Analysis of Carbon Monoxide in Air

GML Technical Procedure

Contents

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1. Purpose

This document provides the technical procedures for analysis of carbon monoxide (CO) in air by Vacuum Ultraviolet Resonance Fluorescence Spectroscopy (VURF) and Quantum Cascade Tunable Infrared Laser Direct Absorption Spectroscopy (QC-TILDAS).

2. Scope

NOAA/GML provides compressed gas standards (reference materials) to the WMO/GAW community. Natural air or modified natural air gas standards are analyzed for CO. Carbon monoxide dry air mole fractions are determined by Quantum Cascade Tunable Infrared Laser Direct Absorption Spectroscopy (QC-TILDAS) and Vacuum Ultraviolet Resonance Fluorescence Spectroscopy (VURF), relative to the WMO CO mole fraction scale. The WMO CO mole fraction scale is derived from gravimetrically-prepared primary standards (see TP_primary_gravimetry.doc) and an internal tracer method developed to track growth of CO in the primary standards. The focus of the scale is confined to levels of CO found in the remote and regionally-polluted atmosphere – typically 30 to 1000 10^{-9} mol mol^{-1} (30 to 1000 nmol mol^{-1}). It is not intended for heavily urbanized environments where CO mole fractions above 1 µmol mol^{-1} are common. The procedures described here only pertain to CO analysis for which a certificate of analysis is issued.

Growth of CO in high pressure aluminum cylinders, termed drift, is a known problem. CO typically grows in Al cylinders at rates of 0 – 1.0 nmol mol^{-1} per year (for size AL150 cylinders, growth rates for smaller cylinders would be higher), although the rate is highly cylinder dependent and can be non-linear. Procedures are in place to determine and correct for drift in the NOAA primary and secondary standards (see section 5.3) to maintain a stable scale. However, over the short period of time of a typical tertiary standard calibration episode (4-6 weeks) we cannot assess the stability of any individual cylinder. We recommend that users return tertiary cylinders to NOAA approximately every 2-3 years for recalibrations so that the stability of individual cylinders can be determined.

3. Informative References

JCGM 100:2008 Evaluation of Measurement Data – Guide to the Expression of Uncertainty in Measurement (ISO GUM 1995 with minor corrections), Joint Committee for Guides in Metrology (2008); http://www.bipm.org/utils/common/documents/jcgm/JCGM_100_2008_E.pdf

Novelli, P.C., J.E. Collins, Jr., R.C. Myers, G.W. Sachse, and H.E. Scheel, Reevaluation of NOAA/CMDL carbon monoxide reference scale and comparisons with CO reference

gases at NASA Langley and the Fraunhofer Institute (1994), J. Geophys. Res., 99, 12833, 1994.

Novelli, P.C., L.P. Steele, and J.W. Elkins (1991), Development and evaluation of a gravimetric reference scale for measurements of atmospheric carbon monoxide, J. Geophys. Res., 93, 13109.

WMO, GAW Report 192 (2010), Guidelines for the Measurement of Carbon Monoxide in the Atmosphere (WMO TD No. 1551), 49 pp. July 2010, http://www.wmo.int/pages/prog/arep/gaw/gaw-reports.html

4. Terms and Definitions

- **Analysis System**: Includes the analytical instrumentation, associated hardware, and software used to analyze CO in compressed gas cylinders (synonymous with **Measuring System)**.

- **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. Dry air mole fraction is the ratio of the number of moles of analyte to the total number of moles in dry air. Within the scope of this TP, all samples are analyzed for dry air mole fraction.

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

- **Reference Cylinder**: Cylinder of dry air designated for the calibration of other standards for quantities of the same kind. The instrument response is normalized relative to the reference cylinder to account for instrument drift over short time scales.

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

- **Response Curve**: A function that relates the instrument response to amount of substance (mole fraction).

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

- **Target Tank**: A tertiary standard used for routine monitoring of system performance. The system should be capable of reproducing the assigned value of the target tank (within expected uncertainties).

- **Tertiary Standard:** A standard whose value is determined through analysis relative to secondary standards, for a quantity of the same kind.

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

5. Procedures

5.1 Gas Handling

Cylinders to be analyzed are stored in a common location and moved to the CO analysis lab when needed. Prior to analysis, a regulator is attached. Several regulator models are used. For CO, regulator purity is generally not an issue although high purity or ultra-high purity models are preferred to preserve the integrity of other trace gases. Upon connecting the regulator, the residual gas in the regulator is purged (flushed) with air from the cylinder. It is left to the analyst to determine the amount of flushing and conditioning time required, as it depends on the history of the regulator and the mole fraction of the gas being analyzed. The cylinder to be analyzed is connected to one of the analysis ports on the analysis system. The outlet pressure of the regulator should be set to 10 – 20 psig.

