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Investigating Adsorption/Desorption of Carbon Dioxide in Aluminum Compressed Gas Cylinders

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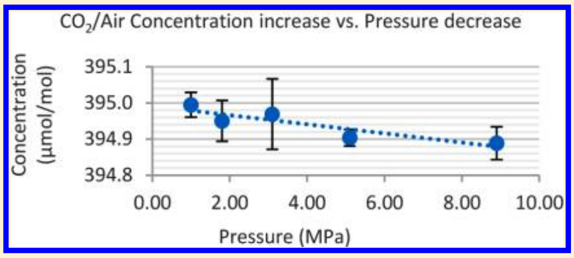
S *Supporting Information*



ABSTRACT: Between June 2010 and June 2011, the National Institute of Standards and Technology (NIST) gravimetrically prepared a suite of 20 carbon dioxide (CO_2) in air primary standard mixtures (PSMs). Ambient mole fraction levels were obtained through six levels of dilution beginning with pure (99.999%) CO_2. The sixth level covered the ambient range from 355 to 404 μmol/mol. This level will be used to certify cylinder mixtures of compressed dry whole air from both the northern and southern hemispheres as NIST standard reference materials (SRMs). The first five levels of PSMs were verified against existing PSMs in a balance of air or nitrogen with excellent agreement observed (the average percent difference between the calculated and analyzed values was 0.002%). After the preparation of a new suite of PSMs at ambient level, they were compared to an existing suite of PSMs. It was observed that the analyzed concentration of the new PSMs was less than the calculated gravimetric concentration by as much as 0.3% relative. The existing PSMs had been used in a Consultative Committee for Amount of Substance-Metrology in Chemistry Key Comparison (K-52) in which there was excellent agreement (the NIST-analyzed value was −0.09% different from the calculated value, while the average of the difference for all 18 participants was −0.10%) with those of other National Metrology Institutes and World Meteorological Organization designated laboratories. In order to determine the magnitude of these losses at the ambient level, a series of "daughter/mother" tests were initiated and conducted in which the gas mixture containing CO_2 from a "mother" cylinder was transferred into an evacuated "daughter" cylinder. These cylinder pairs were then compared using cavity ring-down spectroscopy under high reproducibility conditions (the average percent relative standard deviation of sample response was 0.02). A ratio of the daughter instrument response to the mother response was calculated, with the resultant deviation from unity being a measure of the CO_2 loss or gain. Cylinders from three specialty gas vendors were tested to find the appropriate cylinder in which to prepare the new PSMs. All cylinders tested showed a loss of CO_2, presumably to the walls of the cylinder. The vendor cylinders exhibiting the least loss of CO_2 were then purchased to be used to gravimetrically prepare the PSMs, adjusting the calculated mole fraction for the loss bias and an uncertainty calculated from this work.

Carbon dioxide (CO_2) is an important global warming gas and it is critical to determine its concentration in the atmosphere thus its contribution to the global carbon budget. In order to correctly ascertain the changes of this gas in the atmosphere, it is necessary to develop accurate standards via an absolute method, such as manometry or gravimetry. These standards in turn are used to calibrate atmospheric monitors that are of high accuracy and low uncertainty.

Previous CO_2 calibration scales using manometry have been developed and described.[1,2] The longest available records of atmospheric CO_2 measurements date back to 1957.[3] This record has been maintained at the Scripps Institute of Oceanography (SIO), La Jolla, CA, and is based on manometry. In the early 1980s, the National Institute of Standards and Technology (NIST), then the National Bureau of Standards (NBS), developed a suite of gravimetric primary standard mixtures (PSMs).[4] Three standard reference materials (SRMs), 1670−1672 with (nominal) mole fractions of 330, 340, and 350 μmol/mol, were certified using those PSMs. A comparison of nine of the SRMs between then NBS and SIO showed an absolute average difference of 0.02 μmol/mol with a standard deviation of 0.08 μmol/mol. This comparison showed the equivalence between the manometric and gravimetric techniques used to develop standard scales. The current World Meteorological Organization (WMO) CO_2 scale is championed by the National Oceanic and Atmospheric Administration (NOAA), Boulder, CO.[5−7] The NOAA WMO CO_2 scale consists of a set of 15 CO_2 in air primary standard calibration gases determined using manometry.[8]

