

ISTITUTO NAZIONALE DI RICERCA METROLOGICA  
Repository Istituzionale

An optimized sampling system for highly reproducible isotope ratio measurements (  $^{13}\text{C}$  and  $^{18}\text{O}$ ) of pure  $\text{CO}_2$  gas by infrared spectroscopy

This is the author's submitted version of the contribution published as:

*Original*

An optimized sampling system for highly reproducible isotope ratio measurements (  $^{13}\text{C}$  and  $^{18}\text{O}$ ) of pure  $\text{CO}_2$  gas by infrared spectroscopy / Viallon, Joële; Flores, Edgar; Moussay, Philippe; Chubchenko, Ian; Rolle, Francesca; Zhang, Tiqiang; Mussell Webber, Eric B; Wielgosz, Robert I. - In: METROLOGIA. - ISSN 0026-1394. - 57:5(2020), p. 055004.

*Availability:*

This version is available at: 11696/64270 since: 2021-01-07T10:20:19Z

*Publisher:*

IOP

*Published*

DOI:10.1088/1681-7575/ab948c

*Terms of use:*

Visibile a tutti

This article is made available under terms and conditions as specified in the corresponding bibliographic description in the repository

*Publisher copyright*

Institute of Physics Publishing Ltd (IOP)

IOP Publishing Ltd is not responsible for any errors or omissions in this version of the manuscript or any version derived from it. The Version of Record is available online at DOI indicated above

(Article begins on next page)

**An optimized sampling system for highly reproducible isotope ratio measurements ( $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$ ) of pure  $\text{CO}_2$  gas by infrared spectroscopy**

**Joële Viallon<sup>1</sup>, Edgar Flores<sup>1</sup>, Philippe Moussay<sup>1</sup>, Ian Chubchenko<sup>2</sup>, Francesca Rolle<sup>3</sup>,  
Tiqiang Zhang<sup>4</sup>, Eric B. Mussell Webber<sup>5</sup> and Robert I. Wielgosz<sup>1</sup>**

<sup>1</sup>Bureau International des Poids et Mesures (BIPM), Sèvres, France

<sup>2</sup>D.I.Mendeleev Institute for Metrology (VNIIM), 19 Moskovsky pr., St. Petersburg, 190005 Russia.

<sup>3</sup>Istituto Nazionale di Ricerca Metrologica (INRIM), Strada delle Cacce 91, I-10135, Torino, Italy

<sup>4</sup>National Institute of Metrology (NIM), China, No.18, Bei-San-Huan Dong Str., Beijing 100013, China.

<sup>5</sup>National Physical Laboratory (NPL), Hampton Road, Teddington, Middx, TW11 0LW, UK

Correspondence to: J. Viallon ([jviallon@bipm.org](mailto:jviallon@bipm.org))

**Abstract**

The characteristics of an optimized sampling system for measurements of isotope ratios in pure  $\text{CO}_2$  gas with Isotope Ratio Infrared Spectroscopy measurement systems that has achieved reproducible measurement of  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  values with 0.02 ‰ reproducibility (1  $\sigma$ ) is described. The key elements of the sampling system revolve around almost identical treatment of sample and reference gases allowing two-point calibration of up to 14 samples, and appropriate flushing protocols to remove any biases from memory effects of previously sampled gases. Measurements are performed by the Isotope Ratio Infrared Spectroscopy system at a mole fraction of nominally 700  $\mu\text{mol/mol}$   $\text{CO}_2$  in air, by dilution of pure  $\text{CO}_2$  gas controlled by individual low-flow mass flow controllers (0.07 ml/min), and with a feedback loop to control mole fractions to ensure that differences between references and sample gas mole fraction stay below 2  $\mu\text{mol/mol}$ . This level of control is necessary to prevent biases in measured isotope ratios, the magnitude of which has also been studied with a sensitivity study. The system has been validated using pure  $\text{CO}_2$  samples which range in  $\delta^{13}\text{C}$  delta values of  $-1$  ‰ and  $-45$  ‰ vs VPDB- $\text{CO}_2$ , and in all cases measurement reproducibility over several days of testing of 0.02‰ or better (1  $\sigma$ ) was achieved for both  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$ , with negligible memory effects. The amount

of sample gas used for each measurement was less than 5 ml of CO<sub>2</sub> at (RTP), making the system easily deployable for isotope ratio value assignment of bulk CO<sub>2</sub> gas, and adaptable to atmospheric mole fractions of CO<sub>2</sub> in air, and for value assignments of standards. Using the sampling system described the measurement reproducibility of current Isotope Ratio Infrared Spectroscopy systems approaches measurement reproducibility that can be achieved with some IRMS systems.

