Analysis of Carbon Dioxide in Air

GMD Technical Procedure

Contents

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1. Purpose

This document provides the technical procedures for analysis of carbon dioxide (CO_2) in air by laser spectroscopy. The laser spectroscopic analysis system is used to propagate the CO_2 in air scale, as defined by the manometric system, to standards at lower levels of the calibration hierarchy with high precision to minimize scale transfer uncertainty.

2. Scope

NOAA/ESRL/GMD provides compressed gas standards (reference materials) to the World Meteorological Organization/Global Atmosphere Watch (WMO/GAW) community. Natural air or modified natural air gas standards (tertiary standards) are analyzed for CO_2. Carbon Dioxide dry air mole fractions are determined by laser spectroscopy, relative to the WMO CO_2 mole fraction scale. The WMO CO_2 mole fraction scale is defined by 15 primary standards whose assigned values come from repeated (approximately every 2 years) manometric determinations (see TP_primary_manometer). The scale is transferred to secondary standards and hence to tertiary standards by laser spectroscopy. The procedures described here only pertain to CO_2 analysis for which a certificate of analysis is issued.

3. Informative References

JCGM (2008), International vocabulary of metrology — Basic and general concepts and associated terms (VIM), JCGM 200:2008.

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

Tans, P. P., Crotwell, A. M., and Thoning, K. W.: Abundances of isotopologues and calibration of CO2 greenhouse gas measurements, Atmos. Meas. Tech. Discuss., doi:10.5194/amt-2017-34, in review, 2017.

4. Terms and Definitions

analysis system: Includes the laser spectroscopic instruments, associated hardware, and computer used to analyze CO_2 in compressed gas cylinders (synonymous with measuring system**)**.

CRDS: Cavity ring-down spectroscopy.

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.

NDIR: Non-dispersive infrared spectroscopy.

Offaxis-ICOS: Off-axis integrated cavity output spectroscopy.

primary standard: A measurement standard established using a primary reference measurement procedure, or created as an artifact, chosen by convention. CO_2 primary standards are aluminum cylinders containing dry natural air. The CO_2 mole fraction has been determined by manometric determinations (see TP_primary_manometer).

QC-TILDAS: Quantum cascade tunable infrared laser differential absorption spectroscopy.

reference cylinder: Cylinder of dry, natural air with near-ambient CO_2 mole fraction used to normalize variations in temperature and pressure through an analysis period.

reference material: 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. (JCGM 200:2008, 3.6)

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. These standards are used to calibrate the instrument response. Use of secondary standards for routine 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_2 analysis room when needed. Prior to analysis, a regulator is attached. Several regulators models are used. For CO_2, high purity or ultra-high purity models are preferred to preserve the integrity of the gas. 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. Typically, four flush cycles and 24 hours of conditioning time is used. The cylinder to be analyzed is connected to one of the sample manifold ports on the analysis system. The regulator should be set to approximately 10 – 12 psig. The reference cylinder should also be set to 10 - 12 psig.

Small stainless steel water traps are used on the analysis system to prevent subtle cylinder to cylinder differences in H_2O. The traps are 1/4" O.D. stainless steel tubes immersed in an ethanol bath maintained at -78 °C.

5.2 Analysis System

The CO_2 analysis system is described in Tans et al. (2017). Briefly, the analysis system uses two laser spectroscopic gas analyzers to measure the three major isotopologues of CO_2 ($^{16}O^{12}C^{16}O$, $^{16}O^{13}C^{16}O$, $^{18}O^{12}C^{16}O$) individually. A CRDS instrument is used to measure $^{16}O^{12}C^{16}O$ with either an Offaxis-ICOS or QC-TILDAS instrument for $^{16}O^{13}C^{16}O$ and $^{18}O^{12}C^{16}O$. The Offaxis-ICOS and QC-TILDAS instruments give similar performance and serve as backups for each other as only one is installed at any given time. They are collectively referred to as the isotope analyzer in this document. The instruments are calibrated approximately every two weeks by a suite of 14 secondary standards covering the CO_2 range 250 – 600 μmol mol^{-1}. Each standard is measured relative to a reference cylinder (see below). The assigned total CO_2 of the standards is decomposed into component isotopologue mole fractions using assigned $\delta^{13}C$ and $\delta^{18}O$ of CO_2 values and the method described by Tans et al. (2017). Calibration curves fit to the responses of

