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Cavity ring-down spectroscopy for the certification of the isotopic composition of CO₂ in air CRMs

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Abstract – Carbon dioxide (CO₂) is the most important long-lived anthropogenic greenhouse gas. Studying the ratio ¹³C/¹²C of the CO₂ isotopic composition (δ¹³C-CO₂) in the atmosphere gives useful information for assessing and quantifying the anthropogenic contribution to the continuously growing atmospheric CO₂.

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 CO₂ stable isotope measurement results. In this framework, the realization of gaseous reference materials of CO₂ in air at ambient level and known δ¹³C-CO₂ represents a fundamental and promising activity. This work describes the preparation of the gas mixtures with δ¹³C-CO₂ 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 (δ¹³C) in a gas mixture of carbon dioxide (CO₂) 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 δ¹³C in CO₂ (δ¹³C-CO₂), 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 CO₂ 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 δ¹³C-CO₂ 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 CO₂ 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 δ¹³C-CO₂) for the preparation of gas mixtures with δ¹³C-CO₂ 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 CO₂ in synthetic air and is working to become a producer of candidate CRMs for the isotopic composition of CO₂ in a synthetic air matrix of the

same gas mixtures. In this way, a correct determination of the fraction of anthropogenic emissions of CO₂ in the atmosphere will be enabled for the carbon budget [8]. After the participation in 2024 to the international comparison CCQM-P239 “CO₂ Isotope Ratios (expressed as δ¹³C and δ¹⁸O) 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 δ¹³C-CO₂ will be an outcome.

The present manuscript describes the activity carried out at INRiM for the preparation of reference gas mixtures with atmospheric CO₂ amount fraction and for the analytical procedure based on Cavity Ring-Down Spectroscopy (CRDS) to assign the δ¹³C-CO₂ 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 δ¹³C-CO₂ at INRiM, two pure gas sources of CO₂, having respectively a depleted nominal value of δ¹³C-CO₂ (-42 ‰) and an enriched nominal value of δ¹³C-CO₂ (+1.2 ‰) were used. The CO₂ sources were purchased from SIAD (Italy), and the cylinders were filled to 30 bar, to keep the pure CO₂ in gaseous form to reduce possible fractionation inside the 50 L-cylinders. For the preparation of SA matrix, the following pure gases were used: N₂ 6.0 (Messer Italia, Italy), Ar 5.0 (Air Liquide Italia, Italy), and O₂ 6.0 (Air Liquide Italia, Italy). The CO₂ 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 CO₂ 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 δ¹³C-CO₂ value of the pure gas sources or any sought intermediate value. N₂ was used for all dilution steps, while Ar and O₂ were previously mixed and then added in the last dilution step. The amount fraction of Ar in O₂ 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 δ¹³C-CO₂ value assignment by IRMS.

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

Picarro, USA) was used to assign the δ¹³C-CO₂ value to all the prepared gas mixtures at known isotopic composition with atmospheric CO₂ amount fraction. The set-up for the determination of the δ¹³C-CO₂ 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 δ¹³C-CO₂ 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.

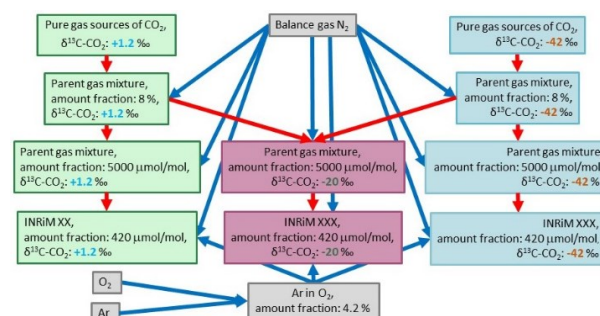


Fig. 1. Scheme of the procedure for the dilution of the pure CO₂ gas sources.

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.

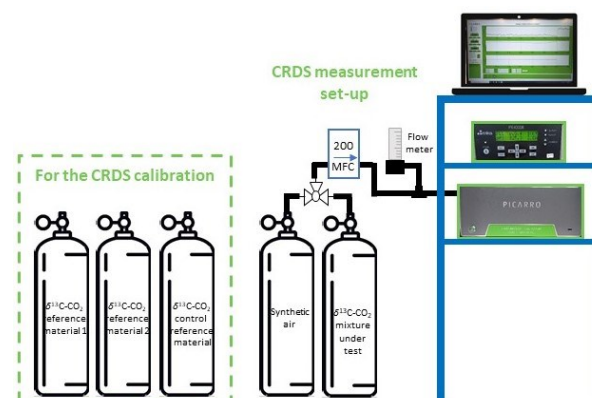


Fig. 2. Scheme of the INRiM set-up for the determination of the δ¹³C-CO₂ value by CRDS. In the green box the gas mixtures used for the CRDS calibration and validation of the calibration curve are reported.

