A notice to users of CO standard gases produced by the WMO central calibration laboratory

A new scale for measurements of CO in the atmosphere is described below. Measurement results since 2000 are revised and reported on the WMO CO X2014 scale.

The WMO CO X2014 scale builds upon the previous X2004 scale by incorporating two additional sets of primary reference gases. X2004 was based upon a suite of nine primary standards prepared using a gravimetric method (Novelli et al., 1992; Hall et al., 2007) during 1999-2000. Primary standards prepared in 2006 and 2011 were made using the same method. The balances and the analytical techniques used to prepare the primaries and their transfer to other standards improved 2000 between 2000 and 2011. Table 1 shows the number of primary standards prepared in each set; their estimated preparation uncertainty and the range of the combined measurement error. The preparation error accounts for the uncertainty the balances plus that introduced by trace amounts of residual CO in diluent air. The preparation error in primary standards decreased by about a factor of two since 2000, largely due to an improved determination of the uncertainties in mole fraction of CO in the diluent air.

Several methods have been used to measure CO: 1) Gas chromatography with hot mercuric oxide reduction and photometric absorption (GC-HgO, used from 2000-2005); 2) Resonance fluorescence in the vacuum ultraviolet (VUVF, 2004-2010); 3) Off-axis Integrated Cavity Output Spectroscopy (ICOS, 2010 to present). Multi-point response curves covering 53 to 398 nmol mol^{-1} defined detector non-linearity on the GC instruments. The VURF instrument, identified as having a linear response from 50 to 500 nmol mol^{-1}, used a single point calibration with reference gases ~ 330 to 400 nmol mol^{-1}. ICOS used response curves based on multiple standards covering the range of 20 to 500 nmol mol^{-1}. Calibration of standards above the range of reference gases on ICOS used response curves extended using primary standards of ~ 1000 nmol mol^{-1}.

In addition to a larger number of primary standards used to define the scale, X2014 incorporates several other modifications to X2004. Four main changes to X2004 were applied in the development of X2014: 1) the GC-HgO response curves do not include an instrument blank; 2) mole fractions assigned the 2000 primary standards were revised based upon their calibration using VURF; 3) corrections for drift were applied to several reference gases; 4) Uncertainties of the assigned mole fraction are now reported as the 2σ combined uncertainty (the combined error of the scale and the measurement repeatability).

Set of standards	N	Range (nmol mol^{-1})	Preparation error (%), k=2
2000	9	53-398	1.8 - 0.5
2006	7	47-498	0.9 – 0.4
2011	14	30-1001	0.7 – 0.4

Table 1: Three sets of primary standards were prepared between 2000 and 2011. Listed are the number of standards in a set, their range of mole fractions, and range of uncertainty.

Development and evaluation of the X2014 scale was aided by measurements of nine surveillance standards calibrated relative to different primary standards between 2001 and 2014. The differences among calibration results using various measurement techniques and reference gases are generally less than 1 nmol mol^{-1}. The combined uncertainty of the calibration results are mole fraction dependent: ~ 1.2 nmol mol^{-1} or 0.6% (k=2), whichever is greater. Preliminary results on X2014 from 2000 to present are available at www.esrl.noaa.gov/gmd/ccl/refgas.html.

Results of this revision are still considered preliminary. We do not recommend converting your standards to X2014 at this time as mole fractions assigned the CCL standards may change slightly. For standards with CO above 350 nmol mol^{-1} measured between 2008 and 2011 the preliminary results are likely high by several nmol mol^{-1}.

Comparisons of the mean CO mole fractions assigned surveillance standards based on either X2014 or x2004 show differences of 1.1 nmol mol^{-1} or less (Table 2). Within the combined uncertainties there is no difference between the results determined by the two scales (the combined error includes the scale and measurement uncertainties).

Table 2: Mole fractions assigned surveillance cylinders using X2004 (measured over 2004-2009) and X2014 (2012). * Standards first measured in 2008, all others in 2004.