In 2009, the Gas Sensing Metrology Group at the NIST began a program to support climate change research. It has developed a new suite of CO_2 PSMs in a balance of dry, CO_2-scrubbed, whole air. These standards were produced using gravimetry and serial dilution from pure natural abundance CO_2. Six levels of PSMs (nominal 10, 4, 1, 0.4, and 0.1 % mol/

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mol and ambient) were prepared in this manner. The final level consists of eight PSMs in the ambient range from 355 to 404 μmol/mol. The first five levels of PSMs were verified against existing PSMs in a balance of air or nitrogen with excellent agreement observed (the average percent difference between the calculated and analyzed values was 0.002%). The ambient-level PSMs were compared to an existing suite (prepared between 1984 and 1987) of PSMs, also developed using gravimetry.[4] The comparison revealed that the analyzed mole fractions were different from the gravimetrically calculated values by 0.5−1.0 μmol/mol. The existing PSMs had been used in a Consultative Committee for Amount of Substance-Metrology in Chemistry (CCQM) Key Comparison (K-52).[9] The results of that comparison indicated excellent agreement with other National Metrology Institutes and WMO designated laboratories.

This difference between the older NIST suite of PSMs (also prepared in aluminum compressed gas cylinders) and the newly developed suite suggested that there could be losses of CO_2 in the aluminum cylinders used to prepare the new standards, which were made of a different aluminum alloy. NOAA described problems related to losses of CO_2 in their manometric system and the choice of surface materials needed in the system to avoid those losses.[2] The adsorption of CO_2 in aluminum and steel compressed gas cylinders was reported by Leuenberger et al.,[10] suggesting that this loss is due to adsorption of the CO_2 molecules onto the surface of the cylinder wall and due to chemisorption.

Therefore, it was possible that losses were occurring either in the manifold system (constructed of metal materials) or in the cylinders used to prepare the PSMs. Increases in the mole fraction of CO_2 in air mixtures, contained in nominal 30 L aluminum cylinders, have been observed with reduced cylinder pressure.[5] As pressures approached 2.1 MPa, the CO_2 mole fraction was observed to increase by +0.4 and +2.8 μmol/mol at 0.7 MPa. It was theorized that one possible reason for this phenomenon might be the presence of water vapor within the cylinder and a possible relationship between the water vapor and desorption of CO_2. These results may also suggest the possibility of CO_2 adsorbing onto the cylinder walls during preparation, a phenomenon between the aluminum and CO_2.

An investigation into the source(s) of the CO_2 loss was undertaken using a technique called "daughter/mother" testing. In these tests, a gas mixture containing CO_2 in a balance of air from a "mother" cylinder was transferred into an evacuated "daughter" cylinder. These cylinder pairs were then analyzed using a cavity ring-down spectrometer (CRDS) and directly compared using the mother cylinder as a control. The control was run frequently (every third cylinder) during the analytical sequence in order to correct for any drift in the instrument response. The ratio of the daughter response to that of the mother was calculated, with the resultant deviation from unity being a measure of the CO_2 loss or gain.

EXPERIMENTAL PROCEDURES

Cylinders. Six new 5 L aluminum compressed gas cylinders with stainless steel (SS) DIN-1 valves were purchased from Air Products and Chemicals (AP), Vilvoorde, Belgium. These cylinders were pretreated with their proprietary Experis treatment to passivate the inner cylinder walls. In addition, five new 6 L aluminum cylinders with brass CGA 590 valves had been purchased from Airgas, Riverton, NJ. These cylinders had been treated by the vendor for ambient air service. All of these cylinders were received with 2 atm of synthetic air. Three steel size 8.50 m^3 cylinders containing 17.2 MPa of (nominal) 390 μmol/mol of CO_2 and 0.9% mol/mol of argon in a balance of synthetic air (O_2/N_2) were purchased from Airgas to act as mother cylinders.