Since CRDS allows direct measurements of δ¹³C-CO₂, the measurement procedure consisting of the following steps was established:

- Selection of two reference mixtures with known δ¹³C value bracketing the expected δ¹³C-CO₂ 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 $\delta^{13}\text{C-CO}_2$ 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 $\delta^{13}\text{C-CO}_2$ 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]:

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

where:

- y is the calculated value of $\delta^{13}\text{C-CO}_2$ (‰) 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 $\delta^{13}\text{C-CO}_2$ value is assigned to each measurement carried out. The final $\delta^{13}\text{C-CO}_2$ 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 $\delta^{13}\text{C-CO}_2$ 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.

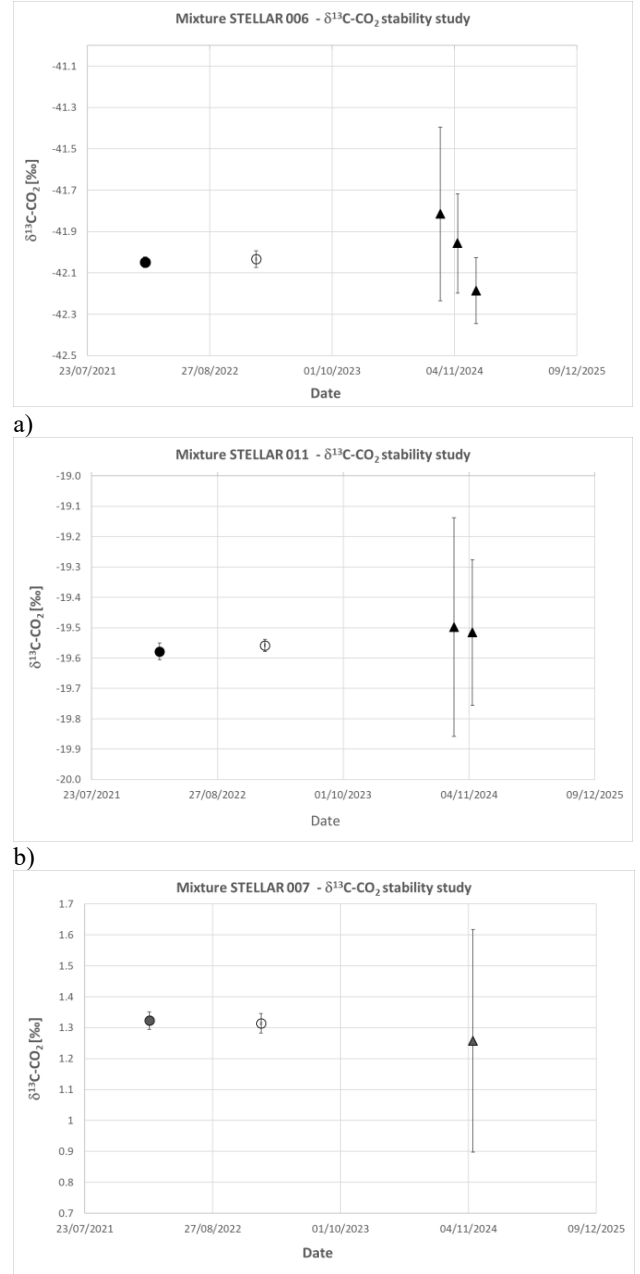


Fig. 3. Stability studies of $\delta^{13}\text{C-CO}_2$ values: a) Mixture STELLAR 006, b) Mixture STELLAR 011, c) Mixture STELLAR 007. The error bars represent the expanded uncertainty ($k = 2$) associated with the analytical values. ●: gravimetric values; ○: IRMS values; ▲: CRDS values.

