Cavity ring-down spectroscopy for the certification of the isotopic composition of CO_2 in air CRMs

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Abstract – **Carbon dioxide (CO_2) is the most important long-lived anthropogenic greenhouse gas. Studying the ratio $^{13}C/^{12}C$ of the CO_2 isotopic composition ($\delta^{13}C$-CO_2) in the atmosphere gives useful information for assessing and quantifying the anthropogenic contribution to the continuously growing atmospheric CO_2.**

INRiM, the Italian National Metrology Institute, is deeply involved in supporting the efforts of the metrological community to achieve the comparability of results and to assure accuracy and metrological traceability to CO_2 stable isotope measurement results. In this framework, the realization of gaseous reference materials of CO_2 in air at ambient level and known $\delta^{13}C$-CO_2 represents a fundamental and promising activity. This work describes the preparation of the gas mixtures with $\delta^{13}C$-CO_2 values in the range from +1.3 ‰ to -42 ‰ and the analytical procedure for the value assignment based on Cavity Ring-Down Spectroscopy. Preliminary stability studies are also shown.

I. INTRODUCTION

The characterization of the carbon isotopic composition ($\delta^{13}C$) in a gas mixture of carbon dioxide (CO_2) in air is fundamental in various scientific and environmental applications, including the study of the carbon cycle, the anthropogenic contribution of greenhouse gas emissions and the paleoclimate research [1]. To ensure the validity and comparability of the obtained data, it is essential to establish the metrological traceability of the measurement results to recognized international standards. In the context of $\delta^{13}C$ in CO_2 ($\delta^{13}C$-CO_2), at present, the metrological traceability is an exception in the CIPM MRA, it relies on an unbroken chain of calibrations linking the measurement to the international primary carbon isotope delta scale (VPDB - Vienna Pee Dee Belemnite) [2]. The International Atomic Energy Agency (IAEA) is the custodian of stable isotope ratio measurement scale for carbon. The Max Planck Institute for Biogeochemistry (MPI-BGC) is responsible for the maintenance of the international primary scale Jena reference air set (JRAS-06) which is anchored to the VPDB scale. JRAS reference mixtures of CO_2 in air matrix used for the realization of this scale are characterised by isotope-ratio mass spectrometry (IRMS) [3]. Due to the lack of traceability to SI units and since the values assigned to the primary reference materials are based on consensus values, these materials are not listed as certified reference materials (CRMs) in the Appendix C of the BIPM Database [4]. At present, many National Metrology Institutes (NMIs) equipped with specific instrumentation are working to gain the skills for the production of $\delta^{13}C$-CO_2 RMs traceable to the VPDB scale following the requirements of the International Standard ISO 17034:2016 [5].

INRiM, the Italian National Metrology Institute, is significantly engaged in supporting the metrological community to attain result comparability and guarantee the accuracy and metrological traceability of CO_2 stable isotope measurement outcomes. By the participation in the European EMPIR Projects 16ENV06 SIRS [6] and 19ENV05 STELLAR [7], INRiM developed the experimental set-up and competences for the determination of the isotopic composition (in term of $\delta^{13}C$-CO_2) for the preparation of gas mixtures with $\delta^{13}C$-CO_2 in the range from +1.3 ‰ to -42 ‰ in a synthetic air (SA) matrix. INRiM is currently an official producer of CRMs for the amount fraction of CO_2 in synthetic air and is working to become a producer of candidate CRMs for the isotopic composition of CO_2 in a synthetic air matrix of the

same gas mixtures. In this way, a correct determination of the fraction of anthropogenic emissions of CO_2 in the atmosphere will be enabled for the carbon budget [8]. After the participation in 2024 to the international comparison CCQM-P239 *"CO_2 Isotope Ratios (expressed as $\delta^{13}C$ and $\delta^{18}O$) in Carbon Dioxide in air mixtures"* [9], if successful, the submission of specific Calibration and Measurement Capabilities (CMCs) in the KCDB of BIPM will be the next intended step. The activation of an internationally recognised service available to customers for the distribution of these candidate CRMs for the $\delta^{13}C$-CO_2 will be an outcome.

