Geophysical Research Abstracts
Vol. 21, EGU2019-18692, 2019
EGU General Assembly 2019

Carousel Calibration and Sampling System for Isotope Ratio value assignment of pure CO_2 reference gases

Edgar Flores (1), Ian Chubchenko (1), Francesca Rolle (2), Joele Viallon (1), Philippe Moussay (1), and Robert Wielgosz (1)

(1) Bureau International des Poids et Mesures, Sevres, France, (2) Istituto Nazionale di Ricerca Metrologica, Torino, Italy

Measurements of the isotopic composition of CO_2 in air constitute a tool to discriminate man-made emissions from natural contributions. Historically, analytical methods based on mass spectrometry have been used almost exclusively to accurately quantify the isotopic ratios of CO_2 in air sampled in flasks (13C/12C, 18O/16O, and 17O/16O). More recently analyzers based on laser absorption techniques demonstrated interesting performances to perform in situ monitoring of CO_2 isotopic ratios, driving a need for different reference materials, more appropriate for high flow-through measurements in air. The quality infrastructure for these types of measurements is still under development.

This paper describes measurement protocols that can be applied to ensure accurate measurements of the isotopic composition of pure CO_2 samples, expressed as δ13C and δ18O on the VPDB scale with an Isotope Ratio Infrared Spectrometer (IRIS) (in this case a Delta Ray (Thermo Fisher Scientific)). A carousel calibration and sampling system, with a 16 position valve controlled by the instrument user interface Qtegra software, has been developed at the BIPM, including bracketing reference gas inlet and dilution systems to allow rapid and accurate analysis of prepared gas mixtures by Isotope Ratio Infrared Spectroscopy. This has allowed the precise comparison of the predicted and measured isotopic compositions.

The low flow rate control systems in the carousel calibration and sampling system ensure relatively small samples of CO_2 can be accurately characterized. CO_2 samples have been prepared by the accurate blending of different pure CO_2 sources with very different isotopic compositions (-1 ‰ to -45 ‰ δ13C vs VPDB). Cryogenic trapping and transfer to ten 50 mL cylinders have allowed multiple samples to be produced and analyzed by the IRIS system. The target isotopic ratios, 13C/12C and 18O/16O, can be adjusted by accurate flow measurements using molbloc technology, and compared to measured values.

During the presentation the measurement/calibration facilities will be described, together with validations studies (homogeneity, linearity, stability) performed. As well as a demonstration of the accuracy of δ13C and δ18O measurements that can be achieved with Isotope Ratio Infrared Spectroscopy. The system is designed to allow value assignment of pure CO_2 gases either as reference materials for calibration of other instruments or for preparation of samples for comparisons/round-robins.