 adsorbed to the walls, expressed as a fraction of total CO_2 in the cylinder, was typically about 0.004% (Table 3). This corresponds to 0.016 ppm CO_2 at 400 ppm.

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 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}) tests, and measured significant temperature gradients on the cylinder surfaces during the high-flow tests, but not during the low-flow tests. They concluded that both adsorption and fractionation were occurring at high flow. 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 cylinders. 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 4). Figure 1, which represents a typical low-flow decanting result, suggests that the increase due to desorption from the cylinder walls should be far smaller than 0.06 ppm at 50% of the original cylinder pressure. Because mother/daughter tests appear to be subject to both thermal fractionation and surface adsorption, we estimated $X_{CO2,ad}$ exclusively from the Schibig et al. (2018) low-flow data (Table 3).

Results and Discussion

Five standards were prepared gravimetrically, with CO_2 mole fractions ranging from 357 to 492 ppm, and evaluated by analysis using laser spectroscopy (Tans et al., 2017). 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 (~25%) and the molecular weight of air (~65%) . For MW_{air}, the uncertainty is partially limited by our ability to measure O_2 and calibrate the O_2 analyzer.

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 CO2 scale, relative to that of CB11941, and fit with a linear function (Figure 2, Table 5). 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-^{16}O, 626). Differences in the residuals from a linear fit were less than 0.005 ppm compared those derived using the response derived from X2007 assignments (Table 5).

Table 5 shows the best-fit results and residuals (difference between best fit and prepared mole fraction). All standards agree (within expanded uncertainties) with the 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 μ_MW_{air}, standard uncertainties for each standard are 40-60% lower than when μ_MW_{air} 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, compared to a standard uncertainty of 0.046 ppm. Thus, 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 3). 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 CO_2 from one 5-mL container to another on a vacuum line (using liquid N_2), without additional flushing, by 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 CO_2-free air, in addition to heating, would improve the transfer efficiency of the CO_2 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.

We also can compare these standards to the WMO X2007 CO_2 scale. The mean ratio, comparing the gravimetrically assigned mole fractions to values assigned on the WMO X2007 scale is 1.00052 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 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/GAW mole fraction scale for CO_2.

Acknowledgments

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

Supporting Information

Table_1_landscape.docx

References

Brewer, P. J., Brown, R. J. C., Miller, M. N., Miñarro, M. D., Murugan, A., Milton, M. J. T., and Rhoderick, G. C.: Preparation and Validation of Fully Synthetic Standard Gas Mixtures with Atmospheric Isotopic Composition for Global CO2 and CH4 Monitoring, Anal Chem, 86, 1887-1893, 10.1021/ac403982m, 2014.

Brewer, P. J., Brown, R. J. C., Resner, K. V., Hill-Pearce, R. E., Worton, D. R., Allen, N. D. C., Blakley, K. C., Benucci, D., and Ellison, M. R.: Influence of Pressure on the Composition of Gaseous Reference Materials, Anal Chem, 90, 3490-3495, 10.1021/acs.analchem.7b05309, 2018.

Dlugokencky, E. J., Myers, R. C., Lang, P. M., Masarie, K. A., Crotwell, A. M., Thoning, K. W., Hall, B. D., Elkins, J. W., and Steele, L. P.: Conversion of NOAA atmospheric dry air CH4 mole fractions to a gravimetrically prepared standard scale, Journal of Geophysical Research: Atmospheres, 110, 10.1029/2005JD006035, 2005.

Keeling, C. D., Guenther, P. R., and Moss, D. J.: Scripps reference gas calibration system for carbon dioxide-in-air standards: revision of 1985, WMO;, 1986.

Keeling, C. D., Guenther, P. R., Emanuele, G., Bollenbacher, A., and Moss, D. J.: Scripps reference gas calibration system for carbon dioxide-in-nitrogen and carbon dioxide-in-air standards: revision of 1999, Scripps Institution of Oceanography; , 2002.

Leuenberger, M. C., Schibig, M. F., and Nyfeler, P.: Gas adsorption and desorption effects on cylinders and their importance for long-term gas records, Atmos. Meas. Tech., 8, 5289-5299, 10.5194/amt-8-5289-2015, 2015.

Machida, T., Tohjima, Y., Katsumata, K., and Mukai, H.: A new CO2 calibration scale based on gravimetric one-step dilution cylinders in National Institute for Environmental Studies – NIES 09 CO2 Scale, 165-169, 2011.

