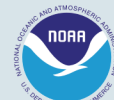


Review of NOAA/GMD CO measurements: methods and reference gases

P.C. Novelli¹, A. Croftwell^{1,2}, K.A. Masarie¹, B.D. Hall¹, P.M. Lang¹

¹ NOAA/ESRL/GMD, 325 Broadway, Boulder, Colorado, 80305, USA,
² CIRES, University of Colorado, Boulder, Colorado, 80303, USA



I. Introduction.

We have measured CO in air since 1989 using several instruments based on different analytical techniques and calibration approaches. A wide range of reference gases have been used. GMD standard gases are tied to gravimetric standards prepared in 1989, 1992, 1997, or 2000. Calibrations prior to 2004 were made using gas chromatography with HgO reduction detection (GC). Measurements from 1999 through 2001 were revised in 2002 to correct for drift in working standards.

Between 2002 and 2004, reference gases were calibrated using both GC and resonance fluorescence in the VUV (VUVF) and differences between methods were observed. A correction was applied in 2005 to all measurements made using GC between 2001 and 2004 to account for possible low standard assignments and drift. A time line of the measurements and corrections is shown in Figure 1.

Here we examine the consistency of our CO reference gases. The differences in measurement techniques, reference gases and a correction to measurements applied in 2005 are discussed. We present reasons why our flask measurements are lower than cylinder calibrations at the low end of the tropospheric range.

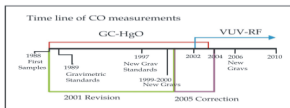


Figure 1. Time line of measurements and corrections since 1989. The 2002 revision is discussed in detail by Novelli et al., JGR, 108, 2003.

II. Methods.

Since 1989 GCs were used for calibration of standards and analysis of air in flasks. These used multi-point response curves with standards ranging from ~50 to 200 ppb to correct for the detector non-linear response. Zero air through I.O. served as a blank.

Beginning 2002 a VUVF instrument was run beside a GC. The VUVF initially used dilutions of a NIST SRM (2.65 (±2%) ppm) as the reference, later gravimetric standards prepared in 2000 (300-400 ppb) were used.

III. 2000 Gravimetric Standards.

CO-in-air standards, with mixing ratios between 50 and 500 ppb were produced using a gravimetric method during 1999-2000. These standards were greater than the original scale and were the basis of a revision of the NOAA scale in 2002.

Beginning 2002, gravimetric and working standards were compared to dilutions of a NIST SRM using VUVF. Calibration curves showed the VUVF linear to within 0.6% over the range of 0-400 ppb (Figure 2). Due to its high reproducibility, repeatability, linearity and capability to use high CO standards, measurements using VUVF are considered superior to our GC.

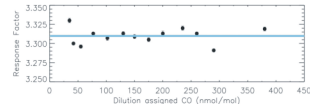


Figure 2. Response factors from the VUVF based on dilution of a NIST SRM with 9.65 ppb CO. The blue line is the average response factor.

IV. Evaluation of the 2000 gravimetric standards

The 2000 gravimetric standards were calibrated using VUVF with dilution of a NIST SRM as the reference. The results (Table 1) show 2-3 ppb difference between the measured and prepared (gravimetric) values below ~125 ppb.

Table 1. Prepared CO vs dilution of a NIST SRM

Tank ID	Prepared	Measured
04016	53.1	55.1
04014	70.5	73.0
03995	116.3	113.1
04025	125.9	127.5
04012	164.8	163.4
03955	205.6	203.2

* Mixing ratios are reported in ppb by mole fraction, * nmol mol⁻¹
¹ CO determined using VUVF with dilution of a 9.65 NIST SRM as the reference. VUVF instrument was from Ana-Lab, GmbH model AD01.

A set of primary standards were first calibrated in 2002-2003 using both GC and VUVF GC, was referred to the suite of 2000 grams, VUVF to dilution of a SRM and one of two 2000 high CO gravimetric standard - Table 2.