the entire suite of secondary standards, referred to as response curves, relate mole fraction of each isotopologue to instrument response (relative to the bracketing reference aliquots). Total CO_2 values assigned to the secondary standards come from calibration of the secondary standards by the primary standards in an analogous manner. The $\delta^{13}C$ and $\delta^{18}O$ assigned values for the secondary standards come from measurement by the Stable Isotope Laboratory at the Institute of Arctic and Alpine Research, University of Colorado, Boulder. The resulting individual isotopologue specific abundances of the samples are then combined into total CO_2, $\delta^{13}C$, and $\delta^{18}O$ values accounting for the rare unmeasured isotopologues following Tans et al. (2017).

The cylinder to be analyzed is compared to a reference cylinder in an alternating, A-B-A-B-A... sequence. The reference cylinder is natural air with CO_2 mole fraction of the local ambient conditions at Niwot Ridge on the day of filling. The reference gas typically closely resembles the remote troposphere. The same reference cylinder is used during instrument calibration episodes and during routine measurement of cylinders to account for slow drift in the analyzers between calibration episodes. A 4-port switching valve is used to simultaneously measure reference gas on one analyzer and sample (or standard during calibration episodes) on the other, alternating back and forth (see Fig 1). Each analysis cycle includes a measurement of reference gas and sample gas on both instruments. Each analysis episode should consist of 8 cycles to match the cycles used when constructing the response curves.

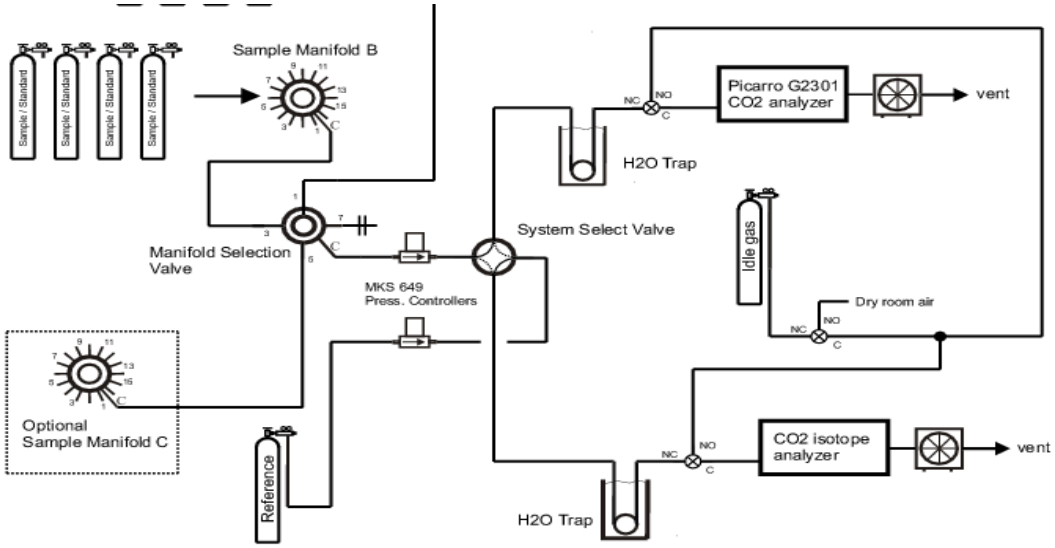

Figure 1: Plumbing diagram of CO_2 calibration system.

