One-Step Preparation of Gravimetric CO_2-in-air Standards

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INTRODUCTION

Atmospheric CO_2 measurements typically rely on high-pressure gas standards for calibration. Calibration scales are traceable to primary standards developed using absolute methods, such as manometry or gravimetry. Both methods can be influenced by the adsorption of CO_2 to surfaces. We have recently identified a potential bias (~0.04%) in our manometric measurement related to adsorption of CO_2 into or through Viton o-rings.

Recent advances in our understanding of the behavior of CO_2 in aluminum cylinders, along with a new method of transferring aliquots of pure CO_2 to cylinders, has enabled us to prepare gravimetric CO_2 standards with relatively low uncertainty.

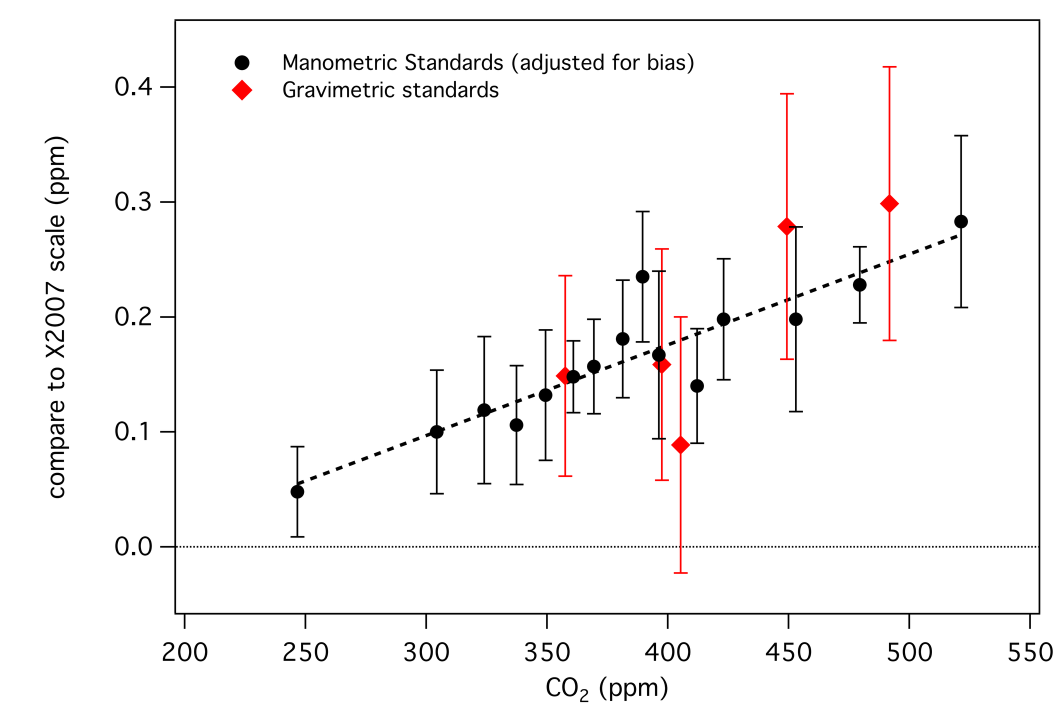
We used gravimetric standards to independently verify the WMO-GAW CO_2 calibration scale and aid our assessment of pending bias corrections.

WHAT WE LEARNED

By using well-characterized cylinders and introducing a mixture of liquid and gaseous CO_2, we can prepare gravimetric CO_2 standards with low uncertainties.

The gravimetric standards show good agreement with a proposed scale update that includes manometer bias correction. Independent lines of evidence indicate that the X2007 CO_2 scale is ~0.04% low.

A scale update is underway and will be applied to all GMD data back to approximately 1980. While the magnitude of the scale update is relatively small, it will be significant with respect to network compatibility within WMO-GAW.