Miller, W. R., Rhoderick, G. C., and Guenther, F. R.: Investigating Adsorption/Desorption of Carbon Dioxide in Aluminum Compressed Gas Cylinders, Anal Chem, 87, 1957-1962, 10.1021/ac504351b, 2015.

Rhoderick, G. C., Kitzis, D. R., Kelley, M. E., Miller, W. R., Hall, B. D., Dlugokencky, E. J., Tans, P. P., Possolo, A., and Carney, J.: Development of a Northern Continental Air Standard Reference Material, Anal Chem, 88, 3376-3385, 10.1021/acs.analchem.6b00123, 2016.

Schibig, M. F., Kitzis, D., and Tans, P. P.: Experiments with CO2 -in-air reference gases in high-pressure aluminum cylinders, Atmos. Meas. Tech. Discuss., 2018, 1-38, 10.5194/amt-2018-42, 2018.

Sutour, C., Stumpf, C., Kosinski, J. P., Surget, A., Hervouët, G., Yardin, C., Madec, T., and Gosset, A.: Determination of the argon concentration in ambient dry air for the calculation of air density, Metrologia, 44, 448, 2007.

Tans, P. P., Crotwell, A. M., and Thoning, K. W.: Abundances of isotopologues and calibration of CO2 greenhouse gas measurements, Atmos. Meas. Tech., 10, 2669-2685, 10.5194/amt-10-2669-2017, 2017.

Trolier, M., White, J. W. C., Tans, P. P., Masarie, K. A., and Gemery, P. A.: Monitoring the isotopic composition of atmospheric CO2: Measurements from the NOAA Global Air Sampling Network, Journal of Geophysical Research: Atmospheres, 101, 25897-25916, doi:10.1029/96JD02363, 1996.

Zhao, C. L., Tans, P. P., and Thoning, K. W.: A high precisionmanometric systemfor absolutecalibrations of CO2 in dry air, J. Geophys. Res., 102, 5885-5894, 1997.

Zhao, C. L., and Tans, P. P.: Estimating uncertainty of the WMO mole fraction scale for carbon dioxide in air, J. GeoPhys. Res., 111, 10.1029/2005JD006003, 2006.

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

	Components						
Cylinder	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	6.80E-03	2.24E-05	1.36062	0.00008	2515.637	0.033	3.1070E-02
CB11906	7.28E-03	1.25E-05	1.52917	0.00007	2542.399	0.026	3.4911E-02
CB11941	1.07E-02	1.25E-05	1.51156	0.00015	2470.262	0.030	3.4589E-02
CB11976	7.32E-03	1.18E-05	1.66307	0.00011	2445.198	0.014	3.7954E-02
CB12009	7.72E-03	1.81E-05	1.71751	0.00007	2307.305	0.039	3.9200E-02

			Adjustments				Amount Fraction
Cylinder	n_{air}	μ_ n_{air}	$X_{CO2,ad}$	μ_$X_{CO2,ad}$	$X_{CO2,dil}$	μ_$X_{CO2,dil}$	X_{CO2}
	mol	mol	ppm	ppm	ppm	ppm	ppm
CB11873	86.8596	0.0144	-0.015	0.001	0.01	0.01	357.569
CB11906	87.7836	0.0146	-0.015	0.002	0.01	0.01	397.523
CB11941	85.2929	0.0142	-0.017	0.001	0.01	0.01	405.363
CB11976	84.4275	0.0140	-0.020	0.002	0.01	0.01	449.330
CB12009	79.6664	0.0133	-0.022	0.001	0.01	0.01	491.795

Note: Entries preceeded by " μ_" represent standard uncertainties (~68% Confidence Level)
CO_2_a = initial mass of CO_2 in cylinder (based on analyzed mole fraction and mass of air)
CO_2_b = mass of CO_2 aliquot in 5-mL container and added to cylinder
Air = mass of air
n_{CO2} = total moles of CO_2 (0.99997 purity correction applied)
n_{air} = total moles of air
$X_{CO2,ad}$ = correction applied to account for adsorption to cylinder walls
$X_{CO2,dil}$ = correction applied to account for CO_2 in the dilution gas
X_{CO2} = mole fraction of CO_2

Table 2: CO_2 purity assessment.