Preparation of the Daughter Cylinders. Six AP cylinders and a 30 L aluminum compressed gas cylinder containing 13.8 MPa of dry, CO_2-free (<200 nmol/mol), whole air were purchased from Scott Marrin, Inc., Riverside, CA. They were connected to a manifold with SS transfer lines. The AP cylinders were vented and evacuated to <0.53 Pa of mercury (Hg) pressure. Air from the Scott Marrin, Inc., cylinder was transferred to the new aluminum cylinders to a pressure of 1.4 MPa and vented to the atmosphere. This process was done four times, and the daughter cylinders were then evacuated to <0.53 Pa of Hg. A cylinder of air containing nominal 390 μmol/mol CO_2 (mother) was then connected to the manifold, and the system was evacuated to <0.53 Pa of Hg. The air was transferred to equilibrium into the daughter cylinders. The daughter and mother cylinders were then moved to the analytical laboratory and allowed to temperature-equilibrate overnight.

Instrument and Analysis System. For analysis, the mother and daughter cylinders were connected to a computer-operated gas analysis system (COGAS) using SS sample lines. COGAS is an automated gas sampling system developed to connect multiple gas cylinders to a manifold and program the automatic sequence of sample streams delivered to an analyzer. One can program the amount of time the sample will purge the analyzer before measurements are taken, the frequency of the measurement outputs, and the number of measurements averaged. In addition, the analyst can also program how many times each sample is tested. Because of instrument concentration limits, daughter/mother testing was conducted using three different instruments.

CO_2 Mole Fractions of 0.02−0.03 mol/mol. For those daughter/mother tests involving cylinders containing CO_2 mole fractions of 0.02−0.03 mol/mol, the COGAS output line was connected to an Agilent (Santa Clara, CA) Micro gas chromatograph with a thermal conductivity detector (GC/TCD). The sample flow out of the COGAS system was set to 100 mL/min. The COGAS system was operated in the continuous-flow mode. The GC/TCD's internal sample pump draws 10 mL/min for 100 ms before injecting the collected volume onto the head of the column. The components were separated with an 8 m × 0.32 mm PLOT Q glass capillary column operated isothermally at 70 °C and a column head pressure of 0.28 MPa. The TCD was operated in the high-sensitivity mode with a detector data rate of 200 Hz. The COGAS sequence was set up with the mother cylinder as the control. It was sampled by the analyzer after two daughter cylinders were sampled. In this way, the response of the mother cylinder could be corrected for instrument drift.

CO_2 Mole Fractions of 0.0026−0.0025 mol/mol. For those daughter/mother tests involving cylinders containing CO_2 mole fractions of 0.0026−0.0025 mol/mol, the COGAS output line was connected to a PerkinElmer (Waltham, MA) Clarus gas chromatograph equipped with a flame ionization detector (GC/FID). The GC was equipped with a methanator to convert CO_2 to methane (GC/Meth/FID). The sample flow out of the COGAS system was set to 30 mL/min. The COGAS system was set up to flush the sample loop for a period of 90 s. The gas sampling valve was switched to inject the sample and

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then returned to a rest port. The components were separated using a 2.44 m × 203 mm SS column packed with 80/100 mesh Porapak Q and a 0.1 mL sample loop. The column was operated isothermally at 60 °C with a carrier gas (UHP helium) flow rate of 34 mL/min. The FID and methanator catalyst (nickel) were maintained at 400 °C. The COGAS sequence was operated in the same manner as that described in the previous section.

CO_2 Mole Fraction of 0.00039 mol/mol. For those daughter/mother tests involving cylinders containing a CO_2 mole fraction of 0.00039 mol/mol, the COGAS output line was connected to a Picarro (Santa Clara, CA) CO_2 CRDS. This CRDS has the capability of measuring $^{12}CO_2$ and $^{13}CO_2$ separately, and in this analysis, these two channels were added together to form a total CO_2 value. The COGAS sequence was set up with the mother cylinder as the control, which would be sampled by the analyzer after two daughter cylinders were sampled. The sample flow out of COGAS was set to allow a bypass flow of 100 mL/min more than the 50 mL/min the CRDS requires. The sample flow from each cylinder purged the instrument for 2 min. Each daughter cylinder was compared to the mother cylinder a minimum of six times during an analytical period.