Either a small amount of drying agent, $Mg(ClO_4)_2$ or a cryogenic bath at ~ -70°C is used to remove moisture before analysis. Gas from both the reference cylinder and sample cylinder are passed through the drying agent or cold trap. The drying agent or trap should be inspected after analysis of a series of moist air samples, and replaced as necessary. The vast majority of samples analyzed on this system are dry (dew point < -70 °C) so the drying agent and traps do not need to be replaced frequently.

5.2 Analysis System

Three analytical techniques have been used to propagate the CO mole fraction scale since 2007, Vacuum Ultraviolet Resonance Fluorescence Spectroscopy (VURF), Off-Axis Integrated Cavity

Output Spectroscopy (OA-ICOS), and Quantum Cascade Tunable Infrared Laser Direct Absorption Spectroscopy (QC-TILDAS). The current analysis system uses QC-TILDAS.

Instrument responses are determined regularly using suites of standards (Primary, Secondary, or dilution standards made by the internal tracer method, discussed in section 5.3.1) analyzed during dedicated instrument calibration episodes. Typically, 30-60 second averages are used for each measurement point (the instruments typically have a 1 Hz data rate). Each measurement of a standard is bracketed by measurement of a reference gas used to normalize for span drift of the instruments. In addition, a CO-free air sample (zero air scrubbed by a Sofnocat trap) is measured between each standard or reference aliquot on the VURF to correct for zero drift in the analyzer. Typically 6-8 replicate analyses are made for each standard. A 2nd order polynomial orthogonal distance regression (ODR) fit to the normalized response of the suite of standards is used to define the mole fraction vs instrument response of the instrument. These calibration curves (or response curves) are then used for converting subsequent sample analyses to mole fractions. New calibration curves are produced approximately bi-weekly to monthly, or whenever the reference cylinder is changed.

Sample tanks are analyzed in a similar method, 6-8 replicate 30-60 second measurement averages with each bracketed by a reference measurement. The normalized response is used with the most recent calibration curve to determine the CO mole fraction.

5.3 Standards

5.3.1 Primary Standards

Primary standards for carbon monoxide were prepared gravimetrically in 2011 as described in Technical Procedure TP_primary_gravimetry. There are 14 primary standards covering a nominal range of 30 to 1000 nmol mol^{-1} CO. The CO primary standards contain ambient N_2O mole fractions (~300 – 330 nmol mol^{-1}). A backup set of primary standards covering the same nominal range was prepared gravimetrically in 2015.

Growth of CO in high pressure aluminum cylinders, termed drift, is a known problem. An internal tracer method has been developed to track growth of CO in the primary standards. This method takes advantage of the stability of the CH_4 scale and the assumption that CO growth in cylinders is a wall effect and is not mole fraction dependent, thus very high mole fraction standards will have similar CO drift rates as low mole fraction standards. Three very high mole fraction gravimetric mixtures of CO and CH_4 in air were made. These "parent" tanks contain 0.1 – 1% CO and ~ 3% CH_4. They were made gravimetrically such that the CO:CH_4 ratio is known with small uncertainty. Typical growth rates of CO in cylinders, a few nmol mol^{-1} per year at the most, is insignificant compared to the amount of CO in the parent tanks giving a stable CO:CH_4 ratio.

Static dilutions from the parent tanks are made by blending small aliquots of parent gas with scrubbed zero air in 5.9 L aluminum Luxfer cylinders. By varying the size of the parent aliquot, various CO mole fractions can be targeted to cover the range of the primary standards. The CH_4 mole fractions in these "dilution standards" are measured relative to the WMO CH_4 scale and used with the known CO:CH_4 ratio of the parent tank to assign a CO value to the dilution standard (correcting for CH_4 and CO in the diluent gas). Dilution standards can be made repeatedly from the stable parent tanks (total uncertainties range from 0.2 to 1.2 nmol mol^{-1}, 68% confidence intervals). Suites of 12-16 dilution standards are made and used to prepare an instrument response curve to calibrate the primary standards. This is done approximately once per year to allow the rate of change of CO in the primary standards to be determined.