5.3 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 can easily determine when the system is performing normally. Indicators of performance include, but are not limited to, the spectral fit of the instruments, repeatability of 8 repeat aliquots during the run, and temperature and pressure stability. Short term target tanks are measured approximately bi-weekly, long term target tanks are measured 2-3 times per year. Target tanks are key indicators of system performance (assuming long-term changes in mole fraction due to drift are known).

6.0 Calculations

6.1 Mole Fraction

The amount of the three major isotopologues of CO_2 in the unknown sample are determined by comparing the instrument responses (for each isotopologue) of the unknown sample, relative to the reference tank, to isotopologue specific response curves.

The response of the CRDS instrument is linear within the uncertainty of the standards. A linear function is used to relate mole fraction of the $^{16}O^{12}C^{16}O$ isotopologue to the normalized response ratios.

$$X(626) = c_0 + c_1 * R \quad (1)$$

Both isotope analyzers show some non-linear behavior and a quadratic polynomial is used to relate mole fraction of the $^{16}O^{13}C^{16}O$ and $^{18}O^{12}C^{16}O$ isotopologues to normalized response ratios.

$$X(636) = c_0 + c_1 * R + c_2 * R^2 \quad (2)$$
$$X(826) = c_0 + c_1 * R + c_2 * R^2 \quad (3)$$

Where c_i are the coefficients of the fit to the secondary standards and R is the instrument response of the sample divided by the average instrument response of the bracketing reference aliquots for CRDS and Offaxis-ICOS or the instrument response of the sample minus the average instrument response of the bracketing reference aliquots for the QC-TILDAS instrument (both resulting values are referred to as a "response ratio" even though in the latter case it is a difference).

The coefficients for the response function are determined using orthogonal distance regression, taking uncertainties (one standard deviation) of both independent and dependent variables into account. The mole fraction of an unknown is determined from the response curve (1) – (3) and the instrument response ratio, *R,* determined for the unknown.

The isotopologue specific mole fractions determined for the unknown are converted into total CO_2, $\delta^{13}C$, and $\delta^{18}O$ values, accounting for the unmeasured rare isotopologues, using the method from Tans et al. (2017). The total CO_2, $\delta^{13}C$, and $\delta^{18}O$ values are saved in the SQL database. Isotopologue specific mole fractions are not saved but can be regenerated.

The current WMO CO_2 scale was developed in 2007 (as an update to the prior CO_2 scale) and transferred to secondary standards since then using NDIR and now laser spectroscopy.

6.2 Uncertainties

Two estimates of uncertainty are reported for each sample. The first is the expanded uncertainty associated with the value assignment (see TP_primary_manometer), and is derived from uncertainties in the primary standards that define the scale, scale transfer, and any other significant uncertainties. Expanded uncertainties are calculated using the GUM (JCGM, 2008) as a guide. The second quantity reported is the long-term reproducibility of the system based on repeated analysis of multiple cylinders (95^{th} percentile) (see section 10.3). Reproducibility is an estimate of our ability to propagate the scale over time periods of several years. It provides an estimate of our ability to detect possible drift in cylinders over time scales of typical use, and is useful for assessing the role of reference materials with respect to inter-laboratory compatibility. The expanded uncertainty of the WMO/GAW calibration scale, based on uncertainties associated with primary standards and scale transfer, is not useful for assessing possible drift or inter-laboratory compatibility among laboratories on a common scale. For the purposes of CO_2 analysis within the WMO/GAW community, reproducibility is the key quantity.

Current estimates of expanded uncertainty and reproducibility, for CO_2 in the ambient mole fractions range (~350 to 450 μmol mol^{-1}) are 0.2 μmol mol^{-1} and 0.02 μmol mol^{-1}, respectively. The reproducibility the historical NDIR system (0.06 μmol mol^{-1}) needs to be considered when comparing measurements of a cylinder by both techniques.

