

Subdocument Technical Procedure
Analysis of Carbon Monoxide in Air
version 1.2
filename: TP_analysis_CO_v1.2.pdf

Approved by



31 Aug '15

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Analysis of Carbon Monoxide in Air

GMD Technical Procedure

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1. Purpose

This report serves to provide the technical procedures used to prepare, maintain and validate a reference scale suitable for application to measurements of carbon monoxide (CO) in natural-air and mixtures of CO in scrubbed natural air (CO and hydrocarbons removed). The focus of the scale is confined to levels of CO found in the remote and regionally-polluted atmosphere – typically 30 to 500 10^{-9} mol mol⁻¹ (30 to 500 nmol mol⁻¹). It is not intended for heavily urbanized environments where CO mole fractions above 1 μ mol mol⁻¹ are common.

2. Scope

This procedure describes a system of operations to develop and maintain a reference scale applicable for measurements of atmospheric CO. The gravimetric procedure used to prepare primary reference CO-in-air mixtures is briefly described, followed by the approach to transfer the primary scale to one or more sets of secondary standards, and tertiary standards. Methods are described to ensure high quality assurance/quality control and long-term stability of the scale.

3. References

Hall, B.D, G.S. Dutton and J.W. Elkins (2007), The NOAA nitrous oxide standards scale for atmospheric observations, *J. Geophys. Res.*, 112, D09305, doi:10.1029/2006/JD007954.

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/utis/common/documents/jcgm/JCGM_100_2008_E.pdf

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.

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 NASALangley and the Fraunhofer Institute (1994), *J. Geophys. Res.*, 99, 12833, 1994.

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

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calibration: An operation, under specified conditions, to establish a relation between instrument response and measurement standards, with corresponding uncertainties. The operation allows value assignment for quantities of the same kind (e.g dry air mole fraction of CO in air).

combined uncertainty (of a measurement): Uncertainty of measurement results when obtained from uncertainties of a number of other quantities, weighted according to how the measurement result varies with changes in these quantities.

comparability: Comparability of measurement results for quantities traceable to the same reference.

drift (of reference material): Change in measurement results of an analyte from a reference material (gas sample) which cannot be attributed to the uncertainty of the measurement or measurement methods.

LGR: Los Gatos Research off-axis integrated cavity output spectroscopy (off-axis ICOS) instrument used for CO analysis.

mole fraction: The ratio of the number of moles of analyte to the total number of moles (expressed as $\mu\text{mol mol}^{-1}$, or ppm for CO_2). 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 scale: Mole fractions corresponding to a particular set of primary standards used to assign mole fractions to lower-order standards.

repeatability (of results of measurements): Closeness of the agreement between results of successive measurements of a sample carried out under the same conditions

response factor: Ratio of an instrument signal provided by measurement of an analyte to the quantity of analyte that produced the signal

secondary standard: Measurement standard established through calibration with respect to a primary measurement standard(s) for a quantity of the same kind. These standards are used to periodically calibrate the instrument. For CO, values for secondary standards

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may also be assigned by comparison to other secondary standards, with verification performed by comparison to primaries.

target (transfer) cylinder: Gas mixture with sufficiently well-defined mole fraction used to routinely establish quality of measuring instruments or reference materials.

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

working standard: Measurement standard that is used routinely to calibrate or verify measuring instruments or systems. On the CO calibration system these are typically secondary standards.

5. Procedures

5.1 Analytical methods.

5.1.1. Introduction

Methods with high reproducibility and repeatability are necessary to provide response functions consistent with acceptable uncertainties of the measurement results. Instruments based on enhanced off-axis integrated cavity output spectroscopy (ICOS) meet these requirements.

5.1.2. Measurement procedure

ICOS provides a one second signal response. Response curves are created using 5-8 determinations of the standard response, each containing 30 one-second measurements. Each determination is bounded by that of a reference gas. Response curves are built using the ratio of the standard signal to that of the reference signal. A polynomial fit determined using orthogonal distance regression is used to define instrument response over the range of analysis.

5.1.3. Reproducibility and Repeatability

The repeatability of a measurement result is defined as the standard deviation of the mean for multiple determinations during a single calibration event. Reproducibility is the variance among distant calibrations events separated by some period of time.

5.2 Hierarchy of standards.

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The hierarchy of standards denotes their designation relative to reference gases having the highest metrological qualities. In this technical procedure, CO-in-air mixtures created using a gravimetric method define the primary standards. Their mole fractions and uncertainties constitute the scale. Secondary standards are assigned mole fractions through calibration against primary standards; lower hierarchical standards may be directly or indirectly tied to secondary standards.