Component	Fraction	Method
CO_2 (source)	0.99994	
CO_2 (aliquot)*	0.99997	
H_2O	0.00003	electrolytic
CH_4	0.00002	laser spectroscopy
CO	0.00001	laser spectroscopy
N_2O	$2\cdot10^{-8}$	GC-ECD
ethyne	$3\cdot10^{-9}$	GC-GCMS
ethene	$2\cdot10^{-9}$	GC-GCMS
propane	$2\cdot10^{-9}$	GC-GCMS
other hydrocarbons	$< 2\cdot10^{-8}$	GC-GCMS
total non-condensible	0.00002	residual pressure

*Since the CO_2 aliquots were cryogenically purified to remove non-condensible gases, we calculate the aliquot purity based on H_2O only. Non-condensibles include e.g., N_2, O_2, Ar, H_2, CO, and CH_4.

Table 3: Summary of CO_2 adsorption experiments. For each cylinder, the test was repeated N times. Adsorbed CO_2 is expressed as a fraction of the total CO_2 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%

Table 4: Results of mother/daughter testing on 29.5-L aluminum cylinders. Note: Final pressures do not sum correctly due to thermal differences.

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	
CB11941	daughter	5.72	after transfer	401.828
change in mother				0.060
daughter - mother			after transfer	-0.160
CB11088	mother	13.80	initial	408.125
CB11088	mother	6.69	after transfer	408.188
CB11873	daughter	0.03	initial	
CB11873	daughter	6.55	final	407.995
change in mother				0.063
daughter - mother			after transfer	-0.193

Table 5: Analysis of CO_2-in-air standards. "Best-fit" values were determined from a linear fit (response vs. prepared CO_2) using orthogonal distance regression. 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	357.569	0.058	0.881915	0.000028	357.535	-0.034
CB11906	397.523	0.062	0.980465	0.000025	397.527	0.004
CB11941	405.363	0.073	1.000000	0.000025	405.455	0.092
CB11976	449.330	0.074	1.108007	0.000025	449.285	-0.045
CB12009	491.795	0.077	1.212741	0.000039	491.787	-0.008

Atmos. Meas. Tech. Discuss., https://doi.org/10.5194/amt-2018-273
Manuscript under review for journal Atmos. Meas. Tech.
Discussion started: 3 September 2018

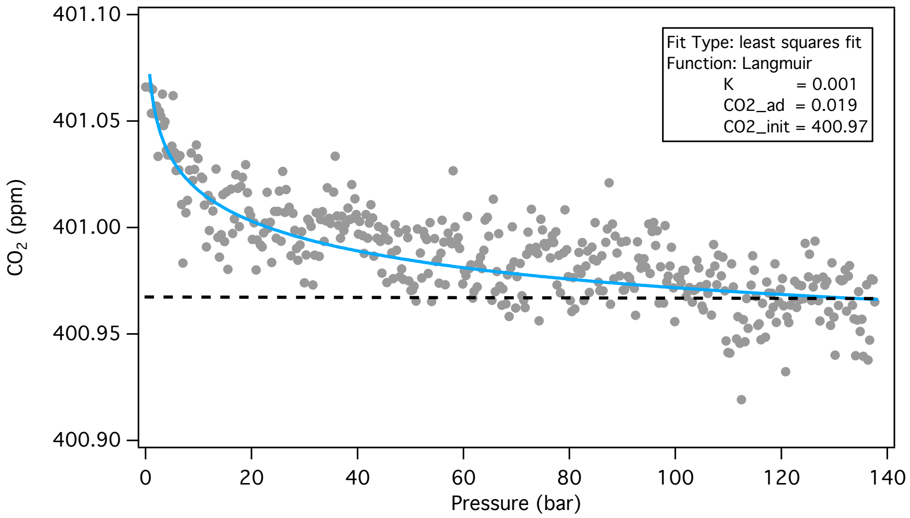

Figure 1: Typical result from CO_2 decanting experiments showing an increase in X_{CO2} with decreasing cylinder pressure. The fraction of CO_2 adsorbed was found by comparing the area under the Langmuir isotherm (blue line) with the area under the Langmuir isotherm but above the initial CO_2 mole fraction (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).

