Reference Materials

GML Technical Procedure

Contents

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1. Purpose

This document provides the technical procedures for the filling of gas cylinders to be used as Certified Reference Materials (CRM) for CO_2, CH_4, CO, N_2O, and SF_6.

2. Scope

In addition to providing calibration services for laboratories associated with WMO/GAW, NOAA/GML also prepares reference materials, as calibrated air mixtures in high-pressure cylinders, for use within GML and the WMO/GAW community. GML has maintained a filling site in the Colorado mountains in cooperation with the University of Colorado Mountain Research Station for the purpose of filling gas cylinders with natural or modified natural air. These air mixtures are calibrated and used as reference materials within WMO/GAW-contributing programs. An important note is that these reference materials are not intended to be atmospheric samples. The filling procedures, materials, and air collection conditions were designed to achieve air mixtures with near-background mole fractions of targeted trace species and varied individual trace gas concentrations. Reference materials should not be interpreted as being free of all artifacts.

3. Informative References

ISO 17034:2016 General requirements for competence of reference material producers.

ISO Guide 31:2015 Reference materials – Contents of certificates, labels, and accompanying documentation

Kitzis, D., (2009), Preparation and stability of standard reference air mixtures, GML website, https://gml.noaa.gov/ccl/airstandard.html

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, https://doi.org/10.5194/amt-8-5289-2015, 2015.

Schibig, M. F., Kitzis, D., and Tans, P. P.: Experiments with CO_2- in-air reference gases in high-pressure aluminum cylinders, Atmos. Meas. Tech., 11, 5565–5586, https://doi.org/10.5194/amt-11-5565-2018, 2018.

4. Terms and Definitions

- **C-1**: The cylinder filling facility located at 3040m asl. on the southeast side of Niwot Ridge, Colorado. This facility is about 3 km ESE of the long-term GML monitoring site, NWR.

- **Concentration**: For this TP, concentration is synonymous with mole fraction.

- **Gas Standard**: A cylinder of compressed gas with mole fractions assigned by metrological methods or by comparison to higher-level standards, used to characterize the response of an instrument for calibration or quality control purposes. For the purposes of this TP, primary, secondary, and tertiary standards are gas standards.

- **Mole Fraction**: The ratio of the number of moles of analyte to the total number of moles present.

- **Niwot Ridge (NWR):** Long-term GML monitoring site, located at 3523m asl. on the upper section of Niwot Ridge, Colorado (40.053° N, 105.586° W).

- **Primary Standard**: A measurement standard established using a primary reference measurement procedure, or created as an artifact, chosen by convention. (JCGM 200:2012, 5.4)

- **Pump**: An oil-free, breathing-air compressor used to pressurize cylinders.

- **Reference Material (RM):** A material sufficiently homogeneous and stable with respect to one or more specified properties, which has been established to be fit for its intended use in a measurement process

- **Regulator**: A device used to reduce the pressure in a gas cylinder (input) to a lower pressure (output). High-purity and Ultra-high purity regulators are used.

- **Secondary Standard**: A standard whose value is determined through analysis relative to primary standards, for a quantity of the same kind. These standards are used to calibrate the instrument response. Use of secondary standards for routine calibration prolongs the life of primary standards.

- **Spiking Gas**: Any gas mixture of higher than ambient concentration used to increase the mole fraction of one or more trace gases.

- **Tertiary Standard:** Measurement standard established through calibration with respect to secondary measurement standards for a quantity of the same kind.

- **Ultra-pure Air:** Natural air, from which many trace gases have been removed, mainly CO_2, CO, and CH_4. Ultra-pure air contains noble gases, such as argon, and may also contain trace levels of CO, N_2O, SF_6, halocarbons, and hydrocarbons.

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

5. Procedures

5.1 Cylinder Handling

Luxfer (Riverside, CA) aluminum cylinders are used for most reference materials. Luxfer cylinders are sourced in two versions, which differ with respect to the interior surface: 1) un-treated aluminum (Praxair, Los Angeles, CA; Mesagas, Santa Ana, CA) and 2) Aculife™-treated aluminum (Airgas, Plumsteadville, PA). Unless specified by the customer, only Ceodeux brass pack-less valves are used on aluminum cylinders. Generally, cylinders are filled at our semi-remote filling facility (C-1). Occasionally, a customer may specify to have a cylinder filled by a third party with subsequent calibration by GML.

All new, re-valved, or reconditioned cylinders contain dry ultra-pure air or nitrogen upon receipt from the vendor. Cylinders can be stored at a wide range of temperatures. Storage conditions are generally not critical for intended use. Environmental conditions within GML laboratories or outdoors at our filling facility, C-1, do not affect the suitability of cylinders for this work.

5.2 Filling Facility

The air standard preparation facility is located in a biosphere preserve at 3040 m. altitude, 40° 02' N., 105° 32' W, approximately 30 km NW of the Denver metro area. This sub-alpine forested area has limited vehicle access and is usually impacted by air masses with continental background (non-urban) characteristics. Mole fractions of several trace gases have been well characterized in this region through on-going GML atmospheric monitoring programs at a nearby site, known as Niwot Ridge (NWR). The C-1 site was chosen due to the year-round accessibility and predominance of clean, continental background air masses.

