Comparison of cavity ring-down spectroscopy and Fourier transform infrared spectroscopy for the isotopic composition determination of CRMs of CO2 in air

Original
Comparison of cavity ring-down spectroscopy and Fourier transform infrared spectroscopy for the isotopic composition determination of CRMs of CO2 in air / Sega, Michela; Durbiano, Francesca; Pavarelli, Stefano; Pennecchi, Francesca Romana; Rolle, Francesca. - In: EPJ WEB OF CONFERENCES. - ISSN 2100-014X. - 323:(2025), p. 09002. (22nd International Metrology Congress (CIM2025)) [10.1051/epjconf/202532309002].
Availability:
This version is available at: 11696/88619 since: 2026-02-28T09:50:43Z

Publisher:
E D P SCIENCES

Published
DOI:10.1051/epjconf/202532309002

EPJ Web of Conferences **323**, 09002 (2025) https://doi.org/10.1051/epjconf/202532309002
22nd International Metrology Congress

Comparison of cavity ring-down spectroscopy and Fourier transform infrared spectroscopy for the isotopic composition determination of CRMs of CO_2 in air

Michela Sega [1]*, *Francesca* Durbiano[1], *Stefano* Pavarelli[1], *Francesca Romana* Pennecchi[1], and *Francesca* Rolle[1]

[1]INRiM – Istituto Nazionale di Ricerca Metrologica, Applied Metrology and Engineering Division, 10135 Strada delle Cacce 91, Torino, Italy

Abstract. Gaseous Certified Reference Materials (CRMs) characterised for the isotopic composition of carbon dioxide (CO_2) in air at ambient amount fraction are crucial for understanding the anthropogenic contribution to climate change. At INRiM, the Italian National Metrology Institute, the realization of gaseous mixtures, which are candidate CRMs of CO_2 in air at ambient level and known isotopic composition, is ongoing. Fourier transform infrared spectroscopy (FTIR) and cavity ring-down spectroscopy (CRDS) are used to verify the mixtures for their isotopic composition, in terms of $\delta^{13}C$-CO_2 in the range from +1.3 ‰ VPDB to -42 ‰ VPDB. In this work, a comparison between the performances of the two analytical techniques FTIR and CRDS used at INRiM to assign the isotopic composition to the prepared candidate CRMs is presented.

1 Introduction

The past ten years, from 2015 to 2024, have been the warmest years in the 175-year observational record. World Meteorological Organization (WMO) and the international scientific community are actively considering several approaches to enable a prompt reporting on the exceedance of global temperature levels. One of these consists in estimating the warming that results from historical changes in key human drivers of the climate system such as greenhouse gases (GHGs) [1]. GHGs reached record observed levels in 2023 and real time data indicate that they continued to rise in 2024. Carbon dioxide (CO_2) is the most important anthropogenic GHG driving climate change. Its concentration has reached the current level of 420.0 ppm ± 0.2 ppm, which represents an increase of 51 % with respect to the concentration of the preindustrial era (around 278 ppm in 1750) [1]. The annual mean CO_2 value in the global surface atmosphere increased by 2.3 ppm from 2022 to 2023, thus marking the twelfth consecutive year with an increase greater than 2 ppm, which continues an already significant trend. The increase in atmospheric CO_2 is directly related to the amount of carbon emissions from fossil fuels, as it represents the net result of total carbon emissions surpassing total ocean and terrestrial biosphere carbon sinks. GHGs monitoring has to be carried out in a proper way, in order to obtain significant measurements and an objective quantification of emissions and removals, to support effective emissions reduction policies. These measurements must be precise and the instruments performing them well-calibrated, because the information about emissions resides in small gradients in space and time relative to a common global background. A fundamental aspect is also to track progress on climate action, sustaining these measurements over decades. [2]. Sound and affordable certified reference gas mixtures characterised for the isotopic composition of CO_2 in air at ambient amount fraction are requested to support the study of the anthropogenic contribution to climate change. Such mixtures, namely Certified Reference Materials (CRMs), are useful in the isotope measurement field, in particular for the spectroscopic techniques. On a broader scale, sound metrological references are fundamental to support the efforts ongoing in the metrological community to achieve the comparability of results and to assure accuracy and metrological traceability to the isotopic measurements of CO_2.