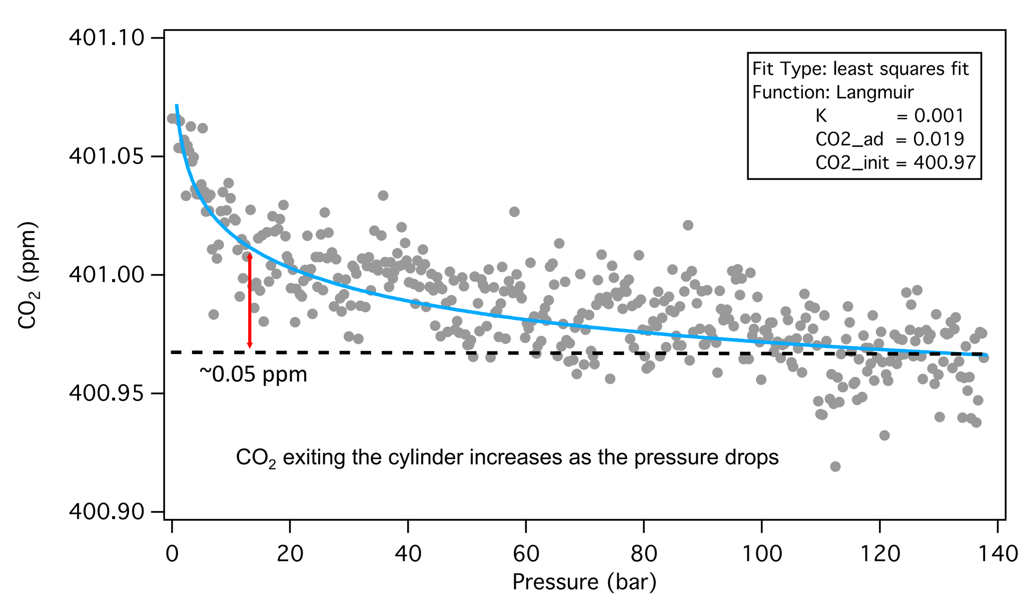


MATERIALS and METHODS

1 High-purity CO_2

Component	Purity 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

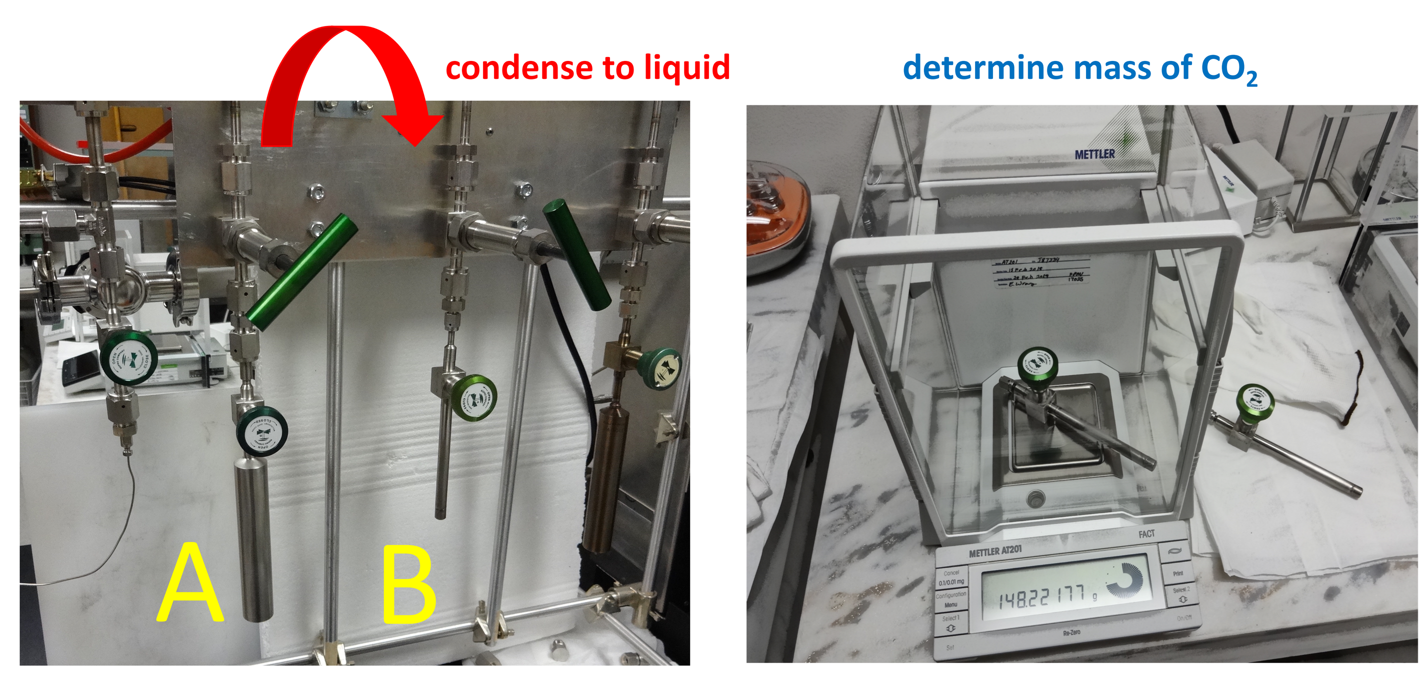
2 Well-characterized cylinders



Air was decanted at 300 cc/min from cylinders multiple times to determine how much CO_2 adsorbs to interior surfaces. The CO_2 mole fraction exiting the cylinder increases as the pressure drops. Comparing the area above the dashed line and below the Langmuir isotherm (blue) to the area below the Langmuir isotherm, we calculated the fraction of CO_2 adsorbed to cylinder walls (Schibig et al., 2018).

