2025 IMEKO Joint Conference
TC8 - TC11 - TC25
Torino, Italy, September 14-17, 2025

Metrological traceability paths for stable isotope measurements of CO_2 in air

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***Abstract* – Measurements of carbon stable isotopes ^{13}C and ^{12}C and of their ratio $^{13}C/^{12}C$ in atmospheric carbon dioxide ($\delta^{13}C$-CO_2) are indicators of the anthropogenic contribution to CO_2 emissions. At present, $\delta^{13}C$-CO_2 falls within the CIPM MRA traceability exception. Gaseous Certified Reference Materials (CRMs) are needed as proper references to support the scientific community dealing with $\delta^{13}C$-CO_2 in atmospheric measurements. The paper presents an approach to assign $\delta^{13}C$-CO_2 values to CO_2 gas mixtures at atmospheric amount fraction following two independent traceability paths, leading to candidate CRMs with established metrological traceability to the Vienna Pee Dee Belemnite scale, which represents an international recognized primary scale in this framework. INRiM is working towards the attainment of internationally recognized Calibration and Measurement Capabilities in the CIPM MRA framework for the production of such CRMs, which represents a fundamental step to meet the increasing demand of proper references for stable carbon isotopes measurements in atmosphere.**

I. INTRODUCTION

Measurements of carbon stable isotopes ^{13}C and ^{12}C and of their ratio $^{13}C/^{12}C$ ($\delta^{13}C$) in atmospheric carbon dioxide ($\delta^{13}C$-CO_2), are indicators of the anthropogenic contribution to CO_2 emissions. These measurements provide useful data to monitor the anthropogenic CO_2 impact on climate change. Indeed, the carbon isotopic composition of atmospheric CO_2 has substantially changed compared to the pre-industrial era mainly due to human activities which influence the natural carbon cycle [1]. As a result, while the atmospheric CO_2 concentration is continuously raising [2], the value of $\delta^{13}C$-CO_2 decreases [3]. In order to ensure the reliability of CO_2 amount fraction and $\delta^{13}C$-CO_2 measurement results, they have to be traceable to internationally recognized references, which enable data comparability in time and space. However, delta value isotope ratio measurements that cannot be traceable to SI fall in a traceability exception of the CIPM Mutual Recognition Arrangement (CIPM MRA) and should be made traceable to materials recognised as International Standards [4]. Since at present, values assigned to these materials are based on consensus values, these materials are not listed in the Appendix C of the BIPM Database [5]. Concerning $\delta^{13}C$ in CO_2, its metrological traceability relies on an unbroken chain of calibrations linking the measurement results to the international primary carbon isotope delta scale, namely the Vienna Pee Dee Belemnite (VPDB) [6]. The International Atomic Energy Agency (IAEA) is recognized as the custodian of stable isotope ratio measurement scales for light elements, including carbon. The VPDB isotope reference defines the zero point of the carbon stable isotope scale describing the relative abundance of ^{13}C and ^{12}C. At present, the standard and associated VPDB scale for $\delta^{13}C_{VPDB}$ in CO_2 are artefact-based and rely on the CO_2 production from carbonate material through its reaction with (over)saturated phosphoric acid. They are used to transfer the scale to CO_2 in air measurements. The Max Planck Institute for Biogeochemistry (MPI-BGC), in its capacity as World Metrological Organization (WMO) Central Calibration Laboratory, developed the Jena reference air set (JRAS) which is anchored to the VPDB scale [7]. However, the use of this method is limited to specialized laboratories and gaseous Certified Reference Materials (CRMs) are needed to meet increasing demand. Recently, another carbon isotope delta scale, the VPDB-LSVEC (LSVEC – lithium carbonate prepared by H. J. Svec), was accepted as another international primary scale by the scientific community expert on the subject of stable isotopes [6]. VPDB-LSVEC is also an artefact-based scale and, as carbon isotope delta values reported on the VPDB and VPDB-LSVEC scales can differ, conversion models between the two scales can be established and used but they will introduce additional uncertainty contribution.

At INRiM, following the participation in the European Joint Research Projects EMPIR 16ENV06 SIRS [8] and EMPIR 19ENV05 STELLAR [9], and in compliance with the prescriptions of the relevant ISO standard [10], gravimetric mixtures of CO_2 at atmospheric amount fraction in air, considered as candidate CRMs for isotopic composition, are under development [11,12]. They are based on two different traceability paths, both linked to the VPDB scale. The first path relies on pure CO_2 sources having different $\delta^{13}C\text{-}CO_2$ values considered as references, which are diluted to ambient amount fraction to produce the candidate CRMs. The second one starts from certified reference mixtures, which are employed to calibrate a cavity ring-down spectrometer (CRDS) used to assign the isotopic values to the same candidate CRMs. This work presents the two traceability paths and their application to three case studies at different $\delta^{13}C\text{-}CO_2$ values.