## 1 Introduction and aims

The measurement of stable isotopes of carbon provides a powerful analytical tool being applied in many scientific and technological application fields, including geological applications, food and product authenticity, clinical diagnosis, atmospheric monitoring and sports drug testing to name a few. Historically this has predominantly been performed by mass spectrometry (IRMS – Isotope Ratio Mass Spectrometry). Whilst the compound in which the carbon isotope ratios is to be determined is often a complex organic, the actual molecule analysed is CO<sub>2</sub>, and any compound analysed must be converted to CO<sub>2</sub> for stable isotope ratio measurements, with a variety of preparation techniques described for example by Coleman[1]. To express the result of carbon isotope ratio analysis on the internationally agreed scale VPDB (Vienna Pee Dee Belemnite), laboratories must perform the measurements relative to certified isotope reference materials (iRMs). A possible calibration hierarchy to conventional international standards, following IUPAC recommendations[2], for measurements of CO<sub>2</sub> gas with an Isotope Ratio Infrared Spectroscopy (IRIS) system is depicted in Figure 1. This scheme corresponds to a currently available traceability chain including standards recommended by the provider of the Delta Ray analyser. It ensures an unbroken chain of calibrations, though the resulting combined standard uncertainty based on currently available reference materials, is potentially too large for certain requirements in the field, in particular for monitoring isotopic ratios of CO<sub>2</sub> in ambient air. End users of IRIS only need gaseous CO<sub>2</sub> with a certified isotope ratio, provided it was value assigned on the VPDB scale by a reference laboratory. The reference laboratory can either value assign CO<sub>2</sub> working standards by IRMS relatively to CO<sub>2</sub> evolved from a carbonate reference material such as the most recent IAEA-603[3], or relatively to other CO<sub>2</sub> isotope reference materials such as the series of glass ampoules manufactured by the National Institute of Standards and Technology (NIST) in the 1990's (RM8562, 8563 and 8564) [4], suitable for IRMS instruments but not directly for IRIS in view of the small amount of gas available.

CO<sub>2</sub> gas isotope reference materials are critical and they were developed as early as the 1980's to serve various scientific applications, with NBS-16 and NBS-17 developed by the United States Geological Survey (USGS), but quickly exhausted[5]. The series of three glass ampoules developed by NIST followed in the 1990's, with their value assignment performed by an ensemble of 13 expert laboratories[4]. Those iRMs are still used, as reported for example in a recent publication by Srivastava *et al.*[6], which also contains an explanation of the difference between VPDB and VPDB-CO<sub>2</sub>. There are currently several efforts worldwide e.g. EURAMET EMPIR JRP 16ENV06 "SIRS" [7] to use pure CO<sub>2</sub> to develop gravimetrically based iRMs of CO<sub>2</sub> in CO<sub>2</sub>-free dry air in high pressure gas cylinders at desired abundance levels and isotopic composition values. The goal is to calibrate isotope ratio measurements performed in the atmosphere, which is one of the most challenging applications, with compatibility goal as low as 0.01 ‰ for δ<sup>13</sup>C-CO<sub>2</sub> being set by experts to allow meaningful observations[8].

