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Novel Instrumentation for Measurements of Isotopic Carbon Dioxide

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Fast, precise, and accurate measurement of δ^{13}C (^{13}C/^{12}C in CO_2), δ^{17}O (^{17}O/^{16}O in CO_2) and δ^{18}O (^{18}O/^{16}O in CO_2) of carbon dioxide is desirable for a number of applications including (but not limited to) atmospheric chemistry, meteorology, and carbon sequestering. Recent advances in laser absorption spectroscopy, including cavity enhanced techniques, have enabled field portable instruments which have a number of advantages over traditional, laboratory-based isotope ratio mass spectroscopy systems. We report on the recent developments and improvements of an analyzer, based on a patented laser absorption technique (off-axis integrated cavity output spectroscopy or Off-Axis ICOS), which simultaneously measures δ^{13}C, δ^{17}O and δ^{18}O in CO_2 along with CO_2 mole fraction. The analyzer can provide measurements of continuously flowing air at a data rate of 5 Hz for applications that require extremely fast flow response (e.g., eddy covariance flux). The analyzer may also be configured for measurements of discrete gas samples via manual injection (automated gas injection is in development). The instrument provide high precision measurements (δ^{13}C and δ^{18}O better than 0.08‰ δ^{17}O better than 0.2‰ (1σ) in less than 2 minutes of averaging on CO_2 mole fractions typically present in ambient air.

For ambient levels of CO_2 (350 to 500 ppm), the analyzer operates with a gas volume of about 50 (standard) mL, which includes sufficient sample to flush instrument prior to measurement. With appropriate dilution, smaller sample volumes of higher mole fractions of CO_2 may be analyzed. In the case of pure (100%) CO_2 samples, only about 1 milliliter of sample is required.

The instrument employs a continuous wave quantum cascade laser, appropriate optics and photodetector to measure high-resolution absorption lineshapes from the strongest CO_2 vibrational bands near 4.3 microns (2310 cm^{-1}). Details concerning instrument performance, operation, sample dilution procedure, and calibration will be presented.