Overview of the World Meteorological Organization Global Atmosphere Watch Central Calibration Laboratory for Greenhouse Gases

T. K. Mefford[1,2], A. Crotwell[1,2], S. DeVogel[1,2], B. Hall[2], D. Kitzis[1,2, Retired], J. Mund[1,2], and G. Petron[1,2]

[1]Cooperative Institute for Research in Environmental Sciences (CIRES), University of Colorado, Boulder, Colorado 80309

[2]NOAA Global Monitoring Laboratory (GML), Boulder, Colorado 80305

Introduction

The World Meteorological Organization (WMO) Global Atmosphere Watch (GAW) community has long recognized the need for minimizing bias in data across monitoring networks to ensure fluxes interpreted from spatial gradients are real. The WMO GAW community recommends the use of a common calibration scale maintained and disseminated from a designated central calibration laboratory for atmospheric monitoring applications to ensure data is comparable across networks. The NOAA Global Monitoring Laboratory (GML) is the WMO Central Calibration Laboratory (CCL) for Carbon Dioxide (CO_2), Methane (CH_4), Carbon Monoxide (CO), Nitrous Oxide (N_2O) and Sulfur Hexafluoride (SF_6). We have been the CCL for CO_2 since 1995 and since 2003 for the other four species. As the CCL, responsibilities include:

- Maintenance and distribution for the mole fraction scales of CO_2, CH_4, CO, N_2O, and SF_6.
- Formal and informal comparisons with independent primary scales.
- Complete disclosure of all relevant data in the maintenance and distribution of the primary scales.
- Provide calibrated trace gas standards at lowest possible cost.
- Provide a backup in case of a catastrophic event.
- We are charged with ensuring that the mole fraction scales are well understood over decadal time scales. This ensures that observed changes in trends and spatial gradients are robust.

Current WMO Mole Fraction Scales

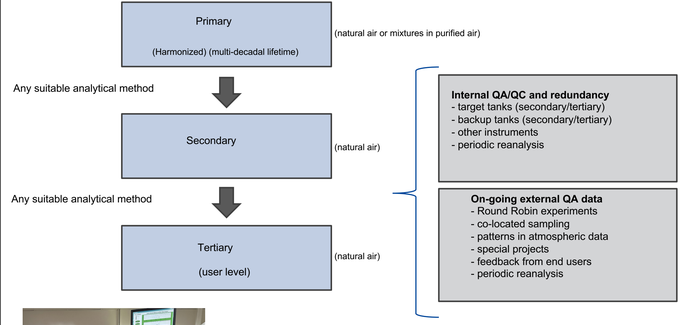
SPECIES	WMO SCALE RANGE	UNITS[1]	SCALE NAME[2]
CO_2	250 – 800	µmol mol^{-1}	WMO X2019
CH_4	300 – 5000	nmol mol^{-1}	WMO X2004A
CO	30 – 500	nmol mol^{-1}	WMO X2014A
N_2O	260 – 370	nmol mol^{-1}	WMO 2006A
SF_6	2 - 20	pmol mol^{-1}	WMO X2014

[1] µmol mol^{-1} = parts per million (ppm), nmol mol^{-1} = parts per billion (ppb), pmol mol^{-1} = parts per trillion (ppt)

[2] WMO mole fraction scales are named according to year of adoption.

CCL Standards Calibration Hierarchy and Mole Fraction Scale Transfer

The CCL uses a hierarchy of standards to distribute the mole fraction scales.



CO_2 and CH_4 Scale Transfer System

- The inclusion of the secondary level increases the lifetime of the primary standards helping to ensure consistency over time.
- The current CO_2 primary standard set, which has been in use since the mid 1990s, is getting low on pressure. A new CO_2 primary set has been made and is currently being evaluated.

How Are Standards Made?