The present manuscript describes the activity carried out at INRiM for the preparation of reference gas mixtures with atmospheric CO_2 amount fraction and for the analytical procedure based on Cavity Ring-Down Spectroscopy (CRDS) to assign the $\delta^{13}C$-CO_2 value. Moreover, since one of the important steps for CRM development regards the stability assessment, examples of periodical analysis of the gas mixtures are presented.

II. MATERIALS AND METHODS

For the production of gaseous reference materials characterised for the $\delta^{13}C$-CO_2 at INRiM, two pure gas sources of CO_2, having respectively a depleted nominal value of $\delta^{13}C$-CO_2 (-42 ‰) and an enriched nominal value of $\delta^{13}C$-CO_2 (+1.2 ‰) were used. The CO_2 sources were purchased from SIAD (Italy), and the cylinders were filled to 30 bar, to keep the pure CO_2 in gaseous form to reduce possible fractionation inside the 50 L-cylinders. For the preparation of SA matrix, the following pure gases were used: N_2 6.0 (Messer Italia, Italy), Ar 5.0 (Air Liquide Italia, Italy), and O_2 6.0 (Air Liquide Italia, Italy). The CO_2 gas mixtures were prepared in 5 L high-pressure cylinders of aluminium alloy (Luxfer, UK) by gravimetry [10, 11], which is a primary method, following the requirements described in the International Standard ISO 6142-1 [12]. Figure 1 shows the dilution procedure used to reach the atmospheric CO_2 amount fractions (nominal value of 420 μmol/mol) starting from pure gas sources. The dilution process is broken down into several steps because a significant mass of gases needs to be introduced into the cylinders to ensure the weighing system functions accurately. The final gas mixtures can have either the same $\delta^{13}C$-CO_2 value of the pure gas sources or any sought intermediate value. N_2 was used for all dilution steps, while Ar and O_2 were previously mixed and then added in the last dilution step. The amount fraction of Ar in O_2 was calculated to be 4.2 % in such a way that the synthetic air matrix obtained in the final gas mixtures, was similar to the natural one. All the values reported in Figure 1 are nominal.

Some of the prepared gas mixtures, were sampled in 1 L-glass flasks and sent to MPI-BCG for $\delta^{13}C$-CO_2 value assignment by IRMS.

At INRiM, a CRDS spectrometer (model G2131-i,

Picarro, USA) was used to assign the $\delta^{13}C$-CO_2 value to all the prepared gas mixtures at know isotopic composition with atmospheric CO_2 amount fraction. The set-up for the determination of the $\delta^{13}C$-CO_2 value is reported in Figure 2. A calibrated 200 standard cubic centimeters per minute (sccm) Mass Flow Controller (MFC) (MKS Instruments, USA) was set to have an optimised flow from the gas mixtures to the CRDS. A two-way valve allows switching the flow between the $\delta^{13}C$-CO_2 mixture under test and synthetic air without having to disconnect the cylinders. A flow meter located between the MFC and the CRDS inlet enables the flow excess to come out.
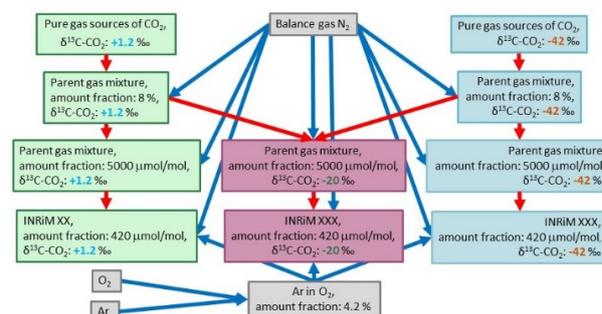

Fig. 1. Scheme of the procedure for the dilution of the pure CO_2 gas sources.