This level of agreement between laboratories is very challenging to achieve, as has been observed, for example, in the comparison exercise organised in 2002 by the Institute for Reference Materials and Measurements (IRMM) of the European Commission, with the code IMEP-8[9]. It included 27 participants in Europe from various application fields (geochemistry, atmospheric and food chemistry), who received two samples of pure CO<sub>2</sub> each to measure. In this study, after removal of two obvious outliers, results agreed within 1 ‰ for δ<sup>13</sup>C, and within 2 ‰ for δ<sup>18</sup>O (after correction of a bias in the calculation algorithm employed by half of the participants). Improved inter-laboratory compatibility was achieved during a comparison organised in 2003 by the National Institute for Environmental Studies (NIES) for atmospheric science expert laboratories, with samples distributed for measurement having two different isotope ratios (NARCIS-I and II)[10]. The comparison involved 20 laboratories, which achieved agreement at 0.1 ‰ for δ<sup>13</sup>C. This is slightly better than observed during the last round-robin on air samples organised by the National Oceanic and Atmospheric Administration (NOAA), in which the standard deviation of results reported by 14 laboratories was 0.15 ‰ for δ<sup>13</sup>C-CO<sub>2</sub>.

As mentioned in the report of the 19<sup>th</sup> WMO/IAEA Meeting on Carbon Dioxide, Other Greenhouse Gases and Related Measurement Techniques (GGMT-2017), laboratories are still encouraged to take part in comparisons and to investigate possibilities for improving their compatibility[11].

In recent years, significant progress has been made with techniques based on infrared light absorption and performances approaching those of IRMS were observed, in particular on air samples with precisions of  $\pm(0.02 \text{ to } 0.25)\text{‰}$  for  $\delta^{13}\text{C}$  and  $\pm(0.02 \text{ to } 2.0)\text{‰}$  for  $\delta^{18}\text{O}$  [12-14]. These instruments are of great interest for field measurements as they can directly sample air, avoiding the use of canisters and subsequent cryo-trapping of  $\text{CO}_2$  from air for IRMS analysis. More recently a few groups have started to use IRIS instruments on other types of geological samples with some success, for example by Sakai et al. [15] who developed a preparation system to evolve  $\text{CO}_2$  from carbonates and obtained a repeatability of 0.1 ‰ for  $\delta^{13}\text{C}$  measurements. A similar instrument was used by the BIPM to perform isotope ratio measurements and was first applied to correct  $\text{CO}_2$  mole fractions measurements performed by Fourier Transform Infrared spectroscopy (FTIR) during the international comparison CCQM-K120[16, 17].

In a global effort to improve the measurements and standards for isotope ratios of  $\text{CO}_2$ , the BIPM and the International Atomic Energy Agency (IAEA) are proposing to coordinate an international comparison of isotope ratio measurements in samples of pure  $\text{CO}_2$  gas (name CCQM-P204). The BIPM has the task of preparing the comparison samples, and the IAEA of assigning their isotopic composition on reference scales using an IRMS with an optimised precision, reaching a combined standard uncertainty of 0.01 ‰ on the  $\delta^{13}\text{C}$  value of the reference material IAEA-603 [3]. The BIPM exploits a preparation facility (not described in this paper) based on blending of pure  $\text{CO}_2$  sources of very different isotopic compositions, followed by cryogenic trapping and transfer to ten 50 mL cylinders. To perform validation studies on samples prepared with this blending system, the BIPM chose to optimise an IRIS analyser, in order to introduce redundancy by the use of different techniques and also to contribute to the development of spectroscopic techniques for isotope ratio measurements. A carousel sampling system with bracketing reference gases calibration and dilution system has been designed to allow rapid and accurate analysis of prepared gas mixtures by IRIS. The values reported in the paper are expressed on the VPDB- $\text{CO}_2$  scale, through measurements on standards performed at the Max Planck Institute for Biogeochemistry (MPI-BGC, Jena), where the scale is realized via JRAS-06 standards (Jena Reference Air Set-2006)[18]. The calibration hierarchy employed in the paper, will not provide accuracy of measurements at the precision levels achieved. This is due to the uncertainties in  $\text{CO}_2$  in air samples employed, as well as type B uncertainties arising from the process of transfer values from  $\text{CO}_2$  in air to pure  $\text{CO}_2$  samples. These uncertainty

components have been estimated to be at the  $\pm 0.3$  ‰ and  $\pm 0.8$  ‰ level for  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  values respectively. Results presented here demonstrate the improved repeatability of measurements, and a full uncertainty budget will be developed after a calibration hierarchy shorter than depicted in Figure 1 is implemented, with samples of the isotopic reference gases analysed by IRMS calibrated with IAEA-603, which is expected to lead to much improved accuracy of the measurement system.

