



UNITED STATES DEPARTMENT OF COMMERCE  
National Oceanic and Atmospheric Administration  
Earth System Research Laboratory  
Global Monitoring Division  
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Boulder, CO 80305-3328

## Certificate of Analysis

NOAA Global Monitoring Division (GMD)

Certificate Number: **CB12202-A**  
Issue Date: **30 October 2017**  
Material: Air, compressed, in an aluminum gas cylinder, nominal pressure 13.6 MPa (2000 psi)  
Intended Use: For the calibration of instruments determining mole fractions of trace gases in air. Experience has shown that high flow applications may lead to changes in mole fraction. For high precision measurement, flow should be less than 0.5 liters per minute.  
Use and Storage: Cylinders should be used under normal laboratory conditions (room temperature). For storage, we recommend -30° to 40° C.  
Period of Analysis: **August 2017**  
Prepared by: **Thomas K. Mefford**

**Cylinder ID: CB12202**

Results are based on analyses performed by the WMO/GAW Central Calibration Laboratories (CCL) located at the NOAA Global Monitoring Division (GMD). The CCL supports monitoring programs that contribute to WMO/GAW by maintaining and propagating scales for relevant atmospheric trace species. Standards traceable to these scales are used to calibrate atmospheric measurements providing comparability across WMO/GAW contributing programs. WMO/GAW mole fraction scales are developed and maintained by GMD in its role as CCL. Results are traceable to the SI-derived unit "amount of substance fraction". Equipment used to develop mole fraction scales and establish traceability to the SI are traceable to national standards for mass, temperature, pressure, and amount of substance fraction (Oxygen in Nitrogen). For more information on calibration scales and analysis methods, see <http://www.esrl.noaa.gov/gmd/ccl>.

## Results

	Mole Fraction <sup>1</sup>	Reproducibility <sup>2,4,6</sup>	Expanded Uncertainty <sup>3</sup>	Unit	Method	Calibration Scale
CO <sub>2</sub>	402.71	0.02	0.20	μmol mol <sup>-1</sup>	LASER SPECTROSCOPY	WMO-CO <sub>2</sub> _X2007

## Informational Values

	Value	Reproducibility <sup>2,4</sup>	Unit	Method	Calibration Scale
CO <sub>2</sub> δ <sup>13</sup> C <sup>5</sup>	-8.5	0.4	per mil	LASER SPECTROSCOPY	VPDB-CO <sub>2</sub>
CO <sub>2</sub> δ <sup>18</sup> O <sup>5</sup>	-1.0	0.4	per mil	LASER SPECTROSCOPY	VPDB-CO <sub>2</sub>

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<sup>1</sup> Mole fraction in dry air, expressed on a WMO/GAW mole fraction calibration scale.

( $\mu\text{mol mol}^{-1}$  = ppm,  $\text{nmol mol}^{-1}$  = ppb,  $\text{pmol mol}^{-1}$  = ppt)

<sup>2</sup> Expected long-term variation of analysis results assuming no cylinder drift (95% confidence level).

<sup>3</sup> Total uncertainty, estimated with coverage factor  $k=2$ , (~95% confidence level). Total uncertainty includes uncertainties associated with preparation and analysis of primary standards, as well as scale propagation. Note that we explicitly express the results with the number of significant figures corresponding to the number of significant figures in the reproducibility estimate. This is deliberate, as it provides important information to WMO/GAW end users.

<sup>4</sup> The reproducibility of the laser spectroscopy system is based on approximately one year of target tank data. This is not a long enough time period to fully quantify this term. A conservative estimate is used at this time and the value will be updated as more information becomes available.

<sup>5</sup> The reported  $\text{CO}_2$  isotopic values are informational only. They are not to be used as a substitute to having cylinders directly measured by IRMS when isotopic standards are required. They are designed to be used only for making isotopic corrections to measurements of atmospheric  $\text{CO}_2$  on instruments that are sensitive to isotopic differences between standards and samples. The values for reference materials used to determine instrument response was provided by the University of Colorado, Boulder, Institute of Arctic and Alpine Research (INSTAAR). Isotopic values are reported as 'delta' values, in per mil units, relative to a standard reference material. The 'delta' notation is (for  $^{13}\text{C}$  for example):

$$\delta^{13}\text{C} = [ (^{13}\text{C}/^{12}\text{C})_{\text{sample}} / (^{13}\text{C}/^{12}\text{C})_{\text{reference}} - 1 ] \times 1000$$

For carbon and oxygen isotopes, the reference is VPDB- $\text{CO}_2$  (Coplen 1995). The current scale at INSTAAR was set using NBS-19 and NBS-20 (carbonates) and VSMOW, GISP and SLAP (waters).