At INRiM, the Italian National Metrology Institute, the realization of CRMs of CO_2 in air at ambient level and known isotopic composition is ongoing starting from the activities carried out within the European Joint Research Projects (JRPs) 16ENV06 SIRS [3] and 19ENV05 STELLAR [4]. CRMs for the CO_2 amount fraction at atmospheric level in synthetic air are realised by the gravimetric method following the ISO standard 6142-1 [5], in high-pressure cylinders of aluminium alloy, achieving preparation uncertainties of 0.33 %. These mixtures are realised from parent mixtures at higher amount fraction, obtained from different pure CO_2 sources. Fourier transform infrared spectroscopy (FTIR) is used to verify the mixtures for their isotopic composition and assign their $\delta^{13}C$-CO_2 value. More recently, a second analytical technique was chosen for

---

* Corresponding author: m.sega@inrim.it

the assignment of the $\delta^{13}C\text{-}CO_2$ values of the gravimetric mixtures, namely cavity ring-down spectroscopy (CRDS). The $\delta^{13}C\text{-}CO_2$ values of the mixtures span in the range from +1.3 ‰ to -42 ‰ VPDB.

In this work, a comparison between the performances of the two analytical instruments, a FTIR and a CRDS spectrometer, in assigning the isotopic composition to the prepared mixtures is presented, focusing on the more depleted $\delta^{13}C\text{-}CO_2$ values from -20 ‰ VPDB to -42 ‰ VPDB. An accurate instrument calibration is mandatory to obtain reliable results from the spectroscopic measurements of isotopic composition, and to carry out stability studies of the reference mixtures over time.

2 Materials and methods

A set of gas mixtures of CO_2 at atmospheric amount fraction in a matrix of synthetic air was gravimetrically prepared at INRiM starting from the following pure gases: CO_2 at +1.3 ‰ VPDB and -42 ‰ VPDB (99.998, SIAD, Italy), oxygen (99.9999, Air Liquide, Italy), argon (99.99999, LINDE, Germany), nitrogen (99.9999, Air Liquide, Italy). For the high precision weighing, the INRiM gravimetric facility is equipped with a mass comparator (PR 10003, Mettler Toledo, Switzerland), having a measurement range of [0.001–10010] g. The mixtures were prepared in cylinders of aluminum alloy (Luxfer, USA) with internal volume of 5 L, filled to a final pressure of 100 bar. After the preparation, the CO_2 amount fraction of each mixture was verified by means of a NDIR photometer (URAS 14, ABB, Switzerland), having a CO_2 measurement range of [0–1000] $\mu mol \cdot mol^{-1}$. Table 1 reports the characteristics of the mixtures, including the nominal $\delta^{13}C\text{-}CO_2$ value assigned on the basis of the information given by the CO_2 supplier.

Table 1. Characteristics of INRiM gas mixtures of CO_2 in synthetic air.

Mixture code	**CO_2 amount fraction $\mu mol \cdot mol^{-1}$**	**$U(CO_2)$ $\mu mol \cdot mol^{-1}$ ($k = 2$)**	**Nominal $\delta^{13}C\text{-}CO_2$ ‰ VPDB**
SIRS 010 (D580461)	390.04	0.40	-20
STELLAR 022 (15914)	404.72	0.40	-42
STELLAR 006 (12997)	409.46	0.40	-42

The mixtures were analysed by both FTIR and CRDS to verify their isotopic composition and assign the $\delta^{13}C\text{-}CO_2$ value. The two analytical techniques require different types of calibrations carried out by means of CO_2 in air reference gas mixtures with known CO_2 amount fraction and $\delta^{13}C\text{-}CO_2$ value. The approach used for FTIR consists of using reference gas standards having $\delta^{13}C\text{-}CO_2$ values similar to the mixture to be characterised and different CO_2 amount fractions bracketing the CO_2 nominal amount fraction of the mixture to be analysed. In CRDS, the reference standards have CO_2 amount fractions similar to the mixture to be characterised and different $\delta^{13}C\text{-}CO_2$ values bracketing the nominal $\delta^{13}C\text{-}CO_2$ value of the mixture to be analysed. In order to obtain the traceability to the VPDB scale [6], all the mixtures used in the present work were sampled in glass flasks and sent to the Max Planck Institute for Biogeochemistry (MPI-BGC) for the isotopic value assignment by isotope ratio mass spectrometry (IRMS).