■ RESULTS AND DISCUSSION

The first source of loss investigated involved the material used to transfer the gas from the mother cylinder to the daughter cylinder. In the first preparation of this suite of standards, Teflon tubing wrapped with braided SS was used in the transfer of gas from the mother cylinder to the daughter cylinder. The losses from using this type of tubing were investigated by transferring gas (to equilibrium) from a mother cylinder to three evacuated cylinders: two using the SS-braided Teflon tubing transfer line and the other using a SS transfer line. In addition, one of the daughter cylinders was used as the mother, and its contents were transferred (to equilibrium) into another evacuated cylinder using a SS transfer line. These cylinders were then connected to the CRDS and compared to each other. The results of these tests are shown in Table 1.

Table 1. Initial CO_2 Loss Study: Transfer-Line Affect

mother		CO_2 concn (μmol/mol)		
FB03265		386.74		
CAL018224		386.38		
mother	daughter[a]	transfer line	ppm loss	% loss
FB03265	APE994663	SS	0.13	0.03
FB03265	CAL018224	Teflon	0.36	0.10
CAL018224	FB03343	SS	0.33	0.08

[a]APE994663: AP with a nickel-plated DIN-1 valve and Experis treatment. CAL018224: Air Liquide America Specialty Gases with a brass CGA 590 valve. FB03343: Scott Marrin, Inc., with a brass CGA 590 valve.

These tests indicated that, although some of the CO_2 loss was because of the material of the transfer line (and/or that of the manifold used), a significant portion was due to the materials of the cylinder that the gas came into contact with. It was observed that there was significantly less loss when the transfer lines were made of SS, and from that point on, all transfer lines were made of that material. Additionally, the results of this testing led to the purchase of AP Experis-treated cylinders.

Testing of the cylinders was initiated after determination of the transfer-line material. AP cylinders were used as the daughter cylinders and were connected to the manifold. They were vented, evacuated, purged with dry, CO_2-scrubbed, whole air, and filled again to equilibrium with a sample from the mother. After temperature equilibrium was achieved, the mother and daughter cylinders were compared using the CRDS. This procedure was done a total of five times with consecutive pressures of 8.9, 5.1, 3.1, 1.8 and 1.0 MPa for each of the six cylinders tested. A minimum of six intercomparisons of the daughter to the mother were conducted at each pressure. The reproducibility of the measured loss for each cylinder at each pressure was 0.02% on average. The CO_2 loss varied from 0.01% to 0.05% relative among the six cylinders. The average CO_2 loss for all five cylinders (grand average) at each pressure averaged 0.02%. The results of these comparisons are shown in Table 2 (data from the other comparisons of the AP cylinders from 5.1 to 1.0 MPa are included in the Supporting Information). A plot of the grand average ratio versus pressure for all AP cylinders is seen in Figure 1.

The data from the AP cylinders indicate that, at higher pressures, greater loss of CO_2 is observed (see Figure 1). Two possible reasons for these results exist. It could be that the loss is permanent, with higher pressure driving more CO_2 into the contacted surfaces than lower pressure, or the loss is temporary, with an equilibrium mechanism allowing more CO_2 to return to the gas state at lower pressure.

Once testing of the cylinders from AP was complete, the procedure was repeated with the five new (daughter) cylinders from Airgas. The procedure was done a total of seven times, with all five cylinders achieving consecutive pressures of 8.9, 5.4, 3.2, 1.8, 1.27, 1.02, and 0.07 MPa. The reproducibility of the measured loss for each cylinder at each pressure averaged 0.02%. The CO_2 loss varied from 0.01% to 0.05% relative among the five cylinders. The average CO_2 loss for all five cylinders (grand average) at each pressure averaged 0.02%. The results from these comparisons are shown in Table 3 (data from the other comparison of the Airgas cylinders from 5.4 to 0.7 MPa are included in the Supporting Information). A plot of the grand average ratio versus pressure for all Airgas cylinders is seen in Figure 2.

The data on CO_2 loss versus pressure for the Airgas cylinders (see Figure 2) is not as clear as that for the AP cylinders (see Figure 1). The Airgas cylinders tested indicate at pressures from 8.8 to 3.2 MPa that there is an increase in CO_2 loss, while from 3.2 to 0.7 MPa, the loss decreases. The reason for these changes in CO_2 loss is unknown.