Table 2. Calibration of primary standards using VUVF, GC and different reference gases

Tank	RG ¹	NIST ²	VUVF ³
15749	51.9	55.9	57.2
15807	70.8	74.9	76.7
17445	100.7	104.5	106.5
16443	132.0	133.7	133.3
17435	151.5	152.2	152.2
17431	203.5	200.9	201.2
16416	291.3	303.8	302.1

¹ Calibration using GC-HgO with response curves based on the 2000 gravimetric standards (-50-200 ppb). The GC used here were from Ana-Lab, GmbH model AD01.
² Calibration using GC-HgO with response curves based on the 2000 gravimetric standards (-50-200 ppb). The GC used here were from Ana-Lab, GmbH model AD01.
³ Calibration using VUVF with 2000 grams (300-400 ppb) as the reference.

V. Correction to 2001-2004 measurements.

The results in Tables 1 and 2 suggested the low-level gravimetric standards were either drifting, assigned low or both. In 2005 a correction was applied to measurements made using GC. The differences between prepared CO and NIST-derived values (Table 1) were fit with quadratic polynomial. These were used to adjust the value of the gravimetric standards (2 ppb at 50/0 ppb at 200).

The remaining differences between the GC and VUVF were attributed to drift and corrected using a linear rate of change (Figure 3).

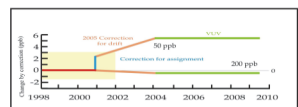


Figure 3. A depiction of the corrections applied to tank calibrations determined between 1998 and 2009 to measurements made using GC at the 50 and 200 ppb level. GC measurements before 2001 are in red, VUVF (VUV) measurements referenced to a ~350 ppb 2000 gravimetric are green, and the time dependent correction in orange. A 2 ppb correction to low-level standards is blue.

VI. Evaluation of the 2005 Correction.

The correction increased CO mixing ratios measured using GC by <1 to 5 ppb over the range of 55 to 200 ppb. Greatest changes were made at lower mixing ratios. Figure 4 shows the differences between the long-term average CO assigned the primary standards using VUVF and the original measurements made using GC in 2002 and 2004.

The corrected CO associated with the 2002 and 2004 measurements are also shown. The correction is time dependent such that a smaller change was applied in 2002 than 2004. Corrected values to measurements made in 2002 remain ~2 ppb high relative to the long-term average, while corrections applied to later measurements are within a ppb of the long-term average (Figure 4).

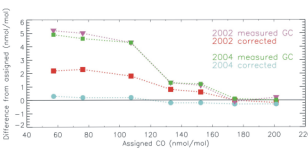


Figure 4. Calibration results determined using GC-HgO reduction in 2002 and 2004 are compared to their revised values.

VI. Evaluation of the 2005 correction (cont'd)

A review of standards first calibrated using GC in the 1990s, revised in 2005, and measured again using VUVF is shown in Table 3.

The corrected values agree well with measurements based on VUVF. There is also no apparent difference between results at low and high CO where the greatest corrections were applied. There remains a 1-2 ppb difference between the corrected and measured CO at low mixing ratios.

Table 3. Original, Corrected and Final Assignments

Year of Original Calibration	Original CO ¹	Corrected ² 2005	Measured ³ 2005
1993	206.7	203.2	203.3
1995	319.0	326.6	348.0
1995	77.2	84.5	86.3
1995	180.1	184.7	185.6
1997	28.1	31.4	31.6
1997	88.0	98.4	99.1
1998	45.5	54.5	54.2
1998	144.0	152.4	153.3
1999	129.0	129.5	130.3
1999	234.7	225.9	224.4
2002	55.1	59.5	60.6
2002	151.0	152.9	151.9

¹ Year CO mixing ratio was first assigned, measured using GC-HgO
² The original CO value (ppb)
³ 2005 corrected value
⁴ 2005 assigned value based on low term average measurements using VUVF

Summary of NOAA/GMD reference gases:

Mixing ratios originally assigned reference gases in the early 1990s using GC were low by as much as 12 ppb at the low end of the scale. Corrections applied in 2002 and 2005 resulted in higher values. Results in Table 3 show that mixing ratios assigned in the 1990s using GC agree well with recent measurements using VUVF. However, results remain 2 ppb low in the 50-100 ppb range.

