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 (Figure 1, top panel), and they give CH$_4$ mole fractions that are a factor of $(1.0124 \pm 0.0007)$ 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](attachment:image.png)

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 $-4.8 \pm 1.1$ nmol mol$^{-1}$ and the slope is 1.0124 $\pm$ 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.