After a PSM was prepared, it was rolled on a cylinder roller to ensure that the components of the mixture were completely mixed before they were analyzed. Two of the AP cylinders were studied to see if there was any change in the CO_2 loss with pressure and if rolling the cylinders made any difference. The two cylinders were vented, purged, and evacuated to less than 0.53 Pa of Hg. The mixture from the mother cylinder (nominal 390 μmol/mol CO_2/air) was transferred to equilibrium (10.34 MPa) to the two daughter cylinders. The cylinders were not rolled but were put into the analytical laboratory to temperature-equilibrate overnight and then connected to a COGAS unit using SS sample lines. The cylinders were compared as before using the CRDS. They were compared over a 5 day period, with the pressure in one cylinder going from 10.34 to 6.72 MPa and in the other from 10.34 to 0.31 MPa.

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Table 2. Daughter/Mother Testing of CO_2 Loss at 8.9 MPa in AP Cylinders at (Nominal) Ambient CO_2 Mole Fraction

	data collected on 7/2/12 and 7/3/12								
sample	ratio daughter/ mother	ratio daughter/ mother	ratio daughter/ mother	ratio daughter/ mother	ratio daughter/ mother	ratio daughter/ mother	average ratio daughter/mother	std dev	% rsd
ND43669	1.0000								
APEX1005614	0.9994	0.9997	0.9997	0.9998	0.9999	0.9998	0.9997	0.0001	0.01
	0.9997	*0.9998*	*0.9997*	*0.9997*	*0.9998*	*0.9997*			
APEX1005674	0.9997	0.9998	0.9997	0.9998	0.9997	0.9996	0.9997	0.0001	0.01
	0.9998	*0.9997*	*0.9997*	*0.9997*	*1.0000*	*0.9997*			
APEX1005689	0.9993	0.9997	0.9994	0.9997	0.9999	0.9996	0.9995	0.0004	0.04
	0.9983	*0.9997*	*0.9994*	*0.9998*	*0.9997*	*0.9998*			
APEX1005690	0.9993	0.9997	0.9997	0.9997	0.9998	0.9998	0.9997	0.0001	0.01
	0.9995	*0.9997*	*0.9997*	*0.9999*	*0.9996*	*0.9997*			
APEX1005715	0.9996	0.9995	0.9996	0.9997	1.0008	0.9997	0.9998	0.0003	0.03
	0.9998	*0.9996*	*0.9997*	*0.9997*	*0.9997*	*0.9996*			
APEX1005721	0.9997	0.9999	0.9999	0.9996	0.9998	0.9998	0.9997	0.0001	0.01
	0.9996	*0.9995*	*0.9998*	*0.9999*	*0.9996*	*0.9997*			
						grand ave =	0.9997	0.0003	0.03
						loss of CO_2 =	0.03%		

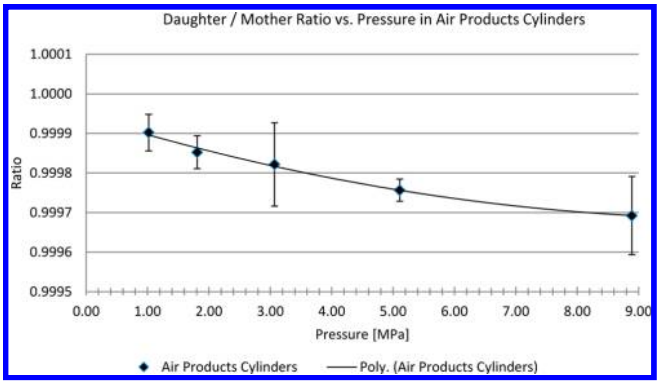

Figure 1. Plot of pressure versus daughter/mother ratio in AP cylinders at (nominal) ambient CO_2 mole fraction (bars indicate the standard deviation of the ratio).

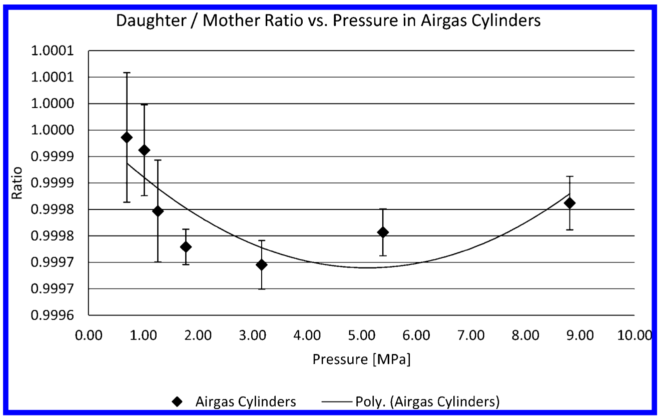

Figure 2. Plot of pressure versus daughter/mother ratio in Airgas cylinders at (nominal) ambient CO_2 mole fraction (bars indicate the standard deviation of the ratio).

