Development of a New Flask-air Analysis System for the Global Greenhouse Gas Reference Network

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The Carbon Cycle Greenhouse Gases group (CCGG) of NOAA GMD monitors the major long-lived greenhouse gases CO_2 , CH_4 , N_2O , and SF_6 (along with CO and H_2) by collecting discrete air samples (flask samples) from a global network of surface sites through its Global Greenhouse Gas Reference Network (GGGRN). In addition to the surface sites, the CCGG aircraft project collects flask-air samples by light aircraft to provide vertical profiles through the free troposphere. Air samples are returned to Boulder for analysis on a single analytical system to provide high internal consistency of the measurements. The current flask-air analysis system, which measures all six species simultaneously, has been in use since 1997 and has measured more than 300,000 discrete air samples.

New analytical techniques based on laser spectroscopy have become commercially available that may lead to improvements in measurement uncertainty. However, these instruments are often developed for *in situ* applications where sample gas is unlimited. For flask-air samples, the amount of gas available is limited by the size of the sample collected and the needs of additional measurements performed on the flasks after the CCGG analysis.

We describe here the development and testing of a new flask-air analysis system using laser spectroscopic techniques for CO_2 , CH_4 , N_2O , and CO (along with gas chromatographic techniques for SF_6 and H_2) that minimizes gas usage while improving the analytical repeatability for CO_2 (±0.02 µmol mol⁻¹), CH_4 (±0.1 nmol mol⁻¹), and N_2O (±0.05 nmol mol⁻¹). The analytical performance for CO (±0.2 nmol mol⁻¹), SF_6 (±0.04 pmol mol⁻¹), and H_2 (±1.0 nmol mol⁻¹) is the same as for the current system. Other improvements in consistency of sample/standard gas treatment, time of analysis, and efficiency of operation will be highlighted.



Figure 1. Flasks filled from a calibrated cylinder of air are used to compare the performance of the N₂O measurements on the new flask-air analysis system using laser spectroscopy (red squares, average difference from the assigned value of the cylinder = 0.03 ± 0.05 nmol mol⁻¹) with the current flask-air analysis system which uses gas chromatography with an electron capture detector (black circles, average difference = -0.06 ± 0.4 nmol mol⁻¹).