

A New Reference Scale for Measurements of Carbon Monoxide in the Atmosphere

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The Global Monitoring Division Carbon Cycle Group serves as the World Meteorological Organization (WMO)/Global Atmosphere Watch Central Calibration Laboratory for measurements of Carbon Monoxide (CO) and several other trace gases. Here we describe a new reference scale (denoted as WMO X2014) which builds upon the previous X2004 scale (WMO, 2010). WMO X2014 is based upon three sets of primary reference gases prepared in 2000, 2006 and 2011 using a common gravimetric method (Novelli et al., 1992; Hall et al., 2007). Several analytical methods were used to measure the primary standards and produce secondary and working standards. These include: 1) Gas chromatography with hot mercuric oxide reduction (GC-HgO, 2000-2005), 2) Resonance fluorescence in the Vacuum UltraViolet (VUV, 2004-2010), and 3) Off-axis Integrated Cavity Output Spectroscopy (ICOS, 2010 to present). Development and evaluation of the X2014 scale was aided by measurements of eight surveillance standards relative to different primary standards and calibration schemes between 2001 and 2014. A preliminary estimate of the scale uncertainty is mole fraction dependent: 1.2 nmol mol⁻¹ or 0.6% at k=2, whichever is greater. Calibration results determined prior to 2000 will be revised to X2014.

The figure below shows preliminary estimates of the uncertainties in mean mole fractions assigned surveillance cylinders using three sets of primary standards as reference. GC-HgO used the 2000 primary standards with mole fractions revised by their calibration by VURF_2000. The VURF_2000 results are based on two 2000 primary standards with CO > 300 nmol mol⁻¹; VURF_2006 results were referenced to primary standards prepared in 2006. The ICOS results are based on primary standards made in 2011. The table compares preliminary mean CO mole fractions assigned surveillance cylinders against the X2014 scale by ICOS to calibration results using VURF and reference gases on X2004. N = 10-12 for 2004, 4 for 2011, the error (2 sigma) includes estimates of both scale and measurement errors.

Tank ID	2004 scale	2014 scale
ND15747	57.6 (1.2)	58.7 (1.3)
ND17435	153.3 (1.6)	153.7 (1.4)
ND16416	301.5 (3.3)	302.6 (2.1)

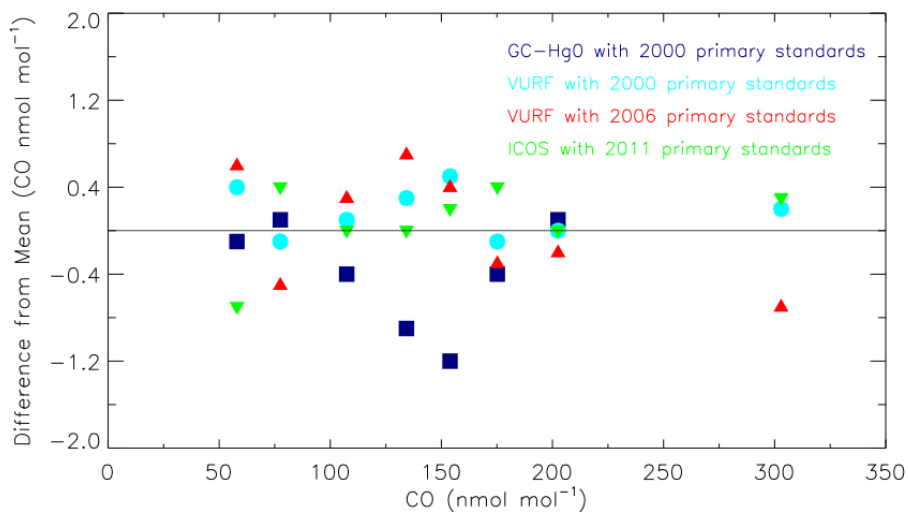


Figure 1. Differences between mean mole fractions assigned surveillance cylinders over 2000-2012 and CO assigned using different sets of primary standards and different analytical methods.