Tank ID	2004 scale	2014 scale
ND33423	41.5 (1.3)*	41.9 (1.2)
ND15747	57.6 (1.8)	58.7 (1.3)
ND15807	76.9 (1.8)	77.7 (1.3)
ND17445	107.3 (2.0)	107.2 (1.4)
ND16443	133.3 (2.1)	134.1 (1.3)
ND17435	153.3 (2.1)	153.7 (1.1)
ND16439	174.2 (2.2)	174.9 (1.4)
ND17431	202.5 (2.8)	202.5 (1.4)
ND16416	301.5 (4.4)	302.6 (2.1)
ND33960	478.1 (6.2)*	483.8 (3.3)

Mole fractions assigned non-surveillance standards may have greater combined uncertainties. Figure 1 shows differences between CO assigned standards on the X2014 or X2004 scales. The results in Figure 1 are binned by increasing larger range of mole fractions, as there are fewer standards measured above ~ 300 nmol mol^{-1}. Greater differences at higher mole fractions are expected as the scale uncertainties increase with mole fraction. In addition, extended response curves used for calibration of high CO standards are incomplete. The preliminary differences above 500 may be several nmol mol^{-1} high.

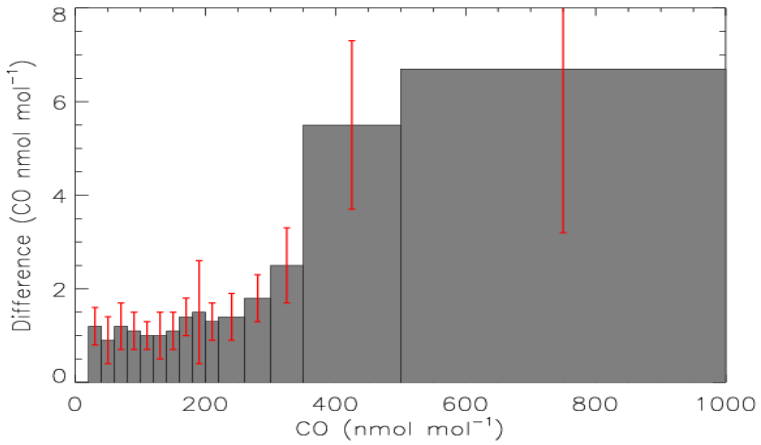

Figure 1. Mean mole fractions assigned on X2014 minus those on X2004. Results below 220 are binned by 20 nmol mol^{-1} intervals, bin intervals then increase from 40 to 500 nmol mol^{-1}. Differences are the mean of 10-20 samples. Plotted are the 2σ of the mean.

Measurements made by GC-HgO between 2000 and 2004 have been revised. Their revision is based on mole fractions of the 2000 primary standards re-assigned by their calibration using VURF-2000. Figure 2 shows the consistency of mole fractions determined for surveillance cylinders using three methods and three sets of primary standards measured between 2000 and 2013.

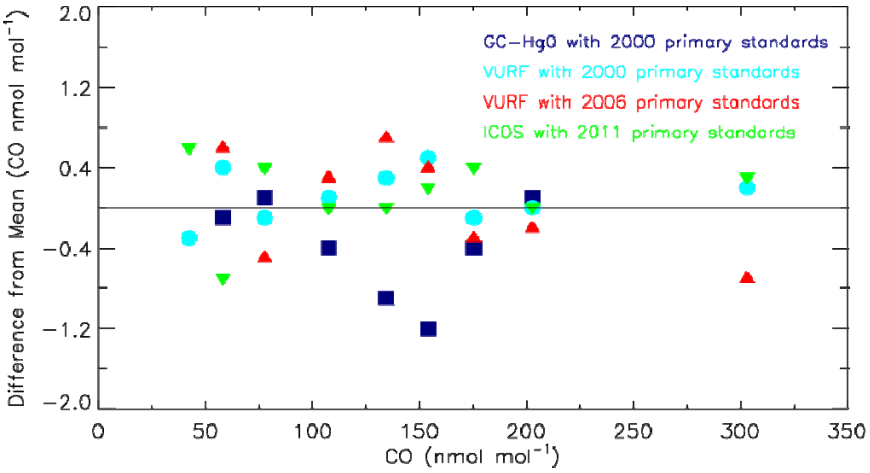

Figure 2. Residual mole fractions assigned surveillance cylinders based on preliminary X2014 revision results minus assignments based on previous scales . Four instrument/scale combinations are shown. The line depicts no difference from the mean. At ~500 nmol mol^{-1} the differences from the mean (not shown) for VURF and for ICOS measurements were 2.9 nmol mol^{-1}.

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