Conversion of NOAA Atmospheric CH_4 Mole Fractions to a Gravimetrically-Prepared Standard Scale

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Sixteen gas mixtures were prepared using a gravimetric technique to define a CH_4 standard gas scale covering the nominal range 300 to 2600 nmol mol^{-1}. This scale, which has been accepted by the community of experts within the Global Atmosphere Watch program as the WMO X-CH_4 scale, is designed to cover a range of measurements for methane in air extracted from glacial ice through contemporary background conditions. All standards were prepared in passivated, 5.9-L high-pressure aluminum cylinders. Methane dry-air mole fractions were determined by gas chromatography with flame ionization detection (FID), where the repeatability of the measurement is typically better than 0.1% ($\leq$ 1.5 nmol mol^{-1}) for ambient CH_4 levels. Once a correction was made for 5 nmol mol^{-1} CH_4 in the diluent gas, the scale was used to verify the linearity of our FID over the nominal range 300 to 2600 nmol mol^{-1}. The gravimetrically prepared standards were analyzed against the existing CMDL CH_4 scale (Figure1, top panel), and they give CH_4 mole fractions that are a factor of (1.0124 ± 0.0007) greater than the old NOAA scale. In the bottom panel of Figure 1, residuals are plotted from a straight line fitted to the measurements, where different symbols represent different preparation techniques. All CMDL measurements of atmospheric CH_4 will be adjusted to this new scale.

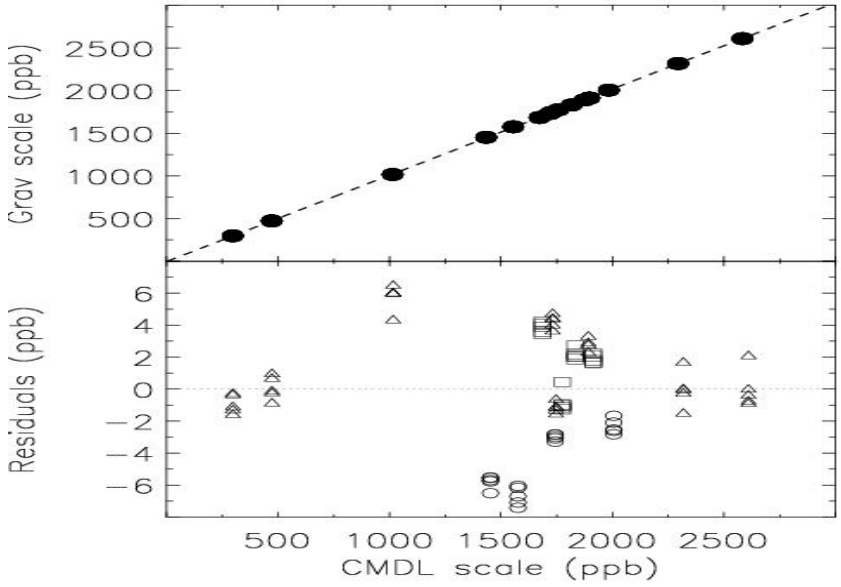

Figure 1. (Top) Plot of prepared gravimetric value for each standard versus the CH_4 mole fraction determined relative to the CMDL scale. The intercept is -4.8 ± 1.1 nmol mol^{-1} and the slope is 1.0124 ± 0.0007. (Bottom) Residuals of the fit in (a) plotted with different symbols for each preparation method: squares are tube expansion method; circles are tube flush method; and triangles are direct dilution method.