7.0 Data Collection and Storage

The sample tank information (serial number, pressure, and regulator) is either entered manually at the start of the analysis or read directly from the refgas manager DB tables by using the CO_2 "to-do" lists.

Data are stored in both raw format (raw instrument response and quality control metadata) on a centrally located computer server and in processed forms (total CO_2, $\delta^{13}C$, and $\delta^{18}O$) in a relational database to facilitate efficient data processing and quality control. The database is backed up once a day and the raw data server has a full backup every two weeks with daily incremental backups.

Mole fractions and isotopic values assigned to primary and secondary standards are stored in a MySQL database, and retrieved by the processing program.

8.0 Safety

It is GMD policy to follow safe working practices when handling compressed gas cylinders and laboratory chemicals. Pressurized 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 in a notebook dedicated to the analysis system. For each analysis, the cylinder number, date, and time 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.

Significant notes relating to the performance and maintenance of the analytical system should be recorded using ELOG (an electronic record system).

10.0 Appendix

10.1 Equipment

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

Item	Manufacturer	Model Number
CRDS	Picarro	G2301
Offaxis-ICOS	Los Gatos Research, Inc.	CCIA-46-EP
QC-TILDAS	Aerodyne Research, Inc.	QCTILDAS-CS
Pressure controllers	MKS Instruments	649B
Multicool	SP Scientific	MC480A
Valves	Valco	EUDA-24UWE, EUTA-2CSD16MWE,

		EUTA-2SD4MWE
Solenoid valves	Parker	009-0143-900

10.2 Sample Calculations (mean mole fraction)

Sample calculations are shown here for a typical analysis. Gas type REF is the reference cylinder used to track slow drift between calibration episodes. Gas type SMP is the unknown cylinder. This example is for the $^{16}O^{12}C^{16}O$ isotopologue mole fraction, X(626). The response curve is determined in a separate mode where the entire suite of standards is run against the reference cylinder. In this instance the response curve for the $^{16}O^{12}C^{16}O$ isotopologue follows equation (1) with $c_o = 0.18436648$ and $c_1 = 395.56334783$.

Table A1: Example calculations for X(626)

X(626) = 0.18436648 + 395.56334783 * R

Type	Date	Time	Sig	Sig_sd	N	Flag	Resp_Ratio (R)	X(626)
REF	2017 01 24	11:35:23	399.7326	0.0152	10	.		
SMP	2017 01 24	11:38:27	390.6285	0.0142	10	.	0.977196045	386.727
REF	2017 01 24	11:41:32	399.7559	0.0127	10	.		
SMP	2017 01 24	11:44:35	390.6413	0.0141	10	.	0.977208386	386.732
REF	2017 01 24	11:47:39	399.7487	0.0114	10	.		
SMP	2017 01 24	11:50:42	390.6465	0.0127	10	.	0.977194138	386.727
REF	2017 01 24	11:53:46	399.7782	0.0080	10	.		
SMP	2017 01 24	11:56:49	390.6461	0.0067	10	.	0.977192038	386.726
REF	2017 01 24	11:59:53	399.7496	0.0101	10	.		
SMP	2017 01 24	12:02:56	390.6503	0.0087	10	.	0.977210122	386.733
REF	2017 01 24	12:05:59	399.7720	0.0141	10	.		
SMP	2017 01 24	12:09:02	390.6477	0.0111	10	.	0.977191518	386.726
REF	2017 01 24	12:12:05	399.7595	0.0094	10	.		
SMP	2017 01 24	12:15:08	390.6520	0.0132	10	.	0.97719213	386.726
REF	2017 01 24	12:18:12	399.7803	0.0108	10	.		
SMP	2017 01 24	12:21:16	390.6662	0.0101	10	.	0.977202228	386.730
			Mean				0.977198326	386.728
			Standard Deviation				0.000007584	0.003

Similar calculations are used for $^{16}O^{13}C^{16}O$ and $^{18}O^{12}C^{16}O$ isotopologue mole fractions using equations (2) and (3). The resulting isotopologue specific values (X(626), X(636), and X(826)) are combined into total CO_2, $\delta^{13}C$, and $\delta^{18}O$ values, which are stored and reported to users. The derivation of the equations used for this is beyond the scope of this TP, the reader is referred to Tans et al. (2017) for details.