II. MATERIALS AND METHODS

In the presented approach, the production of CO_2 mixtures at ambient amount fraction in synthetic air (SA) with known $\delta^{13}C\text{-}CO_2$ value started from two pure gas sources of CO_2, one having a depleted value and the other having an enriched value of $\delta^{13}C\text{-}CO_2$ (SIAD, Italy). Aliquots of the pure CO_2 sources were sampled in 1 L-gas flasks and sent to MPI-BGC for the value assignment by IRMS on the VPDB scale. Blending the two pure CO_2 sources allowed to obtain also a third intermediate $\delta^{13}C\text{-}CO_2$ value.

The pure CO_2 sources were diluted in subsequent steps by applying the gravimetric method [13]. The dilution was carried out using pure gases, i.e. nitrogen (N_2) 6.0 (Air Liquide Italia, Italy), argon (Ar) 7.0 (Linde, Germany), and oxygen (O_2) 6.0 (Air Liquide Italia, Italy), to obtain 3 mixtures of CO_2 at ambient amount fraction in SA, INRiM A, INRiM B, and INRiM C, at different $\delta^{13}C\text{-}CO_2$ values. The mixtures were prepared in 5 L high-pressure cylinders of aluminium alloy (Luxfer, UK).

The gravimetrically prepared mixtures underwent an analytical verification by CRDS (CRDS G2131-i, Picarro, USA). This step allowed to determine an analytical $\delta^{13}C\text{-}CO_2$ value linked to VPDB by an independent traceability path. The CRDS was indeed calibrated by means of CO_2 gas standards in SA previously prepared by gravimetry from different pure CO_2 sources, having $\delta^{13}C\text{-}CO_2$ values assigned via IRMS at MPI-BGC on the JRAS-06 scale.

The entire process is depicted in Figure 1. Details on the various steps are reported in the sub-sections below.

Table 1 summarises the characteristics of the candidate CRMs to be produced following the described procedure.

Table 1. Characteristics of the candidate CRMs of CO_2 in SA at atmospheric amount fraction with known $\delta^{13}C\text{-}CO_2$ values.

Mixture code	Nominal CO_2 amount fraction, µmol/mol	Nominal $\delta^{13}C\text{-}CO_2$ value, ‰
INRiM A	410	+1.2
INRiM B	410	-42
INRiM C	410	-21

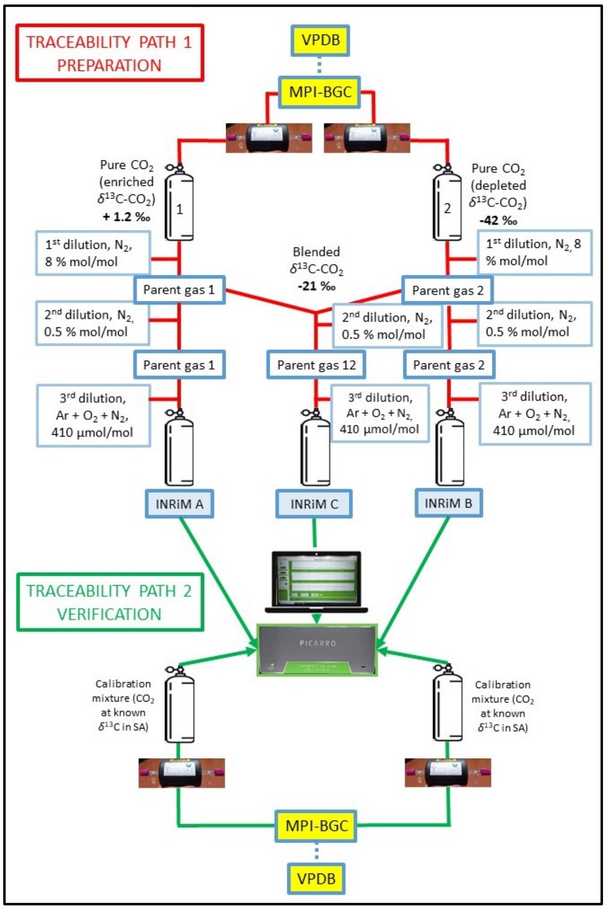

Fig. 1. Schematic of the production process of candidate CRMs of CO_2 in SA at atmospheric amount fraction with known $\delta^{13}C\text{-}CO_2$ values.

III. METROLOGICAL TRACEABILITY PATH 1 – GRAVIMETRIC PREPARATION

The gravimetric preparation of CO_2 mixtures in SA at ambient amount fractions starting from pure gases cannot be carried out in a single step, as illustrated in Figure 1. This is due to the fact that the mass of gases to be introduced into the cylinders must be high enough to guarantee a good performance of the weighing system. The gravimetric dilution has the great advantage that it allows to obtain final mixtures with the same δ^{13}C-CO_2 value of the pure source CO_2.