5.3 Cylinder Preparation and Filling

An oil-free, breathing-air compressor (pump) (Rix Industries, Benicia CA) is used to pressurize cylinders. Natural air is drawn through approximately 30 feet (9 m) of stainless-steel tubing to the compressor, which is located in a weather-proof housing. The air stream is dried by passing

through a 1-micron coalescent filter with a manual drain and then through a magnesium perchlorate ($Mg(ClO_4)_2$) desiccant located downstream of the pump. The $Mg(ClO_4)_2$ trap typically dries the air to less than 2 ppm H_2O vapor. Cylinders can be filled with dry air directly from the compressor, or by transferring air from a series of high-pressure ballast tanks used to store natural air on-site.

Prior to filling, residual gas in a cylinder is expelled through a stainless-steel manifold to atmospheric pressure. If the residual gas was not natural air or was of questionable quality, a flushing procedure (partial pressurization and exhaust to ambient pressure) is performed two or more times. If the residual gas was natural air of known quality, the cylinder can be refilled without the flushing procedure.

Cylinders are typically preconditioned with dry, ambient air. The analyst determines the duration and appropriate gas mixture for conditioning.

Cylinders are filled with natural air, or natural air modified to meet specific criteria, such as higher or lower mole fractions, relative to local ambient conditions. In general, mole fraction targets fall into three categories: ambient, sub-ambient, and super-ambient. Due to the nature of the compressor design and the addition of various components, including any trace gases in the residual air prior to filling, filled cylinders should not be considered representative air samples. Air contained in filled cylinders may not be fully consistent with air sampled in flasks at NWR.

- **Ambient air**: Cylinder is charged to full pressure with natural air.
- **Sub-ambient targeting**: An aliquot of ultra-pure air is introduced into the cylinder and then filling is completed with natural air.
- **Super-ambient targeting**: A small section of the gas filling manifold is isolated and charged with an aliquot of high-concentration spiking gas. This volume is then swept into the cylinder as it is filled with natural air.

After cylinders are filled and transported to the laboratory, a work-order tag is attached denoting targeted mole fractions and calibrations to be performed.

5.4 Quality Control

5.4.1 Assessment of homogeneity (ISO 17034 (7.10)):

After filling, cylinders are stored for at least seven days prior to analysis. Experience shows that this is sufficient to ensure homogeneity.

5.4.2 Assessment of stability (ISO 17034 (7.11)):

GML monitors for stability in the following ways:

a) Multiple analysis of the same reference material over a short time period (weeks)
b) Analysis of the reference material 2-3 years after the initial measurement (WMO/GAW partners are encouraged to send cylinders back for re-analysis)
c) Accelerated stability studies (used to test new materials, but not performed on each RM)
d) Monitoring similar materials
e) Consulting the scientific literature

Experience has shown that a critical variable affecting the stability of CO_2 in aluminum cylinders is the moisture content of the gas. For CO_2, cylinders are more likely to be stable when the water vapor mole fraction is less than 5 ppm. For this reason, pressurized air from the filling equipment is continually analyzed for water vapor during filling. Cylinders that contain more than 5 ppm H_2O are not suitable to be used as CO_2 reference materials. Typical water vapor mole fractions are 0.5–1.0 ppm for air, and are introduced into the cylinder. For other gases, such as N_2O and CH_4, moisture content is not known to affect stability, at least within the range of water vapor mole fractions typically observed.

A number of other factors can affect CO_2 stability. Some cylinders show instability despite efforts to the contrary. Items listed below are suspected to increase chances of CO_2 drift and are avoided:

1. H_2O concentration above acceptable levels
2. Extended period under vacuum prior to spiking or final filling
3. Use below 300 psig
4. Use of untested cylinder valves, untested valve packing, or stainless-steel valves
5. Use of untested thread sealant for valve installation
6. Use at high flow rates (>0.5 L/min)

5.5 Characterization (Value Assignment)

Cylinders (RMs) are submitted to the labs in Boulder for analysis and value-assigned as appropriate. RMs are value-assigned relative to the defined scales following appropriate procedures. See Technical Procedures for analysis systems and data processing for further details.

6. Data Collection and Storage

Notes pertaining to cylinder filling are recorded in a database. A fill code is assigned so that calibration histories can be linked to each separate filling. The following are entered for use and coordination of calibrations:

- Cylinder serial number
- Fill date
- Location
- Gas designation (UN1002 or UN1956)
- H_2O concentration
- Date assigned to a project
- Project institution
- Contact name and information

7. Safety

It is GML policy to follow safe working practices when handling compressed gas cylinders and laboratory chemicals. Pressurized cylinders should be secured whenever possible. Personal protective equipment (PPE) should be used when working with hazardous chemicals or in a high-noise environment.

8. Appendix

8.1 Equipment

The following equipment is used for the functions described in this TP.

Item	Manufacturer	Model Number
Breathing-air compressor	Rix Industries	SA6
Gas blending manifold	Custom	
Gas spectrometer	Picarro	G2401
Trace water vapor analyzer	Meeco	Waterboy