10.3 Reproducibility

Reproducibility of total CO_2 is estimated from repeated analysis of four target tanks over approximately one year (Fig 2). The mean standard deviation of the target tanks is ± 0.007 μmol mol^{-1}. This time period is not long enough to fully access reproducibility but we estimate it to be ± 0.02 μmol mol^{-1} (95% CL) based on these target tank results. The reproducibility of the calibration system will be assessed in the future by longer target tank histories and by repeated measurements of cylinders delivered to outside organizations.

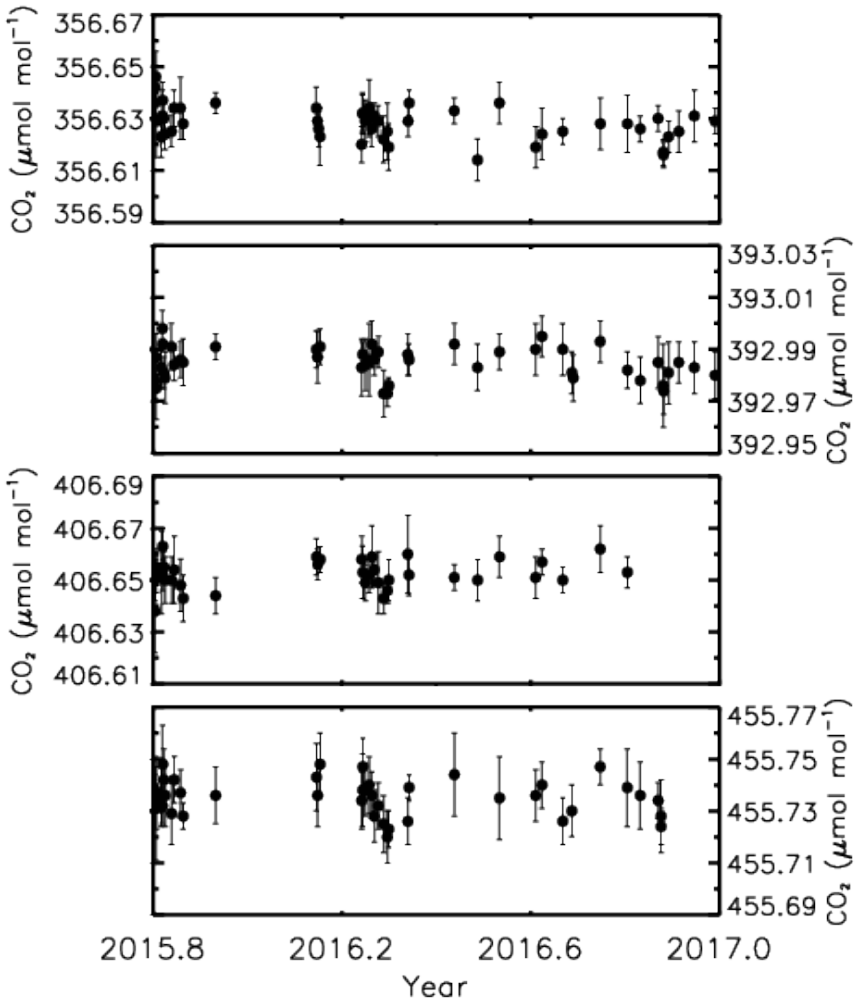

Figure 2: Histories of four target tanks measured over approximately 1 year. Top to bottom: CC71624, CB11127, CA05008, and CB10826