



Realisation of primary mixtures of CO₂ in air at known isotopic composition

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The monitoring of the increasing levels of CO₂ in atmosphere, together with the discrimination between the natural and anthropogenic sources of CO₂, is of utmost importance to support climate change studies and the reduction of the CO₂ emissions from human activities in the close future. The involvement of the metrological community is essential to achieve the comparability of results over space and time, to assure accuracy and metrological traceability, linking all the individual measurement results to common and stable reference standards.

The availability of sound and affordable reference materials for the measurement of the isotopic composition of CO₂ at ambient amount fraction is foreseen to support the researchers operating in the isotope measurement field, by means of spectroscopic techniques, to assure the metrological traceability for the determination of the isotopic composition of CO₂ in air. Reference gas mixtures at known isotopic composition produced by means of primary methods, such as gravimetry, represent a good opportunity for this purpose.

At INRiM, the Italian National Metrology Institute, the realization of gaseous reference materials of CO₂ in air at known $\delta^{13}\text{C-CO}_2$ started within the European Joint Research Project (JRP) 16ENV06 SIRS, and continued with the JRP 19ENV05 STELLAR.

The reference mixtures are realized by the gravimetric method, following the ISO standard 6142-1, in high-pressure cylinders of aluminum alloy, obtaining low preparation uncertainties of 0.33 % for the CO₂ amount fraction at atmospheric level. These mixtures are prepared from parent mixtures at higher amount fraction, realized at INRiM from different pure CO₂ sources.

Non Dispersive Infrared Spectroscopy (NDIR ABB URAS 14, Switzerland) is used to verify the mixtures for their amount fraction values while Fourier Transform Infrared Spectroscopy (FTIR Thermo Scientific Nicolet iS50, USA) is used for the $\delta^{13}\text{C-CO}_2$ value assignment. The $\delta^{13}\text{C-CO}_2$ values of the gravimetric mixtures span in the range from +1.3 ‰ to -42 ‰.

Recently, a Cavity Ring-Down Spectrometer (CRDS G2131i Picarro, USA) was acquired to double-check the isotopic composition of the prepared mixtures. Preliminary tests were carried out for the metrological characterization of the instrument, followed by the set-up of the analytical methodology for the confirmation of the isotopic composition of some mixtures prepared within the STELLAR project and sent to other project partners for analysis in the past two years. The results of the tests carried out are presented in this work, together with some future perspectives for the realization of primary reference mixtures of CO₂ in air at known isotopic composition on a larger scale.