<sup>6</sup> The  $\text{CH}_4$  reproducibility reported here was determined for the GC-FID  $\text{CH}_4$  calibration system. The current CRDS system is expected to be more consistent but has not run long enough to determine a new reproducibility value. The value will be updated as more information becomes available.

## Period of Validity

Recalibrations are highly recommended (see WMO/GAW Report No. 229 for more information about recalibration intervals). At a minimum, it is recommended to perform a final calibration at the end of the cylinder's term of use (pressure  $\geq 24$  atm.). Mole fractions shown are valid for a period of 3 years. The more reactive analyte Carbon Monoxide typically has measurable drift within 2 years.



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## Terms

**LASER SPECTROSCOPY:** generalized method indicating the application of CRDS with OA-ICOS or QC-TILDAS for making total  $\text{CO}_2$ ,  $\delta^{13}\text{C}$ , and  $\delta^{18}\text{O}$  measurements. See [http://www.esrl.noaa.gov/gmd/cc/CO2\\_calsystem.html](http://www.esrl.noaa.gov/gmd/cc/CO2_calsystem.html) and Tans et al. (2017) for details

**CRDS:** cavity ring-down spectroscopy

**OA-ICOS:** off-axis integrated cavity absorption spectroscopy

**QC-TILDAS:** quantum cascade tunable infrared laser differential absorption spectroscopy

**GC-FID:** gas chromatography with flame ionization detection

**WMO/GAW:** World Meteorological Organization, Global Atmosphere Watch



## References

- CO<sub>2</sub>: Tans, P. P., Crotwell, A. M., and Thoning, K. W.: Abundances of isotopologues and calibration of CO<sub>2</sub> greenhouse gas measurements, *Atmos. Meas. Tech.*, 10, 2669-2685, doi:10.5194/amt-10-2669-2017, 2017.
- Zhao, C. L., P. P. Tans, and K. W. Thoning, A high precision manometric system for absolute calibrations of CO<sub>2</sub> in dry air, *J. Geophys. Res.*, 102, D5, pp. 5885-5894, 1997.
- Zhao, C. L. and Tans, P. P., Estimating the uncertainty of the WMO mole fraction scale for carbon dioxide in air, *J. Geophys. Res.*, 111, D08S09, doi:10.1029/2005JD006003, 2006.
- CO<sub>2</sub>δ<sup>13</sup>C and CO<sub>2</sub>δ<sup>18</sup>O: Coplen, T.B., Reporting of stable carbon, hydrogen, and oxygen isotopic abundances, in Reference and intercomparison materials for stable isotopes of light elements. Vienna, International Atomic Energy Agency, IAEA-TECDOC-825, p. 31-34, 1995.
- WMO/GAW: 18<sup>th</sup> WMO/IAEA Meeting on Carbon Dioxide, Other Greenhouse Gases and Related Tracers Measurement Techniques (GGMT-2015), La Jolla, CA, USA, 13-17 September 2015, World Meteorological Organization, Global Atmosphere Watch Report Series No. 229, available at <http://www.wmo.int/pages/prog/arep/gaw/gaw-reports.html>.

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- Regulators can be purchased directly from the manufacturer. We use Scott Gas model 51-14C-590 or Airgas Y12-C144B590. For mass spectrometer measurement of the stable isotopes of CO<sub>2</sub> we use Airgas model Y11-C444A590. The listing of part numbers here does not constitute an endorsement.
  - Amended certificates will not be issued following calibration scale updates. Results are available at <http://www.esrl.noaa.gov/gmd/cc/>
  - This certificate shall not be reproduced except in full, without written approval of the laboratory.
  - Compressed gas cylinders are regulated by U.S. Law under CFR Title 49, parts 106-179. Users should ensure safe handling and storage. Cylinders should not be exposed to temperatures above 130 deg C. (<http://www.luxfercylinders.com/support/temperature-exposure>)