Each of the two pure gas sources of CO_2 was diluted in N_2 6.0 to prepare a first parent mixture having CO_2 nominal amount fraction of 8 % mol/mol; a second parent mixture was then prepared to reach a CO_2 nominal amount fraction of 0.5 % mol/mol.

The mixtures having nominal CO_2 amount fraction of 410 µmol/mol in SA were then prepared by adding proper masses of Ar 7.0, O_2 6.0 and N_2 6.0. Two mixtures, namely INRiM A at about +1.2 ‰ and INRiM B at about -42 ‰, were obtained. A third mixture, INRiM C, was prepared by blending the two CO_2 sources, targeting an intermediate δ^{13}C-CO_2 value of about -21 ‰. To optimise the performance of INRiM gravimetric facility and of its mass comparator, the dilution process did not start from the two pure CO_2, but aliquots of the two parent mixtures of CO_2 in N_2 at 8 % mol/mol were mixed gravimetrically. Two subsequent dilutions were needed to obtain the final INRiM C mixture of CO_2 at atmospheric amount fraction.

IV. METROLOGICAL TRACEABILITY PATH 2 – ANALYTICAL VERIFICATION

The gravimetrically prepared mixtures were verified by CRDS. This analyser allowed the direct measurement of δ^{13}C-CO_2, and was calibrated with two gas standards bracketing the δ^{13}C-CO_2 values of the prepared gas mixtures.

To calibrate the CRDS, its analysis curve was determined by fitting the straight-line model (1) by applying the Weighted Total Least Squares implemented by the INRiM Calibration Curves Computing (CCC) software [14]:

$$y = a + bx \tag{1}$$

where:

y is the calculated value of δ^{13}C-CO_2 in ‰ in the mixture under verification;

a is the intercept of the analysis curve;

b is the slope of the analysis curve;

x is the average of repeated readings ($n = 100$) of the CRDS analyser.

The analysis curve was then used to assign an analytical δ^{13}C-CO_2 value to each gravimetrically prepared mixture.

V. COMPARISON BETWEEN THE TWO PATHS

The procedure described above allows to assign δ^{13}C-CO_2 values to gravimetric prepared mixtures of CO_2 in SA by means of two independent techniques having different traceability chains. Usually, path 2 gives a measurement uncertainty associated with the δ^{13}C-CO_2 value higher than the gravimetric one, as the analytical steps add additional uncertainty sources. However, the possibility of having two independent values is a strong advantage as the analytical result allows also to verify the goodness of the gravimetric preparation. For this purpose, the two values are compared by calculating the normalized error, E_n, defined in Eq. 2:

$$E_{\mathrm{n}} = \frac{y_{\mathrm{grav}} - y_{\mathrm{CRDS}}}{2\sqrt{u_{\mathrm{grav}}^2 + u_{\mathrm{CRDS}}^2}} \tag{2}$$

where:

y_{grav} is the δ^{13}C-CO_2 in ‰ obtained by gravimetry;

y_{CRDS} is the δ^{13}C-CO_2 in ‰ obtained by CRDS analysis;

u_{grav} is the standard uncertainty associated with y_{grav};

u_{CRDS} is the standard uncertainty associated with y_{CRDS}.

If the criterion of Eq. 3 is met

$$-1 \leq E_{\mathrm{n}} \leq 1 \tag{3}$$

the gravimetric value is confirmed, the entire process is demonstrated to be under control and the candidate CRM can be considered valid.

The analytical procedure associated with path 2 can also be used as standalone to directly assign the δ^{13}C-CO_2 value by CRDS to CO_2 mixtures prepared by means of a less accurate process with respect to gravimetry or produced by external laboratories. The resulting mixture will not be a CRM, but a calibrated gas mixture, accompanied by a calibration certificate.

VI. CONCLUSIONS

At present, $\delta^{13}C_{\mathrm{VPDB}}$ measurements represent a traceability exception of the CIPM MRA. Gaseous CRMs are needed as proper and more easily accessible references to support the scientific community dealing with CO_2 stable isotopes in air and δ^{13}C-CO_2 in atmospheric CO_2 measurements. The paper presents an approach to assign δ^{13}C-CO_2 values to gas mixtures of CO_2 in SA at atmospheric amount fraction following two independent traceability paths, thus leading to candidate CRMs with established metrological traceability to VPDB scale. INRiM is working towards the attainment of internationally recognized Calibration and Measurement Capabilities (CMCs) in the CIPM MRA framework for the production of such CRMs. This represents a fundamental step to meet the increasing demand for proper references for stable carbon isotopes in atmosphere.

Acknowledgements

Part of this work has been funded by the Italian Ministry of University and Research (MUR) in the framework of the project “METRO-INN – National Infrastructure for the quality of measurements for sustainable innovation”, under the Fund for the enhancing of public investments and national development (Law n. 160/2019).

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