- Standards are made at a remote biosphere reserve maintained by the National Forest Service and the University of Colorado Niwot Ridge Mountain Research Station.
- The site is located at 40° 02’ N., 105° 32’ W at an altitude of 3040 m (9,773.8 ft).
- Air is pulled into the shack by the RIX SA6B pump, water vapor is removed by a $Mg(ClO_4)_2$ trap, and the dried air is finally stored in several steel ballast tanks.
- A conditioned aluminum cylinder is connected to the cylinder filling apparatus.
- Air from either a zero air tank (lower than ambient targeting) or a spike cylinder (higher than ambient targeting) is first added. Then the cylinder is filled to 2000 psi with ambient air from the ballast tanks.
- The finished standard is then brought down to GML where it will sit for a week to allow the air in the cylinder to mix.
- The standard is then routed to the necessary labs for measurement on dedicated calibration systems.
- Once the standard has finished being measured, it is shipped and a calibration certificate is e-mailed to the client.

Primary Standards

CO_2: The WMO X2019 scale is based on 19 primary standards covering the range of 250 – 800 ppm. Assigned values come from repeated measurements on the CCL manometer.

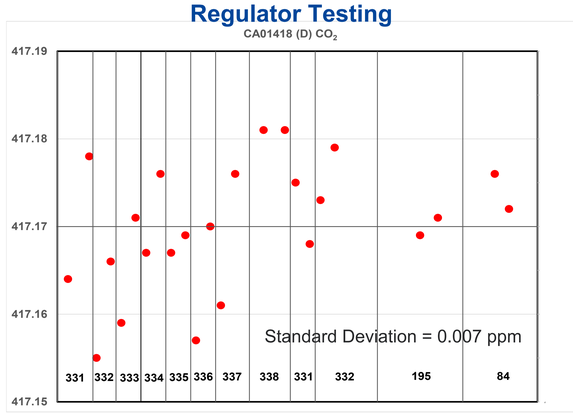
CH_4: The WMO X2004A scale is based on 22 primary standards covering the range of 300 – 5000 ppb. Assigned values come from static gravimetric dilution.

CO: The WMO X2014A scale is based on 14 primary standards covering the range of 30 – 500 ppb. Assigned values come from gravimetric methods. Because CO isn’t stable, drift correction is determined from freshly made standards bootstrapped to CH_4.

N_2O: The WMO X2006A scale is based on 13 primary standards covering the range of 260 – 370 ppb. Assigned values come from static gravimetric dilution methods.

SF_6: The WMO X2014 scale is based on 17 primary standards covering the range of 2 – 20 ppt. Assigned values come from static gravimetric dilution methods.

Regulator Testing



Comparison of 8 brand new regulators (331 – 338) purchased in 2024 with 2 of the same model (195 and 84) that have been in use for several years.

The CCL uses the Airgas Model Y12114C590-AL regulator and a pigtail to connect the standards to the scale transfer systems.

Conclusions:

- Even though gas handling equipment suppliers have undergone consolidation, we still find this regulator performs well.
- High-purity gas regulator prices range from about $300 to $2000. The Y12114-C590-AL satisfies the requirements of the CCL at reasonable cost ($600).

Certificates of Analysis

UNITED STATES DEPARTMENT OF COMMERCE
National Oceanic and Atmospheric Administration
Office of Oceanic and Atmospheric Research
Global Monitoring Laboratory
325 Broadway – David Skaggs Research Center
Boulder, CO 80305-3337

Certificate of Analysis

NOAA Global Monitoring Laboratory (GML)

Certificate Number:	CC510163-A
Issue Date:	8 May 2024
Version:	2020.05.27
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 CO_2 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:	July 2023
Prepared by:	Thomas K. Mefford

Cylinder ID: CC510163

Results are based on analyses performed by the WMO/GAW Central Calibration Laboratories (CCL) located at the NOAA Global Monitoring Laboratory (GML). 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 GML in its role as CCL. Results are traceable to the dimensionless SI-derived quantity “amount of substance fraction”, expressed in units of mole 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. For more information on calibration scales and analysis methods, see http://www.esrl.noaa.gov/gmd/ccl.