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 CO₂ as the most significant long-lived anthropogenic greenhouse gas and the importance of its $\delta^{13}\text{C}$ -CO₂ value in quantifying anthropogenic contributions to atmospheric CO₂ increase. INRiM's active involvement in ensuring the comparability and accuracy of CO₂ stable isotope measurements was underscored, with the development of gaseous reference materials in air at ambient level and known $\delta^{13}\text{C}$ -CO₂ being a key activity. The preliminary stability studies on $\delta^{13}\text{C}$ -CO₂ 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 $\delta^{13}\text{C}$ -CO₂ and, successively, to activate a dissemination service of CRMs characterised both for the amount fraction and for the isotopic composition of CO₂.

V. ACKNOWLEDGMENT

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VI. CITATIONS AND REFERENCES

- [1] Global Monitoring Laboratory, Carbon Cycle Greenhouse Gases, Trends in CO₂, <https://gml.noaa.gov/ccgg/trends>.
- [2] F. Camin, D. Besic, P. J. Brewer, C. E. Allison, T. B. Coplen, P. J. H. Dunn, M. Gehre, M. Gröning, H. A. J. Meijer, J.-F. Hélie, P. Iacumin, R. Kraft, B. Krajnc, S. Kümmel, S. Lee, J. Meija, Z. Mester, J. Mohn, H. Moossen, H. Qi, G. Skrzypek, P. Sperlich, J. Viallon, L. I. Wassenaar, R. I. Wielgosz "Stable Isotope Reference Materials and Scale Definitions—Outcomes of the 2024 IAEA Experts Meeting", Rapid Communications in Mass Spectrometry, vol.39, No.14, 2025. <https://doi.org/10.1002/rcm.10018>
- [3] M. Wendeberg, J.M. Richter, M. Rothe, W.A. Brand, "Jena reference air set (JRAS): a multi-point scale anchor for isotope measurements of CO₂ in air", Atmos Meas Tech. (2013), 6(3):817–822, doi:10.5194/amt-6-817-2013.
- [4] "Decision CIPM/104–26, Traceability Exception: Delta Value Isotope Ratio Measurements," CIPM (2015), <https://www.bipm.org/documents/20126/48101963/Traceability-Exception-QM1>.
- [5] ISO, "General Requirements for the Competence of Reference Material Producers (ISO 17034:2016)," International Organization for Standardization, (2016):1–24.
- [6] <https://projectsites.vtt.fi/sites/SIRS/>
- [7] <http://empir.npl.co.uk/stellarproject/>
- [8] M. Zimnoch, J. Necki, L. Chmura, A. Jasek, D. Jelen, M. Galkowski, T. Kuc, Z. Gorczyca, J. Bartyzel, K. Rozanski, Quantification of carbon dioxide and methane emissions in urban areas: source apportionment based on atmospheric observations, Mitigation and Adaptation Strategies for Global Change, vol. 24, pp. 1051–1071, 2019.
- [9] F. Rolle, F. Durbiano, S. Pavarelli, F. R. Pennechi, M. Sega, Pilot study CCQM-P239 "CO₂ Isotope Ratios (expressed as $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$) in Carbon Dioxide in air mixtures" - INRiM Report, 31, 2024.
- [10] F. Rolle, F. Durbiano, S. Pavarelli, F. R. Pennechi, M. Sega, Comparison of gravimetry and dynamic dilution for the generation of reference gas mixtures of CO₂ at atmospheric amount fraction, Measurement: Sensors 30 (2023) 100937. <https://doi.org/10.1016/j.measen.2023.100937>
- [11] F. Durbiano, F.R. Pennechi, F. Rolle, S. Pavarelli, M. Sega, Stability study and uncertainty evaluation of CO₂ materials for greenhouse gases monitoring, Measurement 232 (2024) 114653. <https://doi.org/10.1016/j.measurement.2024.114653>
- [12] ISO 6142: International Standard ISO 6142-1:2015, Gas analysis - Preparation of calibration gas mixtures - Part 1: Gravimetric method for Class I mixtures, International Standard Organization, Geneva (Switzerland).
- [13] M. Sega, F. Durbiano, S. Pavarelli, F. R. Pennechi, F. Rolle, Comparison of cavity ring-down spectroscopy and Fourier transform infrared spectroscopy for the isotopic composition determination of CRMs of CO₂ in air, Proceedings of the International Metrology Congress CIM 11-14 March 2025, Lyon France.
- [14] CCC Software: <https://www.inrim.it/en/services/software-and-databases/ccc-software>