Assessing LI-COR's Factory CO_2 Calibration

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Abstract

LI-COR performs approximately 1000 CO_2 calibrations annually, including new analyzers, repairs, and recalibrations. These calibrations use 13 working standards to cover the range of 0 to 3000 ppm. The working standards are all re-measured periodically (every time one is replaced – typically 2 or 3 times per year) using a set of primary standards. Before 1998, the primary standards were a set of 11 tanks obtained from a commercial gas supplier in 1986. In 1998, five new tanks were obtained from CMDL (180, 355, 716, 1448, and 2808 ppm), which became the new primary standards and provided an independent check on the previous primaries. In 2005, these five primary tanks were re-measured by CMDL, and 8 additional CMDL tanks (between 250 to 1100 ppm) were obtained. Having 13 primary standards provides the opportunity to answer several important questions: How much error was introduced by not re-measuring the primaries for 7 years? How well do the 13 primary standards fit the assumed behavioral curve (a 5^{th} order polynomial) used by LI-COR analyzers? What is the loss in accuracy of calibrating over 0-3000 as opposed to a more limited range nearer to ambient? How accurate is a LI-COR CO_2 calibration?

Summary

The original 1986 primary tanks (800 ppm and below) were all within 1 ppm of their certified values when measured against the 5 CMDL primary tanks in 1998. The remaining tanks (1500 ppm and above) were 10 to 30 ppm higher than their certified values (1.2% max error).

The 2005 analysis showed the 5 CMDL tanks had drifted < 0.15% in 7 years. A 5^{th} order fit of all 13 CMDL primaries yields residuals < 0.05%. Fitting a range of 0 to 800 ppm reduces the residuals to < 0.02%. Working standard concentrations determined with a 5^{th} order fit of all primaries compared with a method of using successive 3^{rd} order fits of groups of 4 and 5 primaries yields differences < 0.02.

The present protocol of re-measuring the primary tanks every two years (0.05% potential drift) and using a 5^{th} order curve fit to the primaries to determine the working concentrations (0.05% uncertainty) leads to the estimate that LI-COR is calibrating IRGAs to standards that are within 0.1% of the CMDL accuracy.