VII. Analysis of air on a flask system using GC.

Differences between GC and VUVF flask-air analysis are apparent at the lower end of the tropospheric range even after the correction. Table 4 compares calibration of the primary standards using GC to their values assigned by VUVF. Differences of 2-3 ppb are found at the low end of the range (Columns 1 and 2).

Table 4. Comparison of GC results with and without a fixed zero value.

VUVF	GC ¹	GC (no zero) ²
25.4	20.9	25.6
42.0	39.3	42.1
57.7	54.9	57.2
77.0	75.5	77.2
106.7	105.5	106.0
133.3	133.6	133.0
152.8	154.0	153.1
174.5	175.3	174.5
200.8	200.2	201.1
235.6	235.6	236.9

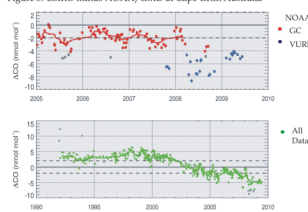
¹ Assigned CO based on VUVF 6 year average, considered the best value.
² GC calibration curve includes zero.
³ GC calibration curve without zero.

The calibration curve is very sensitive to the zero value. The GC calibration curves include a zero air sample providing no quantified response. However a response is visible on the chromatogram. If the zero value is fixed in the calibration curve or left to float, mixing ratios are further reduced relative to the best value (Table 3, Columns 3 and 4).

VIII. CSIRO-NOAA ICP at Cape Grim.

The Inter-Comparison Program (ICP) between NOAA and CSIRO at Cape Grim shows changing differences over time. (Mixing ratios at Cape Grim average ~35 ppb). Figure 5 (top panel) shows a relatively constant offset of 2 ppb for the period 2005 through 2008 that ends with an abrupt decrease of 4 ppb in 2008-2009. This corresponds to a change from analysis by GC to VUVF at NOAA.

Figure 5. CSIRO minus NOAA/GMD at Cape Grim Australia



The long-term ICP at Cape Grim shows two periods of nearly constant offset (1992-2002, and 2005-2008) with a period of transition between 2002 and 2004 and the aforementioned change in 2008.

VIII. CSIRO-NOAA ICP (cont)

Air samples from Cape Grim, measured at NOAA until 2004 may be low. A combination of two problems may have contributed to this low. 1. Corrections assigned working standards < 110 ppb may be 1-2 ppb low. 2. The low end of the calibration curve is sensitive to the zero value. An incorrect zero may force the curve higher and mixing ratios 2-3 ppb lower near 50 ppb.

IX. Summary and Conclusions:

1. Revised CO mixing ratios assigned to reference gases since the early 1990s agree to ~2 ppb with recently measured values. The two NOAA/WMO scales (2000 and 2004) are both in use and the scale name primarily indicates the method used for the analysis - GC (2000) or VUVF (2004). However we note that NOAA/WMO 2000 may be low 2 ppb at CO levels below 110 ppb.
2. Air samples measured using GC may be low by 3-4 ppb at 50 ppb due to under-assigned values for working standards and an effect of the zero value on the instrument response curve fit. After further study, air samples analyzed using GC may be represented using an approach less sensitive to the zero.
3. A correction to the NOAA GC measurements may account for a large part of the GC-VUVF offset in flask air, and the difference in the CSIRO-NOAA ICP.

X. Acknowledgments:

D. Guenther set up the VUVF and built the dilution system. K. Thoning developed the software used in the analysis. Funding from the NASA MOPITT/TERRA validation program provided the VUVF instrument.