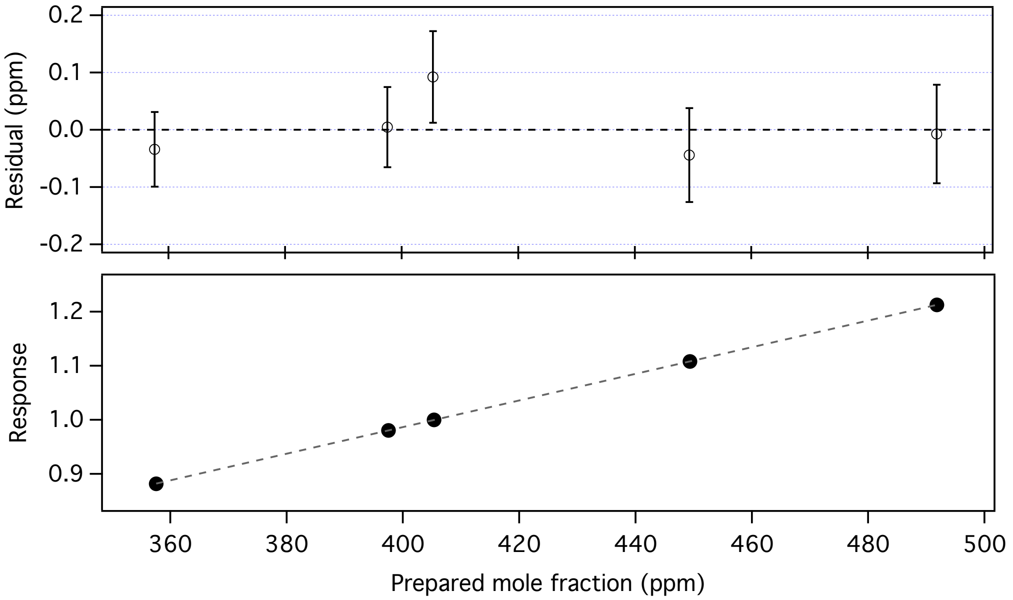

Figure 2: Normalized response of gravimetrically-prepared standards, analyzed by laser spectroscopy (lower panel). Residuals from linear fit are shown in upper panel, along with preparation uncertainties (~68% Confidence Level, or coverage factor k=1).

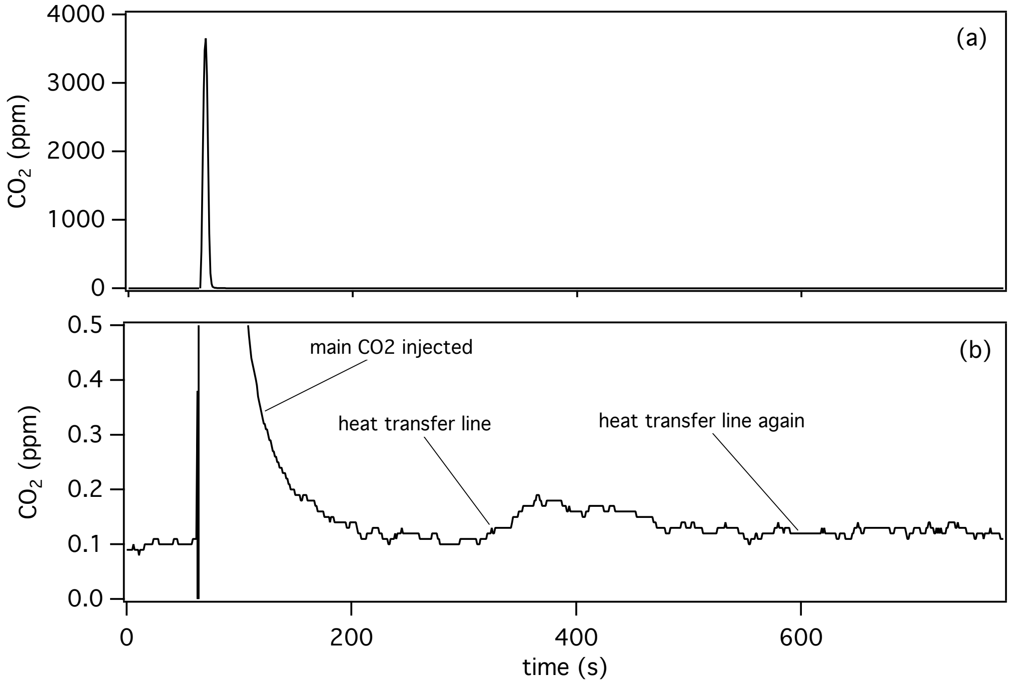

Figure 3: Measure of CO_2 passing through AT-steel transfer line. The peak in (a) results from 0.6cm^3 air containing 10% CO_2 injected into CO_2-free air flowing at 0.2 L min^{-1}. Panel (b) is an expanded view of panel (a), showing a second peak at ~ 400s, which results from CO_2 driven off the tubing by heating.