Results

	Mole Fraction[1]	Reproducibility[2]	Expanded Uncertainty[3]	Unit	Method	Calibration Scale
CO_2	411.34	0.02	0.21	µmol mol^{-1}	LASER SPECTROSCOPY	WMO-CO_2-X2019
CH_4	1919.8	0.2	3.7	nmol mol^{-1}	CRDS	WMO-CH_4-X2004A
CO	174.6	0.8	1.5	nmol mol^{-1}	VURF	WMO-CO-X2014A[4]
N_2O	331.25	0.22	0.4	nmol mol^{-1}	GC-ECD	WMO-N_2O-X2006A
SF_6	9.82	0.03	0.08	pmol mol^{-1}	GC-ECD	WMO-SF_6-X2014

Informational Values

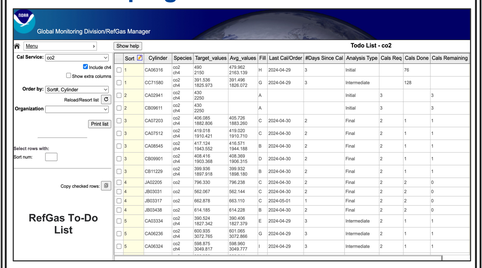
	Value[5]	Reproducibility[2]	Unit	Method	Calibration Scale
CO_2 $\delta^{13}C$	-8.7	0.4	per mil	LASER SPECTROSCOPY	VPDB-CO_2
CO_2 $\delta^{18}O$	-0.8	0.4	per mil	LASER SPECTROSCOPY	VPDB-CO_2

Example of first page of Certificate of Analysis

Every new tertiary standard receives a certificate of analysis that provides;

- Mole fraction, reproducibility, and uncertainty values
- Detailed information about scales, measurement uncertainties, and isotopic measurements
- Period of validity
- Definition of terms
- Peer reviewed references for each species measured
- Regulator information
- Safe handling information

Keeping Track of Standards



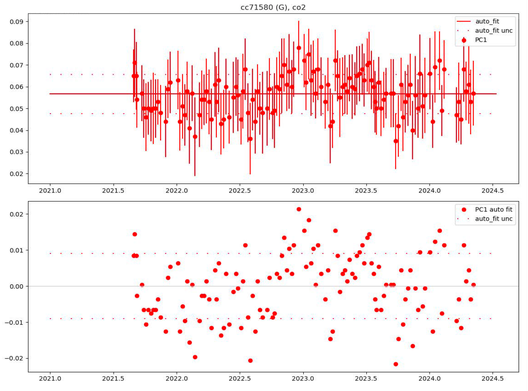
- Orders for standards are managed by a program called RefGas Manager.
- This web based program keeps track of the standards starting with the filling of standards at Niwot Ridge, continuing with the measurements on dedicated systems, and finally shipping to the client.
- Over 400 new tertiary standards are made every year. In addition, standards are shipped back to the CCL to be re-calibrated or receive a final calibration.
- The CCL is a big operation. Good data management is critical.

Instrument History and Efficiency Improvements

Species	Instrument (Method)	Precision (95% CI)	CALIBRATION INTERVAL
CO_2	Licor (NDIR)	±0.06 ppm	Every run
CO_2	Picarro (Cavity Ring Down Spectroscopy)	±0.02 ppm	Every two weeks
^{13}C and ^{18}O of CO_2	Los Gatos Research (Off-Axis Integrated Cavity Output Spectroscopy)	±0.4 ‰	Every two weeks
CH_4	(Gas Chromatography)	±1.0 ppb	Every Run
CH_4	Picarro (Cavity Ring Down Spectroscopy)	±0.1 ppb	Once a month
CO	Aerolaser (Vacuum ultraviolet resonance fluorescence spectroscopy)	±0.4 ppb below 300 ppb	Every two weeks
N_2O	(Gas chromatography with electron capture detection)	±0.15 ppb	Every 3 – 4 weeks
SF6	(Gas chromatography with electron capture detection)	±0.02 ppt	Every 3 – 4 weeks

- **Since July 2017, CO_2 and CH_4 have been measured concurrently on the same Picarro instrument.**
- **Picarro instrument measures the $^{16}O^{12}C^{16}O$ isotopologue.**

Quality Assurance



- In order to verify that the CCL’s dedicated systems and instruments are working properly, “target cylinders” are measured at regular intervals ranging from once a week to once a year.

This research was supported in part by NOAA Cooperative Agreement NA22OAR4320151.

For more information: https://gml.noaa.gov/ccl