The CRDS was calibrated by means of two gas reference materials and the calibration curve was validated with a control mixture, all reported in the green box of Figure 2. These mixtures were connected to the CRDS using the same inlet of the mixture under test.
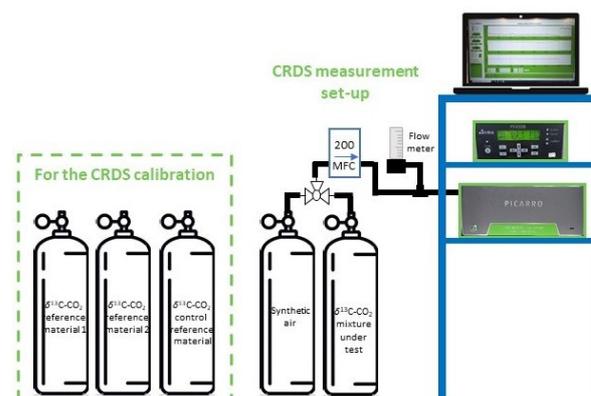

Fig. 2. Scheme of the INRiM set-up for the determination of the $\delta^{13}C$-CO_2 value by CRDS. In the green box the gas mixtures used for the CRDS calibration and validation of the calibration curve are reported.

Since CRDS allows direct measurements of $\delta^{13}C$-CO_2, the measurement procedure consisting of the following steps was established:

- Selection of two reference mixtures with known $\delta^{13}C$ value bracketing the expected $\delta^{13}C$-CO_2 values of the

mixture under test.

- Selection of a control reference mixture to validate the analyzer calibration curve.

- Definition of the analysis sequence of the different gas mixtures under test, using a decreasing order of the nominal δ^{13}C-CO$_2$ values and positioning the reference mixtures at the extremes of the sequence.

- Homogenising the mixtures before the analysis by rolling for at least 15 min.

- Setting a flow of synthetic air for at least 15 min to stabilize the system and remove humidity from the internal lines before starting the sequence.

- Flushing synthetic air for at least 40 s between one measurement and another, ensuring that there is a variation in the signal on the instrument display.

- Performing 3 measurement repetitions for each gas mixture to have multiple measurements and to take into account possible drifts over time.

- Repeating at the end of the sequence the measurement of the first reference mixture to verify by comparison the absence of a drift.

A run of 10 min was set for each mixture in order to obtain a stable signal. The last 100 measurement values (acquired in approximately 2 min) were taken into account and their mean value was calculated.

The calibration approach based on two gas reference materials bracketing the δ^{13}C-CO$_2$ values of the prepared gas mixtures was applied considering that a good linearity of CRDS in the measurement range from +1.2 ‰ to -42 ‰ was observed [13]. The calibration curve was calculated based on a straight-line model (1) using the Weighted Total Least Squares implemented by the INRiM Calibration Curves Computing (CCC) software [14]:

$$y = a + bx \qquad (1)$$

where:
y is the calculated value of δ^{13}C-CO$_2$ (‰) in the mixture;
a is the intercept of the analysis curve;
b is the slope of the analysis curve;
x is the average of CRDS repeated values ($n = 100$).

On the basis of the model equation (1), an analytical δ^{13}C-CO$_2$ value is assigned to each measurement carried out. The final δ^{13}C-CO$_2$ value of a gravimetrically prepared mixture is calculated as the average of the 3 measurement repetitions.

III. RESULTS AND DISCUSSION

Since the stability assessment is a fundamental requirement to be compliant with the International Standard ISO 17034:2016 [5], the CRDS results were also used to carry out preliminary stability studies for the isotopic composition. Figure 3 shows the δ^{13}C-CO$_2$ values obtained over time for 3 mixtures taken as examples to span the range from -42 ‰ to +1.2 ‰ covered by INRiM.