5.3.2 Secondary Standards

There are currently 11 secondary standards covering the range of mole fractions found in the remote to regionally-polluted atmosphere (30 – 1000 nmol mol^{-1} CO). CO mole fractions are assigned to secondary standards using response curves based on measurement of the primary standards. Repeated calibrations of the secondary standards against the primary standards over the life of the secondary standards (typically once per year) allows drift of CO in the secondary standards to be accounted for. The secondary standards are used to calibrate tertiary standards.

5.4 Quality Control

It is critical that assignments made using the analytical system are reproducible. For a sample mole fraction that does not change with time, the system must be capable of reproducing the assigned value (within uncertainties) over the long term.

The experienced analyst determines when the system is performing normally. Indicators of performance include, but are not limited to, the CO response of the reference cylinder, repeatability of repeat injections, cell temperature and pressure stability, and variations in the response curve and residuals. Typically, the response curve is determined once to twice a month by comparing the reference cylinder to the secondary standards. Past testing has shown that it is not necessary to analyze secondary standards more often than this. However, it is up to the technical lead to determine if this frequency is sufficient to define the response curve within the expected uncertainties. In addition, one or more target tanks are analyzed weekly. Target tanks are key indicators of system performance over longer time periods from month to years/decades (assuming long-term changes in CO mole fraction in the target tanks due to drift are accounted for).

6.0 Calculations

6.1 Mole Fraction

The mole fraction of CO in an unknown sample is determined by comparing the instrument response of the unknown sample to that of a suite of standards using CCL procedures as described in TP_analysis_calculations.

Exceptions for CO:
A CO free air sample (zero air scrubbed by a Sofnocat trap) is measured between each sample, standard, or reference aliquot on the VURF to correct for zero drift in the analyzer. The zero correction is applied to each reference, standard, and sample aliquot before determining the normalized instrument response.

6.2 Uncertainties

For CO, a single estimate of uncertainty is reported for each sample as the expanded uncertainty associated with the value assignment. It is derived from uncertainties in the primary standards that define the scale, including drift corrections applied, and the scale transfer uncertainties. Expanded uncertainties are calculated using the GUM (JCGM, 2008) as a guide.

There is currently no distinction made between the total uncertainty and the scale transfer uncertainty provided for other CCL species. Uncertainty for each calibration episode, referred to as "episode uncertainty" in data distributions, and the resulting value assignment is calculated and provided to the customers using CCL procedures as described in TP_analysis_calculations.

7.0 Data Collection and Storage

Processed data and metadata are stored on a centrally located computer server. The raw data (30 second average instrument responses) are archived in text files on a networked server; the processed mole fraction measurements are stored in a relational database. The database is backed up once a day. The raw data server has a full back up every 2 weeks and incremental back-ups every work day. The results (processed data) are also available from a web interface and can be accessed by users according to the cylinder serial number.

8.0 Safety

It is GML policy to follow safe working practices when handling compressed gas cylinders and laboratory chemicals. Compressed gas cylinders should be secured (except when they are being weighed). Personal protective equipment (PPE) should be used when working with hazardous chemicals or in a high noise environment.

9.0 Documentation

Notes pertaining to cylinder analysis are recorded on log sheets dedicated to the analysis system. For each analysis, the cylinder number and date of analysis should be recorded, along with any variables likely to affect the result. It is left to the analyst to determine which, if any, additional data should be recorded. Notes on analysis system maintenance and changes are recorded in an electronic log (ELOG) which is backed up regularly.

10.0 Appendix

10.1 Equipment

The following equipment is critical to the functions described in this TP.

Item	**Manufacturer**	**Model Number**
QC-TILDAS analyzer	Aerodyne	QC-TILDAS N2O/CO
Multi-position valve	VICI (Valco)	Multiple models of SD low pressure selector valves

10.2 Sample Calculations (Mean Mole Fraction)

Sample calculations are shown (Table A1) for a typical calibration episode from the OA-ICOS instrument. Current QC-TILDAS data processing would be treated exactly the same. Eight aliquots of sample were analyzed, each bracketed by reference aliquots. Each sample response is normalized to the average of the two bracketing reference responses to generate response ratios. The response ratios are compared to an earlier, off-line instrument response curve generated by running the secondary standards in a similar fashion to generate mole fractions for each sample aliquot. The average of the mole fractions from the eight aliquots is taken as the best measure of the mole fraction of the sample.