This paper is focused on the setup of the Carousel sampling system (section 2) and the measurement process and data post-processing developed to optimize the reproducibility of measurements (sections 3 and 4). During the development, the dependence of isotope ratios measured by IRIS on the  $\text{CO}_2$  mole fraction in the instrument gas cell was found to be critical, and this is reported in section 5. Finally, the reproducibility of the system is demonstrated in section 6 with series of measurements spanning the range of isotope ratio which could be obtained with the blending system.

## 2 Measurement setup

The full measurement setup, displayed in Figure 2, includes the source gases, a sampling system, and the IRIS analyzer. The sampling system was developed at the BIPM to allow automated sampling of up to fourteen pure  $\text{CO}_2$  samples, while respecting the principle of identical treatment of the sample and the reference gases as much as possible [19].

### 2.1 Gases

Two pure  $\text{CO}_2$  reference gases were used to calibrate the measurements, chosen to span a large range of the  $^{13}\text{C}$  isotopic ratio. The values of the isotopic ratios in both of them were estimated from IRMS measurements performed by MPI-BGC on  $\text{CO}_2$  in air mixtures which had been prepared by the National Physical Laboratory (NPL) using the same  $\text{CO}_2$  pure gases, and taken from the two cylinders described here. Expanded uncertainties were provided by MPI-BGC at 90% level of confidence. Because of potential issues with cylinders containing liquid  $\text{CO}_2$  as well as the unknown biases introduced by mixing  $\text{CO}_2$  with  $\text{CO}_2$ -free air, the values and uncertainties taken from MPI-BGC constitute a temporary solution and are not intended for accurate value assignment. The two reference gases are named REF1 and REF2 and their characteristics are displayed in Table 1, together with other cylinders connected to the

system. Drifts in the values of REF 1 and REF2, cannot be discounted due to isotopic fractionation effects that occur between CO<sub>2</sub> in liquid and in vapour phase[20], with the size of the effect moderated by the size of the CO<sub>2</sub> reservoir and depletion rate. Whilst a drift in values in REF1 and REF2 was not observed on the timescale of the work described here, at the level of precision of measurements made, it has been reported at longer time scales[21], and recommendations developed to use gas cylinders filled below 40 bar to avoid gas/liquid mixtures which can cause shifts in the delta values due to fractionation effects. The use of stable reference gases and application of a calibration hierarchy as in Figure 1, will allow these effects to be quantified in future work.

SMP was used to denote the sample gas used to obtain the results reported in this study. It was chosen so that its <sup>13</sup>C isotopic ratio would be in the calibration range defined by the two references. Its isotopic composition was measured by the IRIS analyzer, as reported later. As this gas was used to estimate the reproducibility of the system, the calibration uncertainty is not relevant and therefore not reported. The sample was normally connected to one port of the 16 positions valve as displayed in Figure 2.

Air (AIR) was used as the carrier gas to dilute the reference and sample gases, so as to obtain the optimal mole fraction of CO<sub>2</sub> in the gas cell of the IRIS analyser.

CREF1 and CREF2 were used to denote two mixtures of CO<sub>2</sub> in air with known mole fractions required by the IRIS analyser during the starting phase (GET READY process further described in section 3). The values of the CO<sub>2</sub> mole fraction was measured by the NIST for previous work[12]. They were kept connected to the dedicated ports of the analyser, although they were only required to be used infrequently as described later.

Other sample gases analysed during this work were generated on site with the preparation facility, which allows filling up to ten aliquots of 50 mL at a pressure of 2 bar with the same gas. The aliquots are made in 316 stainless steel and closed by ball valves (further changed to bellow valves after measurements reported in this paper). No nominal value of the isotope ratio is provided for gases generated with this facility because the traceability has not yet been validated.

