Calibration Strategies for FTIR and Other IRIS Instruments for Accurate $\delta^{13}C$ and $\delta^{18}O$ Measurements of CO_2 in Air

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Over recent years the introduction of Isotope Ratio Infrared Spectroscopy (IRIS), based on various spectroscopic techniques, has advanced stable isotope analysis in the atmosphere, allowing *in situ* field measurements of the isotope ratio of carbon dioxide (CO_2) in air, performed in real time directly on the air sample without separation of CO_2 from air. These instruments also need to be calibrated with CO_2 in air standard mixtures, applying calibration strategies which exploit the specificity of IR absorption spectroscopy, namely its dependency on individual isotopologues amount fraction in the sample.

The BIPM has developed a novel methodology to calibrate a Fourier Transformed Infrared (FTIR) spectrometer using only two standards of CO_2 in air with different mole fractions but identical isotopic composition. A complete uncertainty analysis was performed and measurements of $\delta^{13}C$ and $\delta^{18}O$ with standard uncertainties of 0.09 ‰ and 1.03 ‰, respectively, were demonstrated, at a nominal CO_2 mole fraction of 400 µmol mol^{-1} in air. A different strategy was chosen for another IRIS system (Thermo Delta Ray) which makes use of two standards of CO_2 in air of known but differing $\delta^{13}C$ and $\delta^{18}O$ isotopic composition, reaching standard uncertainties of 0.18 ‰ and 0.48 ‰, for $\delta^{13}C$ and $\delta^{18}O$ measurements, respectively. Both calibration strategies were validated using a set of five Primary Reference Gas Mixtures of CO_2 in whole air or synthetic air in the mole fraction range of 378-420 µmol mol^{-1}, prepared and/or value assigned either by the National Institute of Standards and Technology (NIST) or the National Physical Laboratory (NPL). The standards were prepared using pure CO_2 obtained from different sources, namely: combustion; Northern Continental and Southern Oceanic Air and a gas well source, with $\delta^{13}C$ values ranging between -35 ‰ and -1 ‰. All measurements were compared with values assigned independently on the same samples by Isotope Ratio Mass Spectrometry (IRMS) at the Max Planck Institute for Biogeochemistry Jena (MPI-Jena), providing the traceability to the VPDB-CO_2 scale for $\delta^{13}C$ and $\delta^{18}O$.

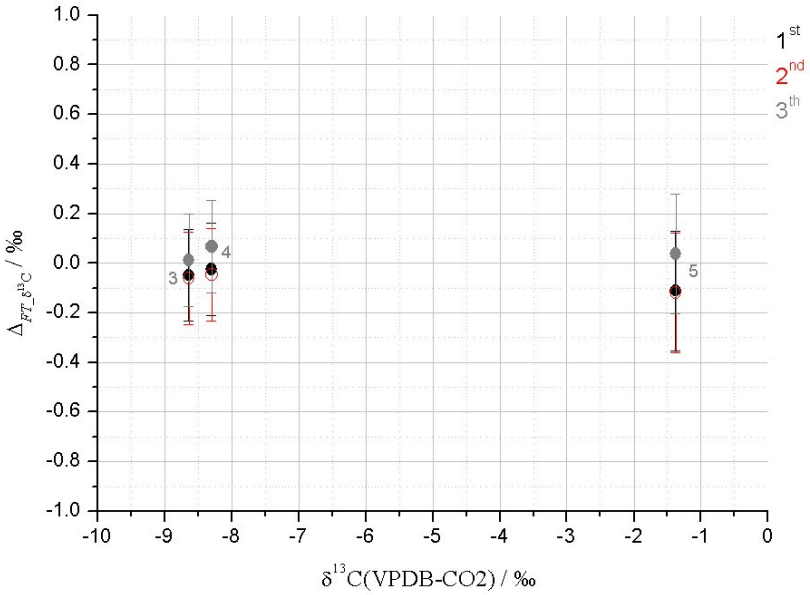

Figure 1. Difference between $\delta^{13}C$ values of the three samples evaluated by FTIR and by IRMS, as measured three times. The error bar represents the expanded uncertainty at a 95% level of confidence.