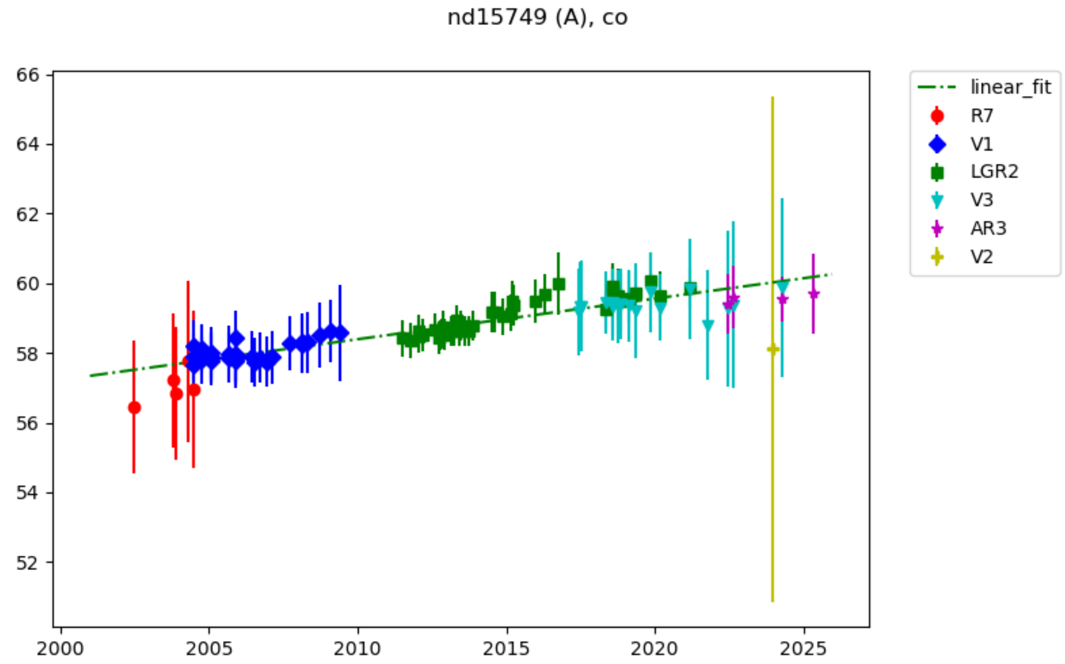
Table A1. Example mole fraction calculations