For each mixture, the values obtained by gravimetric preparation, by IRMS at MPI-BGC, and by CRDS are distinguished. The CRDS values show uncertainty values greater than the IRMS ones, due to the intrinsic nature of the instrumentation measurement principle.

a)

b)
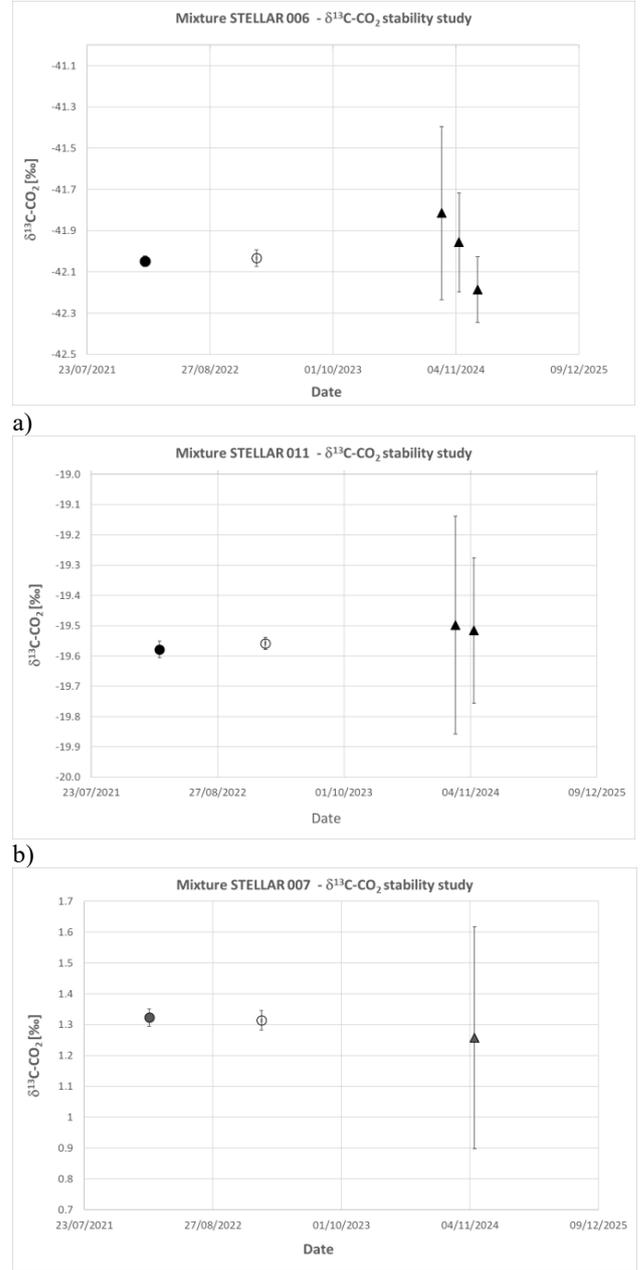
c)

Fig. 3. Stability studies of δ^{13}C-CO$_2$ values: a) Mixture STELLAR 006, b) Mixture STELLAR 011, c) Mixture STELLAR 007. The error bars represent the expanded uncertainty ($k = 2$) associated with the analytical values. ●: gravimetric values; ○: IRMS values; ▲: CRDS values.

13

The results obtained with the different approaches are consistent within their associated uncertainties. This suggests good stability for the 3 mixtures presumably across a longer time. Further measurements with CRDS will be carried out on the mixtures in order to extend the period of their stability and to determine it more accurately.

IV.   CONCLUSIONS

The study addressed the crucial role of CO_2 as the most significant long-lived anthropogenic greenhouse gas and the importance of its $\delta^{13}C$-CO_2 value in quantifying anthropogenic contributions to atmospheric CO_2 increase. INRiM's active involvement in ensuring the comparability and accuracy of CO_2 stable isotope measurements was underscored, with the development of gaseous reference materials in air at ambient level and known $\delta^{13}C$-CO_2 being a key activity. The preliminary stability studies on $\delta^{13}C$-CO_2 values are promising and further work is foreseen to evaluate and determine a suitable stability period for the prepared gas mixtures. The final goal is to complete all the necessary steps for the realization of candidate CRMs characterised for $\delta^{13}C$-CO_2 and, successively, to activate a dissemination service of CRMs characterised both for the amount fraction and for the isotopic composition of CO_2.

V.   ACKNOWLEDGMENT

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