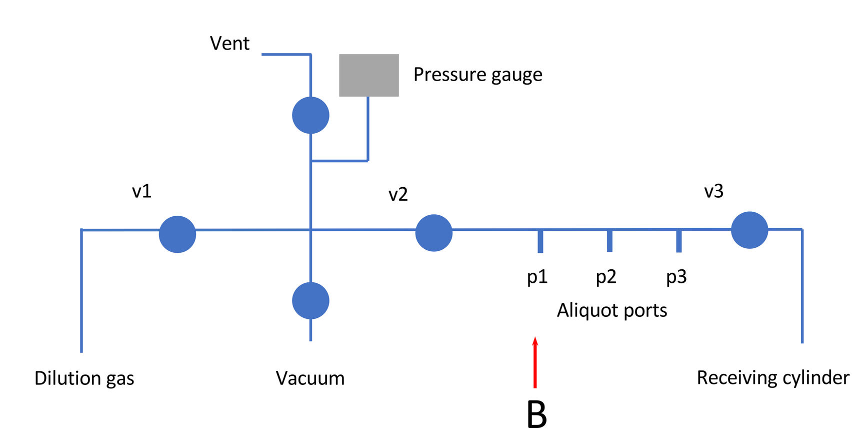
Cylinder	N	CO_2 adsorbed to walls	std. dev.
		%	%
CB11873	5	0.0043%	0.0003%
CB11941	4	0.0042%	0.0003%
CB11906	5	0.0038%	0.0004%
CB11976	5	0.0044%	0.0005%
CB12009	5	0.0044%	0.0002%

3 Cryogenic collection and purification (aliquot).



About 1.5g CO_2 was first transferred into a 50-cc stainless steel tube (A) and cryogenically purified. Then the purified CO_2 was transferred to a 5-cc tube (B) and weighed on a balance with 0.01 mg readability. This allows us to determine the mass of the aliquot with a relative uncertainty of ~0.005%.

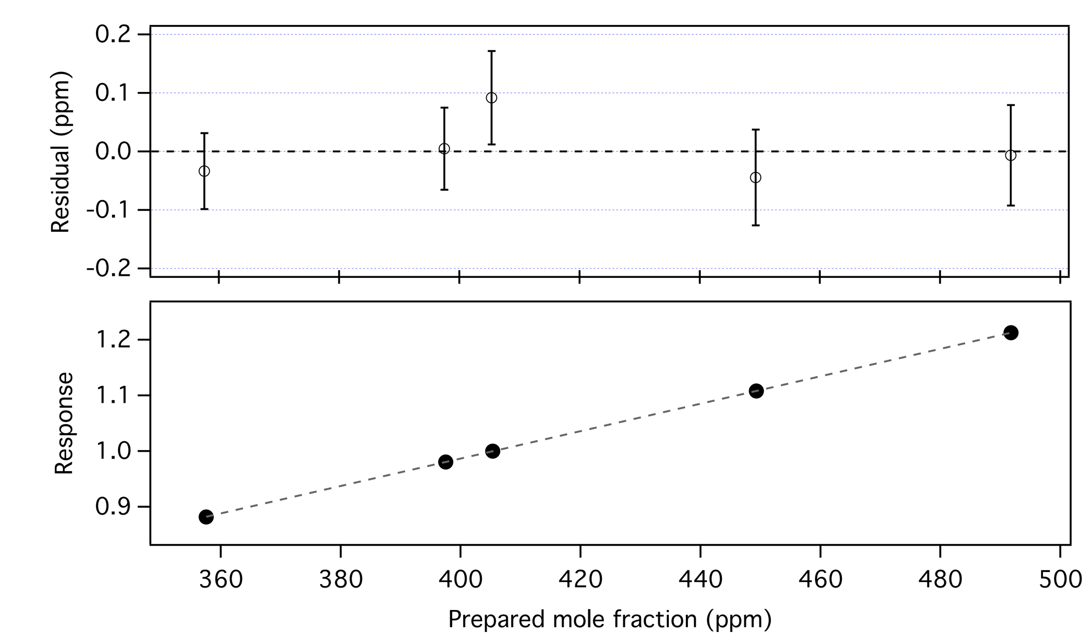
4 Transfer aliquot of CO_2 to partially-evacuated cylinder, and add 2500g CO_2-free air.



5 Calculate the mole fraction of CO_2 in the cylinder, and make minor corrections:

- account for CO_2 in the dilution gas (0.01 ppm)
- account for CO_2 adsorbed to walls (~0.004%)

6 Compare standards using laser-spectroscopy



Cylinder	Prepared	unc.	Response	unc.	Best-fit	Residual
	ppm	ppm			ppm	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

RESULTS

Five gravimetric CO_2 standards show excellent agreement. The standard deviation of residuals from a linear fit was 0.05 ppm. The largest deviation was 0.09 ppm, and this cylinder may have been influenced by residual CO_2 remaining in stainless steel transfer lines following tests with pure CO_2.

This method will be used to support the development of the WMO-GAW CO_2 scale, particularly for mixing ratios higher than 1000 ppm.

Hall, B. D., A. M. Crotwell, B. R. Miller, M. Schibig, and J. W. Elkins (2019), Gravimetrically prepared carbon dioxide standards in support of atmospheric research, *Atmos. Meas. Tech.*, *12*(1), 517-524.

Schibig, M. F., D. Kitzis, and P. P. Tans (2018), Experiments with CO2-in-air reference gases in high-pressure aluminum cylinders, *Atmos. Meas. Tech.*, *11*(10), 5565-5586.

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