After daughter/mother testing of these two daughter cylinders, they were vented, purged, and evacuated to less than 0.53 Pa of Hg. A mixture from a different mother cylinder (nominal 390 μmol/mol CO_2/air) was transferred to equilibrium (6.89 MPa) into two of the AP cylinders. These daughter cylinders were then rolled for 4 h. The cylinders were put in the analytical laboratory to temperature-equilibrate

Table 3. Ratio Summary: Daughter/Mother Testing of CO_2 Loss at 8.9 MPa in Airgas Cylinders at (Nominal) Ambient CO_2 Mole Fraction

	data collected on 6/11/12 and 6/12/12								
sample	ratio daughter/ mother	ratio daughter/ mother	ratio daughter/ mother	ratio daughter/ mother	ratio daughter/ mother	ratio daughter/ mother	average ratio daughter/mother	std dev	% rsd
ND41496	1.0000								
FF13680	0.9994	0.9999	1.0001	0.9998	0.9998	0.9999	0.9998	0.0002	0.02
	0.9999	*0.9999*	*0.9998*	*0.9998*	*0.9999*	*0.9999*			
FF10236	0.9996	0.9997	1.0000	0.9997	0.9998	0.9996	0.9998	0.0001	0.01
	0.9997	*0.9998*	*0.9998*	*0.9998*	*0.9998*	*0.9999*			
FF10239	0.9997	0.9998	0.9999	0.9997	0.9999	0.9997	0.9998	0.0001	0.01
	0.9997	*0.9997*	*1.0000*	*0.9999*	*0.9998*	*0.9997*			
FF10211	0.9998	0.9997	0.9999	0.9998	0.9999	0.9998	0.9998	0.0001	0.01
	0.9998	*0.9996*	*0.9998*	*0.9999*	*0.9997*	*0.9998*			
FF13687	0.9997	0.9999	0.9999	0.9998	0.9999	0.9999	0.9999	0.0001	0.01
	1.0000	*1.0000*	*1.0000*	*0.9998*	*0.9999*	*0.9998*			
						grand average =	0.9998	0.0001	0.01
						loss of CO_2 =	0.02%		

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overnight and then connected to a COGAS unit using SS sample lines. The cylinders were compared as before using the CRDS. They were compared over a 5 day period, rolling for a 2 h period before the start of each analysis. The pressure in one cylinder went from 6.89 to 4.82 MPa and in the other from 6.89 to 0.17)MPa. The results of this testing are illustrated in Figure 3 for one of the cylinders and in Figure 4 for the other.

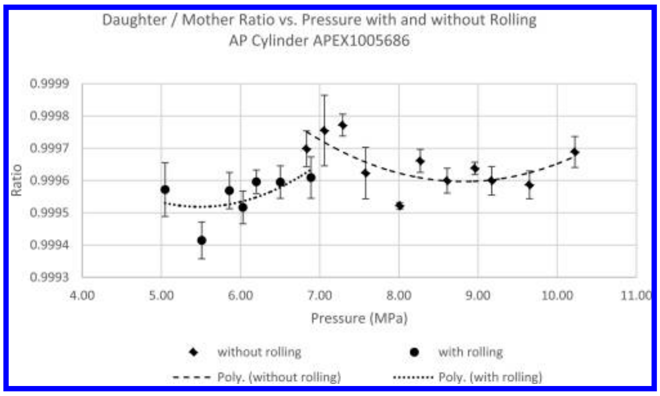


Figure 3. Plot of pressure versus daughter/mother ratio in an AP cylinder APEX1005686 at (nominal) ambient CO_2 mole fraction with and without rolling (bars indicate the standard deviation of the ratio).