2.1 FTIR analysis

A FTIR spectrometer (Nicolet iS50 Thermo Scientific, USA) equipped with a 2 m path length gas cell (Thermo Scientific, USA) and a MCT detector was used to analyse the CO_2 mixtures. A schematic picture of the measurement setup is reported in Figure 1.

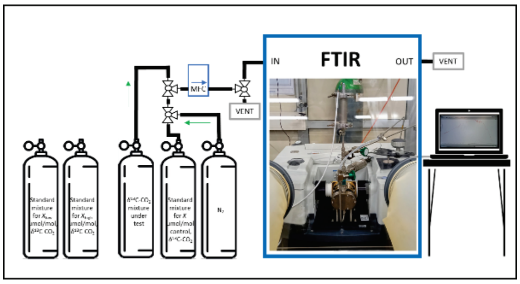


Fig. 1. Schematic of the FTIR measurement setup.

To calibrate the FTIR, two reference mixtures bracketing the CO_2 amount fraction values of the mixtures to be analysed were chosen and used as measurement standards. Moreover, an additional mixture was used as a control mixture to validate the calibration. For the acquisition and fitting of the FTIR spectra, the radiative transfer calculation code named MALT (Multiple Atmospheric Layer Transmission, University of Wollongong, Australia) was employed [7]. MALT uses the HITRAN database spectral lines to generate synthetic infrared spectra of gas phase mixtures. The software B-FOS developed at the Bureau International des Poids et Mesures (BIPM) has been used to interface MALT and the software of the FTIR (Thermo Fisher Scientific Omnic®).

The calibration approach, adapted from the BIPM procedure [8], is based on the use of two CO_2 standard mixtures of different amount fraction but similar isotopic values. The standards were analysed at the beginning and at the end of the analytical sequence in order to account for possible measurement drifts. The mixtures under investigation were analysed in between the two standards and in increasing CO_2 amount fraction value order. The analysis function was calculated according to the model equation (1), by using the

Calibration Curves Computing (CCC) software, developed at INRiM [9]:

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

where:
y is the calculated value of $\delta^{13}C\text{-}CO_2$ (‰) in the mixture;
a is the intercept of the analysis curve;
b is the slope of the analysis curve;
x is the average of repeated FTIR spectra ($n = 6$).

2.2 CRDS analysis

A CRDS spectrometer (G2131*i*, Picarro, USA) was used to analyse the CO_2 mixtures. A schematic picture of the measurement setup is reported in Figure 2.

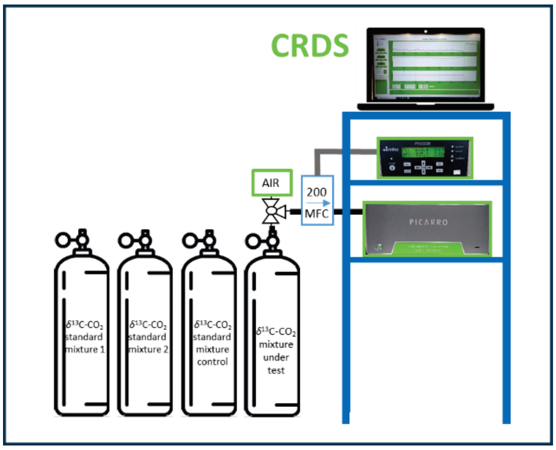


Fig. 2. Schematic of the CRDS measurement setup.

To calibrate the CRDS, two reference mixtures bracketing the $\delta^{13}C\text{-}CO_2$ values of the mixtures to be analysed were chosen and used as measurement standards. Moreover, an additional mixture was used as a control mixture to validate the CRDS calibration. The standard mixtures were analysed at the beginning and at the end of the analytical sequence in order to account for possible measurement drifts. The mixtures under investigation were analysed in between the two standards and in decreasing $\delta^{13}C\text{-}CO_2$ value order. The analysis function was calculated according to the model equation (1), where x is the average of repeated readings ($n = 100$) of the CRDS analyser. The final delta value was calculated as the average of three single measurement values x_i.

