

Original document is generated on May 2002

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The calibration scale for atmospheric CO measurements made by AGAGE derives from the gravimetric scale developed at NOAA/CMDL by Novelli et al. (*J. Geophys. Res.*, Vol. 96, July 20, 1991, pp. 13,109-13,121). The link to the gravimetric scale is via a single standard in a high-pressure (2000 psig) aluminum cylinder (29.5 liter), with a CO mixing ratio (mole fraction in dry air) assigned by NOAA/CMDL of 195.7 parts per billion ( $10^9$ ). This standard is one of five synthetic mixtures of CO<sub>2</sub>, CH<sub>4</sub>, and CO in zero air (with CO mixing ratios spanning the range 30.1 – 195.7 ppb) that were calibrated for CSIRO Atmospheric Research by NOAA/CMDL between 1992 and 1994. (The synthetic mixtures were prepared by Scott-Marrin, Inc., Riverside, California).

Only the standard with the highest CO mixing ratio is used to link to the NOAA/CMDL gravimetric scale because significant discrepancies have been found between CSIRO's and CMDL's determination of relative mole fraction among these five standards, and other high pressure standards exchanged since 1994. The discrepancies have emerged from a series of static dilution experiments conducted at CSIRO between 1993 and 1999. In these experiments the instrument response function of the instrument used at CSIRO for CO measurements (a Trace Analytical RGA3 gas chromatograph system, fitted with a heated mercuric oxide detector) was determined by using zero air to prepare a range of static dilutions of an air standard containing both CH<sub>4</sub> and CO. The dilution ratios were precisely determined by analysis of the CH<sub>4</sub> mixing ratios, on a gas chromatograph with flame ionization detector, whose response function had been determined to be linear.

By using the single standard with a CO mixing ratio of 195.7 ppb as the fixed reference point for linking to the NOAA/CMDL gravimetric scale, the dilution experiments at CSIRO show differences between CSIRO and CMDL of up to 4 ppb at lower CO mixing ratios. These discrepancies are most pronounced at CO mixing ratios less than 100 ppb, and are most likely due to different treatment of instrument non-linearity in each laboratory (Masarie et al., *J. Geophys. Res.*, 106, D17, pp. 20,445-20,464, 2001).

The long-term stability of the CO standards, and variations in instrument response over time, are monitored with ~20 high-pressure cylinder standards maintained at CSIRO Atmospheric Research. These standards have lifetimes of 4 – 10+ years, with CO mixing ratios spanning the range 20 – 400 ppb.

The linearity of the CO measurements at the Mace Head Station, Ireland, was evaluated using a suite of sixteen CO mixtures covering a range of concentrations from 16-290 ppb made by diluting a single parent standard. In each case the dilution factor was calculated by measuring the methane concentrations in the mixtures. In addition a CO-free cylinder of zero air was measured to check for a CO blank. To determine nonlinearity the resulting data were fitted with a cubic polynomial, however this was complicated by the presence of a CO blank. To separate the blank from the nonlinearity required iteration: by using the initially fitted nonlinearity to calculate the blank concentration, and then correcting the concentrations of the dilution standards for the blank and re-fitting the nonlinearity. This was repeated until the blank concentration converged. The resulting CO blank was 8.7 ppb, and the overall non-linearity correction determined from these analyses was +5% at 16 ppb and -1% at 290 ppb. The standard deviation of the measurements

from the fit was 0.23%. For the range of ambient mixing ratios typically observed at Mace Head of between 70-200 ppb, the non-linearity correction was within +3% and -1%.

Additional linearity tests are performed approximately every two weeks at Mace Head using a high concentration (136 ppb) and low concentration (63 ppb) pair of CO calibration standards.

#### Mace Head Carbon Monoxide (CO) calibrations during the period February 1990-June 1996.

Prior to June 1996 the inherent non-linearity of the RGA3 hot mercuric oxide detector was more severe than after June 1996 when a more linear mercuric oxide reactor was installed. Instrumental non-linearity during the 1990-mid 1996 period was determined by regular (every 3-4 months) dynamic dilutions of a NIST CO primary standard with CO-free zero air. The NIST standard contained carbon monoxide in air at a concentration of 1.02 ppm with a stated accuracy of 2%. Based on the approximately quarterly dynamic dilutions of the NIST primary standard a linear regression was fitted to all of the calibration data. The best straight-line fits were: for the concentration range 0-265 ppb:  $Y = -2,865,307 + 45,165X$ , and for the concentration range 266-1020 ppb:  $Y = -5,466,848 + 51,649X$ , respectively.

Mace Head CO observations which had been corrected for the non-linearity of the RGA3 detector were subsequently intercompared during October 1991 with independent CO measurements using an NDIR instrument (R.G. Derwent *et al.*, 28, 2623-2637, 1994). The difference between the monthly means for the two datasets was 0.7% with a correlation coefficient of  $r = 0.99$  (No. of data points = 740). A separate CO intercalibration exercise was conducted during the European EUROTRAC Tropospheric Ozone Research (TOR) project. Results of independent calibrations against two blind standards gave differences of -2.2% and +2.5% from the actual values. These intercalibrations provide confidence that carbon monoxide measurements obtained prior to June 1996, although less robust, can nevertheless be successfully corrected for the non-linearity of the RGA3 detector.