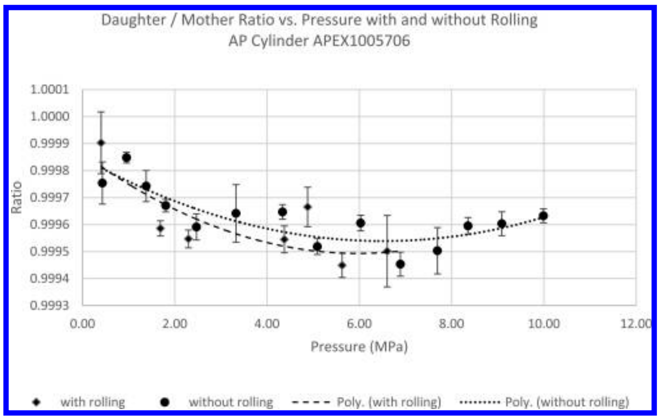


Figure 4. Plot of pressure versus daughter/mother ratio in an AP cylinder APEX1005706 at (nominal) ambient CO_2 mole fraction with and without rolling (bars indicate the standard deviation of the ratios).

A suite of 11 CO_2 in air PSMs were prepared at three levels from pure to ambient using gravimetry. No instrumentation was available to conduct daughter/mother testing of pure CO_2 (level 1) and determine, if any, the losses and uncertainty of those losses. Therefore, at this level, the losses and uncertainties were estimated from data collected on these cylinders during daughter/mother testing at lower CO_2 concentrations. Daughter/mother testing for CO_2 loss was conducted on level 2 and 3 cylinders from AP using either GC/TCD or GC/FID after CO_2 was converted to methane (methanization). The collected data were used to adjust the amount of CO_2 from the mother cylinder delivered to the daughter for all levels except the first. The results of this work are illustrated in Figure 5. The data suggest that, with the AP cylinders at higher levels of CO_2 mole fraction, there may be greater loss of CO_2. The pressures of the cylinders tested (see table in Figure 5) ranged from 1.14 to 3.27 MPa, and it is unsure at this time what effect pressure had on the observed ratios.

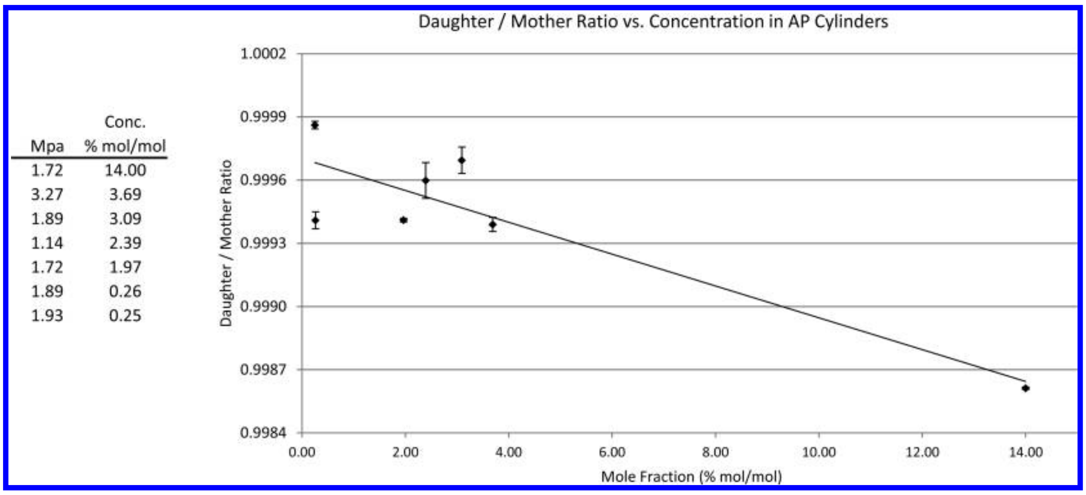
■ CONCLUSIONS

All cylinders tested showed a daughter/mother ratio of <1 and therefore exhibited loss of CO_2. It is suggested that any cylinder used to make CO_2 PSMs be tested for CO_2 loss using the daughter/mother technique to establish the magnitude of the loss and adjust the CO_2 contribution from the mother cylinder in the final mole fraction value.