3 Results and discussion

Table 2 reports the $\delta^{13}C\text{-}CO_2$ values obtained for each mixture with the different techniques.

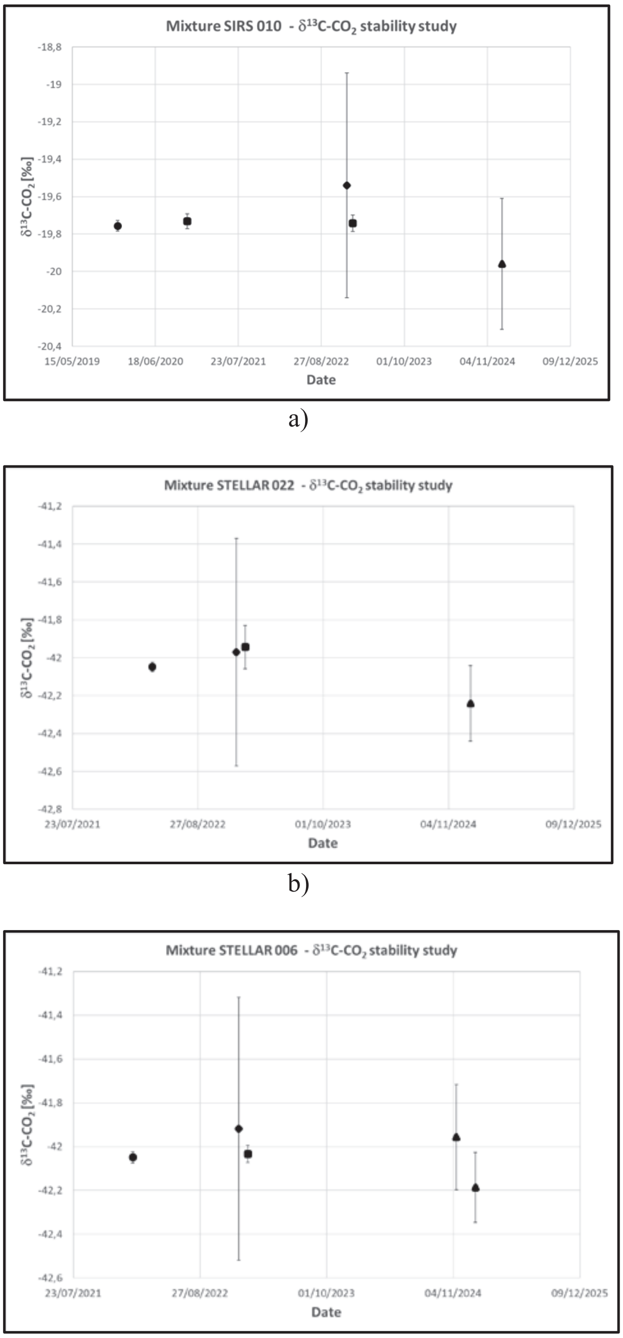
Table 2. $\delta^{13}C\text{-}CO_2$ values expressed in ‰ VPDB obtained by IRMS, FTIR and CRDS with the associated expanded uncertainty ($k = 2$).

Mixture code	**IRMS ‰ VPDB**	**FTIR ‰ VPDB**	**CRDS ‰ VPDB**
SIRS 010 (D580461)	-19.74 ± 0.04	-19.54 ± 0.60	-19.96 ± 0.35
STELLAR 022 (15914)	-41.94 ± 0.12	-41.87 ± 0.30	-42.24 ± 0.20
STELLAR 006 (12997)	-42.03 ± 0.04	-41.92 ± 0.30	-42.19 ± 0.16

The data presented in Table 2 for each mixture are compatible within the associated uncertainties. The spectroscopic measurements have uncertainty values greater than the IRMS, sometimes also by an order of magnitude. Such results are due to the intrinsic nature of the spectroscopic measurement principle.