*Instrument Response Curve: -3.5167 + 127.1777 * R ^ 0.9781*

Type Date Time Response (StdDev) RespRatio nmol mol-1

```
REF   2015-12-31  08:54   120.921   (0.102)
REF   2015-12-31  08:58   120.919   (0.071)
SMP   2015-12-31  09:01   106.766   (0.105)        0.8826        109.04
REF   2015-12-31  09:04   121.015   (0.104)
SMP   2015-12-31  09:07   106.777   (0.100)        0.8823        109.01
REF   2015-12-31  09:10   121.016   (0.159)
SMP   2015-12-31  09:14   106.739   (0.110)        0.8818        108.93
REF   2015-12-31  09:17   121.090   (0.075)
SMP   2015-12-31  09:20   106.771   (0.085)        0.8818        108.94
REF   2015-12-31  09:23   121.077   (0.110)
SMP   2015-12-31  09:27   106.738   (0.113)        0.8817        108.92
REF   2015-12-31  09:30   121.053   (0.114)
SMP   2015-12-31  09:33   106.698   (0.070)        0.8814        108.89
REF   2015-12-31  09:36   121.062   (0.079)
SMP   2015-12-31  09:40   106.744   (0.051)        0.8817        108.93
REF   2015-12-31  09:43   121.062   (0.078)
SMP   2015-12-31  09:46   106.702   (0.049)        0.8815        108.91
REF   2015-12-31  09:49   121.018   (0.070)

                Summary     N=8   Mean           0.8819        108.94
                                  StdDev         0.0004          0.05
```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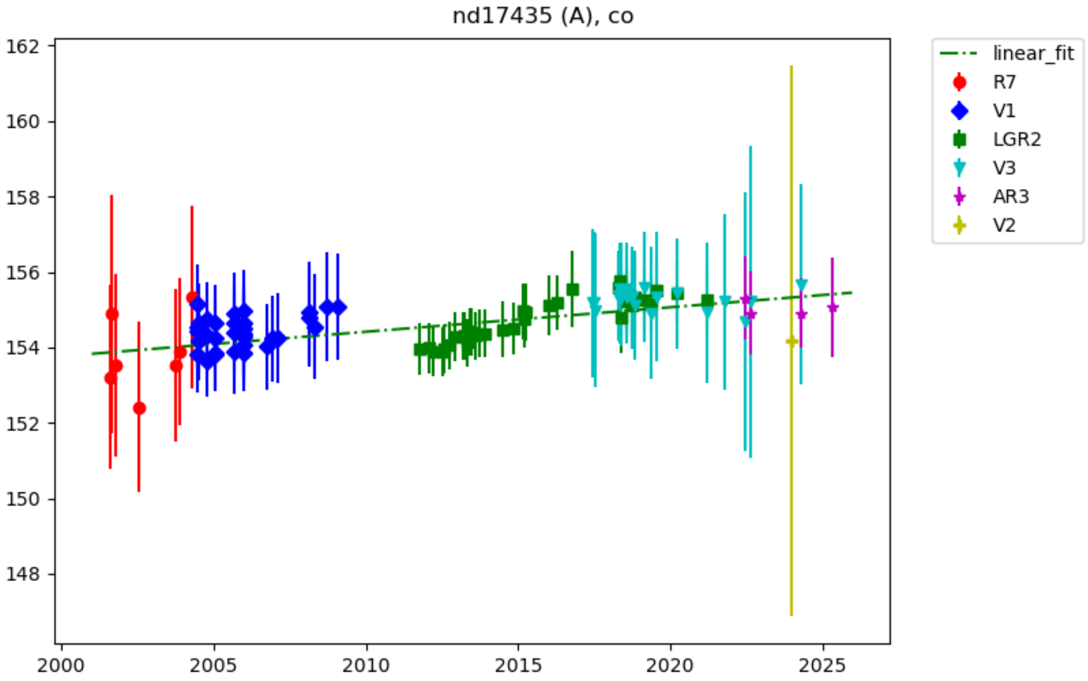
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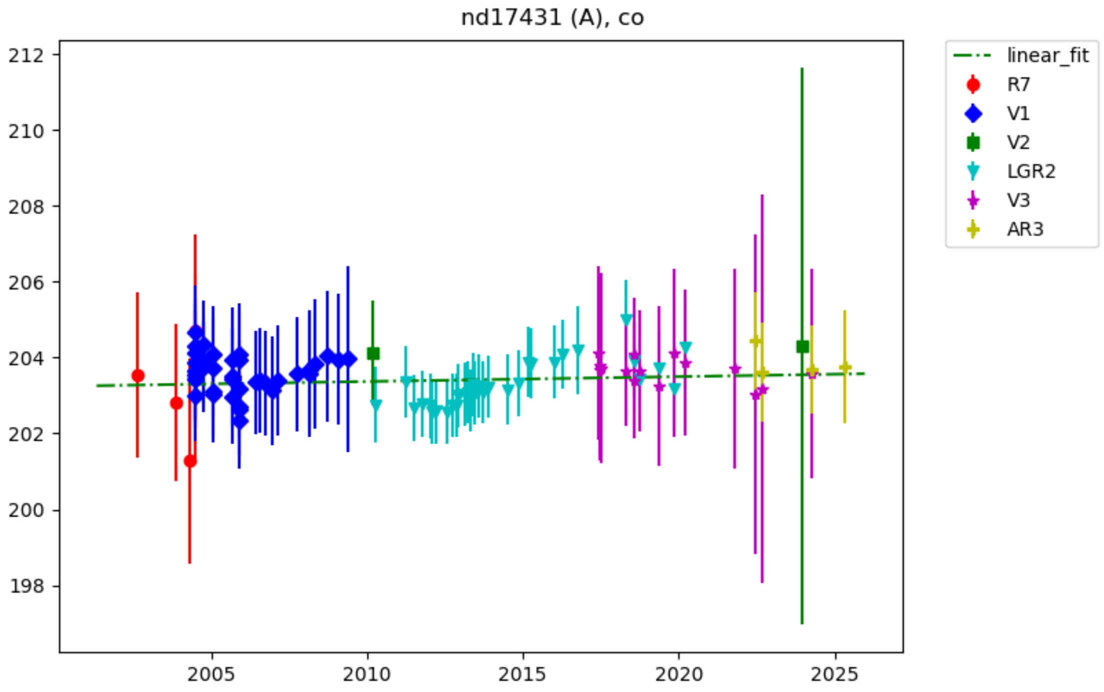

Figure 1: Histories of three of the 12 long-term target tanks color coded by analytical methods, GC_HgO (instrument R7), VURF (instruments V1, V2, and V3), OA-ICOS (instrument LGR2), and QC-TILDAS (instrument AR3). Not all target tanks were available when the GC_HgO measurement technique was in use. The three target tanks exhibit a drift in their CO mole fractions and each tank CO drift rate is determined from a linear fit of the tank calibration results. The standard deviation of the residuals of a linear fit to all of the data is used to determine reproducibility of analytical systems.