The AP cylinders tested showed a decrease in the CO_2 loss with a decrease in the pressure, indicating less loss with decreasing pressure. The Airgas cylinders tested indicated an increase in that CO_2 loss at higher pressure followed by a decrease as the pressure continued to decline.

The testing done on two AP cylinders to see the loss as a function of rolling versus nonrolling had two mother gas cylinders. The data collected indicate the same trend in CO_2 loss whether the cylinder was rolled or not. There was no evidence that rolling had any effect on the magnitude of the loss but does seem to indicate that, because the resultant profiles are different, the observed loss may not be constant with continued reuse of a particular AP cylinder.

There is some indication that at higher CO_2 mole fraction levels there may be greater loss. A more in-depth study of the CO_2 loss is planned for the future. Multiple (new) cylinders



Mpa	Conc. % mol/mol
1.72	14.00
3.27	3.69
1.89	3.09
1.14	2.39
1.72	1.97
1.89	0.26
1.93	0.25

Figure 5. Plot of daughter/mother ratio versus concentration in AP cylinders (bars indicate the standard deviation of the ratios at each mole fraction).

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from four specialty gas vendors to be used as the daughter cylinders will be studied. In addition, four levels of mother gas at 10, 7, 3, and 0.5% mol/mol will be studied to better define the effects of the CO_2 mole fraction on this phenomenon. This study will also investigate the effect on the CO_2 loss in a cylinder with continuous monitoring from high to low pressure as opposed to venting it and refilling to a lower pressure, as was done for this study. In addition, this study will also incorporate the use of different materials for use in transferring the gas from the mother to daughter cylinders. All of these studies were done using small-volume (≈6 L) cylinders. Larger-volume cylinders (20 L and larger) may also be tested because the possibility exists that large volume-to-surface ratios may suppress adsorption/desorption issues.

Until such time as a cylinder preparation/treatment technique and/or manifold materials has been found that show no or reduced loss of CO_2, it is recommended that daughter/mother testing of PSMs containing CO_2 be conducted.

■ ASSOCIATED CONTENT

Supporting Information

Tables S1−S10. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

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Notes

The authors declare no competing financial interest.

Certain commercial equipment, instruments, materials, or processes are identified in this paper in order to specify the experimental procedure adequately. Such identification is not intended to imply recommendation or endorsement by the National Institute of Standards and Technology nor is it intended to imply that the products identified are necessarily the best available.

■ REFERENCES

(1) Keeling, C. D.; Guenther, P. R.; Moss, D. J. *Environmental Pollution Monitoring and Research Programme*; WMO: Geneva, Switzerland, 1986.

(2) Zhao, C. L.; Tans, P. P.; Thoning, K. W. *J. Geophys. Res.* **1997**, *102*, 5885−5894.

(3) Keeling, C. D.; Piper, S. C.; Whorf, T. P.; Keeling, R. F. *Tellus, Ser. B* **2011**, *63*, 1.

(4) Zielinski, W. L.; Hughes, E. E.; Barnes, I. L.; Elkins, J. W.; Rook, H. L. DOE/PR-06010-31, 1986.

(5) *14th WMO/IAEA meeting of experts on carbon dioxide, other greenhouse gases and related tracers measurement technique*, Helsinki, Finland, Sept 10−13, 2007; GAW Report No. 186; WMO: Geneva, Switzerland, 2009.

(6) *15th WMO/IAEA meeting of experts on carbon dioxide, other greenhouse gases and related tracers measurement technique*, Jena, Germany, Sept 7−10 2009; GAW Report No. 194; WMO: Geneva, Switzerland, 2011.

(7) *16th WMO/IAEA meeting of experts on carbon dioxide, other greenhouse gases and related tracers measurement technique*, Wellington, New Zealand, Oct 25−28, 2011; GAW Report No. 206; WMO: Geneva, Switzerland, 2012.

(8) Zhao, C. L.; Tans, P. P. *J. Geophys. Res.* **2006**, *111*, D08S09.

(9) WesselR. M.; et al. *Metrologia* **2008**, *45*, Tech. Suppl. 08011.

(10) Leuenberger, M. C.; Schibig, M. F.; Nyfeler, P. *Atmos. Chem. Phys. Discuss.* **2014**, *14*, 19293−19314.

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