The expanded uncertainty value associated with the IRMS data was evaluated by INRiM on the basis of the MPI-BGC measurement results, taking into account both the maximum uncertainty value for the single analysis and the standard deviation of the analyses carried out on the same mixture (different sample flasks). The FTIR uncertainty associated with the $\delta^{13}C\text{-}CO_2$ measurements takes into account several contributions, e.g. the stability of the FTIR, the HITRAN uncertainty for the CO_2 line parameters and the uncertainty of the regression algorithm, based on classical least squares (CLS), used by MALT. As for CRDS, the uncertainty takes into account the uncertainty of the standards, the instrument repeatability and the scattering among the three different measurement runs. Research activities are currently ongoing at INRiM to improve the measurement repeatability, in particular for CRDS, in order to obtain better estimation of the $\delta^{13}C\text{-}CO_2$ values and lower associated uncertainties.

In order to evaluate their stability in terms of $\delta^{13}C\text{-}CO_2$ values, additional CRDS measurements have been carried out on the mixtures which can be considered as candidate CRMs in accordance with the International Standard ISO 17034 [10]. Figure 3 reports the preliminary data.



a)

b)

c)

Fig. 3. Stability studies of δ^{13}C-CO$_2$ values: a) mixture SIRS 010; b) mixture STELLAR 022; c) mixture STELLAR 006. The error bars represent the expanded uncertainties (k = 2) associated with the analytical values. ●: gravimetric values; ♦: FTIR values; ■: IRMS values; ▲: CRDS values.

The stability study is essential to go towards the production of CRMs of CO$_2$ in air characterised for the isotopic values. Although different techniques show different uncertainty values, the data reported in Figure 3 are in agreement within their expanded uncertainties, thus confirming a good stability of the three mixtures, even for a 5-year period (Figure 3 a).

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).

4 Conclusions

The presented results show a good comparability of FTIR and CRDS for the assignment of δ^{13}C-CO$_2$ values to the mixtures gravimetrically prepared at INRiM. In addition, they are promising in terms of the stability of the mixtures for δ^{13}C-CO$_2$ values. Due to this premise, further activities are foreseen for extensive stability studies in the whole δ^{13}C-CO$_2$ range in order to obtain the international recognition of Calibration and Measurement Capabilities for the production of CO$_2$ in synthetic air CRMs characterised for both CO$_2$ amount fraction and isotopic composition. Starting from the work carried out in the H2020 INFRAIA project “Metrology for Integrated Marine Management and Knowledge-Transfer Network – MINKE” [11], future developments are foreseen also in the application of isotopic measurements to the marine field, for the determination of the stable carbon isotopic content of seawater dissolved inorganic carbon (DI^{13}C).

References

1. World Meteorological Organization (WMO), State of the Climate 2024 - Update for COP29, WMO, 2024, https://library.wmo.int/idurl/4/69075
2. World Meteorological Organization (WMO), WMO Greenhouse Gas Bulletin No. 20 – 28 October 2024 The State of Greenhouse Gases in the Atmosphere Based on Global Observations through 2023, WMO, 2024 https://library.wmo.int/idurl/4/69057
3. https://www.euramet.org/research-innovation/search-research-projects/details/project/metrology-for-stable-isotope-reference-standards
4. https://empir.npl.co.uk/stellarproject/
5. International Standard ISO 6142-1:2015, Gas analysis — Preparation of calibration gas mixtures. Part 1: Gravimetric method for Class I mixtures, ISO, Geneva
6. H. Qi, H. Moossen, H.A.J. Meijer, et al, USGS44, a new high-purity calcium carbonate reference material for δ^{13}C measurements, Rapid. Commun. Mass Sp. **35**, e9006 (2021), https://doi.org/10.1002/rcm.9006
7. F. Rolle, M. Sega, Use of FTIR spectroscopy for the measurement of CO$_2$ carbon stable isotope ratios, in Proceedings of the 19th International Congress of Metrology, Paris, France, 24-26 September (2019), 05002, doi.org/10.1051/metrology/201905002
8. E. Flores, J. Viallon, P. Moussay, D. W. T Griffith, R. I. Wielgosz, Calibration Strategies for FT-IR and Other Isotope Ratio Infrared Spectrometer Instruments for Accurate δ^{13}C and δ^{18}O Measurements of CO$_2$ in Air, Anal. Chem., **89**, 3648 (2017).

https://doi.org/10.1021/acs.analchem.6b05063

9. CCC Software: https://www.inrim.it/en/services/software-and-databases/ccc-software
10. International Standard ISO 17034:2016, General requirements for the competence of reference material producers, ISO, Geneva
11. https://minke.eu/