5.3 Primary Standards.

5.3.1 Preparation of Primary Standards: Primary standards for carbon monoxide are prepared as described in *Technical Procedure: Preparation of primary standards by gravimetric methods*. Primary standards are reported as dry air mole fraction and range from approximately 30 to 1000 nmol mol⁻¹ CO. Preliminary dry air mole fractions are assigned based on the gravimetric preparation with associated measurement uncertainties. Recent CO primary standards include N₂O or N₂O and CH₄.

5.3.2 Primary Standard Mole Fractions: Primary standards are assigned mole fractions from an expression relating instrument response to preliminary mole fraction. The appropriate function will minimize variance in the instrument response factors.

5.4 Scale transfer to Secondary and Working Standards:

5.4.1 Secondary Standards:

Secondary standards span the range of mole fractions found in the remote to regionally-polluted atmosphere. CO mole fractions are assigned to secondary standards using response functions based on measurements of the primary standards or other secondary standards. The sample responses from multiple aliquots are converted to mean response ratio as described in 5.3.2. Multiple determinations define the transfer repeatability.

5.4.2 Tertiary standards:

Regular measurements of secondary standards define instrument response functions. These are used to assign mole fractions to measurements of tertiary standards

6. Calibration scale

6.1. The CO calibration scale used by this laboratory is defined by multiple sets of primary standards prepared by gravimetric methods. The scale covers the range of atmospheric mole fractions in remote and regionally-polluted locations. (40 to 500 nmol mol⁻¹). It can be

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expanded to 1000 nmol mol⁻¹ if needed. Quality assurance/quality control procedures (6.3) maintain the scale for the foreseeable future.

Brad Hall 8/26/15 9:42 AM

Comment: Better statement on uncertainty in next paragraph. This one was redundant.

6.2. Uncertainties:

The uncertainty in the reference scale is estimated from the standard uncertainties assigned for primary (gravimetric) standards, and from the reproducibility of assignments over time. Long-term surveillance cylinders are used to estimate reproducibility. The uncertainty is reconsidered with each new preparation of primary standards. The uncertainty in the reference scale is approximately 1.2 ppb ($k=2$, approx. 95%ile) at 150 ppb.

Typical repeatability of the LGR instrument used for CO analysis is 0.2% (1 s.d. over 8 aliquots). The reproducibility of CO mole fraction assignments (tertiary standards) is ~0.8 nmol mol⁻¹ or ~0.5%, whichever is greater (95%ile). Reproducibility is influenced by uncertainties associated with scale propagation (to secondary and tertiary standards, typically < 0.2% and <0.4%, respectively) and potential drift in primary, secondary, and tertiary standards over time. Reproducibility is estimated from repeated measurements of tertiary standards made at least one year apart, and by mole fraction assignments to secondary and target standards based on different sets of primary standards. Neither method is completely free from the influence of drift, and we are actively engaged in improving ways to estimate and account for drift.

6.3. Quality assurance/control: The carbon monoxide reference scale for atmospheric measurements requires long-term internal stability. Procedures to determine changes in reference gases include:

1. Preparation of new sets of primary standards every 4-6 years (or as otherwise required) to compare with previous primary and secondary standards.
2. Maintenance and comparison of two or more independent sets of target cylinders.
3. Review of the internal consistency of response factors and curve residuals for primary and secondary standards over time.
4. Periodic comparison of primary and secondary standards to high-accuracy dilutions of higher mole fraction standards, prepared internally or obtained from other institutions, such as NIST.

6.4. Stability of the Reference Scale: Changes in mole fraction occur in CO reference gases. The scale may need future correction or revision.

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6.4.1. The stability and consistency of the scale may require correction if drift is determined in primary or secondary standards. Reprocessing of calibration events based on archived measurement signals and estimated rates of drift in reference gases may be necessary.

6.4.2. The scale may need revision if a significant bias is determined in the primary standards currently used to define the scale.

7. Safety

The NOAA policy for safe handling of compressed gas cylinders requires cylinders always be secured. Cylinders are stored in designated areas with their contents clearly labeled.

8. Data archives and Documentation

The parameters of analysis are recorded for each calibration event. Instrument serial numbers, cylinder IDs, regulators, pressures, flow rates and sampling ports are included in data measurement record. Mean 30s digital signals from measurement of standard gases, reference gas, transfer cylinder and samples are stored in a GMD database. Mole fractions are computed and saved with 1 sigma analytical uncertainty.

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