## 2.2 Sampling

The sampling system described in this study was designed to fulfil the requirement of identical treatment of the sample and the reference gases as much as possible, while allowing automated sampling of a minimum of fourteen pure CO<sub>2</sub> samples. The Delta Ray analyser is meant to measure CO<sub>2</sub> in air samples, and it is equipped with two sampling ports: sample A port for pressurised flows of dry air, externally controlled in flow rate around 90 mL min<sup>-1</sup>, and sample B port to analyse ambient air. Inside the analyser, there is a vent after sample A port, while there is a Nafion dryer after sample B port. To analyse CO<sub>2</sub> samples, the manufacturer recommend the use of a separate dilution box (named XPand) in which the gas flows through different capillaries connected to sample A port (to make use of the vent). This box was tested previously and found unsuitable for our needs. It was replaced with the system described in Figure 2, in which the sample and reference gases are diluted with a carrier gas and a vent introduced just before the analyser to allow flushing of tubing just after MPV-4 between two measurements of different gases (references and sample). After the vent, the flow of CO<sub>2</sub>/air is similar to what would be used for measurements of samples of dry ambient air and it was connected to sample B port, which is the default port the analyser always returns to when a measurement sequence is completed. This avoids sampling room air which could introduce moisture inside the tubing. In addition, the Nafion dryer was by-passed as all samples were already dry.

For an automated sampling of up to 14 samples (for comparison purposes), a VICI 16-position dead-end valve (MPV-16) with a micro electric actuator was chosen. Of the 16 available ports, one was connected to a dry nitrogen cylinder at a delivery pressure of 2 bar, which was used outside of measurement periods to prevent contamination of the lines by room air. A second port was connected to a diaphragm vacuum pump (Vacuubrand MV 2) that allowed pressure reduction in the lines down to  $0.5 \times 10^{-3}$  bar when needed. The output of the valve was also connected to the pump via a two-position valve (MPV-2) with pneumatic actuator, in order to evacuate all 16 ports after connection of the samples.

Mass flow controllers (Bronkhorst, MFC1, 2 and 3) were used to control the flow rate of the sample, reference 1 and reference 2 gases accordingly. They allowed flows to be controlled from 0.06 ml/min to 0.7 ml/min with an accuracy of  $\pm 0.5$  % of reading plus  $\pm 0.1$  % of full scale. A



VICI 4-position flow through valve (MPV-4) allowed switching between sample, reference 1 and reference 2. All exit ports of the valve were connected to the exhaust in order to let all three gases to flow at the same rate during the analysis, either to the analyser or the exhaust.

After MPV-4 the pure CO<sub>2</sub> gas was diluted by the carrier gas (AIR). The air flow rate was controlled by a Red-y (Vögtlin) mass flow controller (MFC-4) at a nominal rate of 95 mL min<sup>-1</sup>. The flow of CO<sub>2</sub> in air was connected with a tee to the analyser port B and to an exhaust to evacuate the excess of gas not being used by the analyser.

All lines were made of 1/16 inches tubing in 316 stainless steel coated with SilcoNert 2000®. Valves and pressure reducers were in 316 stainless steel.

With this system, the path of samples and reference gases is identical from MPV-4 up to the analyser gas cell. Results presented in this paper do not reveal observable impact of the path difference introduced before MPV-4.

### 2.3 Analyser

The analyzer was an Isotope Ratio mid-Infrared Spectrometer with the trade name of Delta Ray (Thermo Fisher Scientific, Bremen, Germany), first described by Van Geldern et al.[22] and already used in a previous work on calibration strategies for measurements of the isotopic ratios in CO<sub>2</sub> in air [12]. Its measurement principle relies on a simple direct absorption of the mid-infrared laser light (nominal wavelength 4.3 μm) by the CO<sub>2</sub> molecules in the gas flowing inside the gas cell at a controlled pressure of 100 hPa. The laser is rapidly scanned over a narrow absorption region in which the three major isotopologues of CO<sub>2</sub> display absorption lines. The Delta Ray uses four absorption lines around 4.3 μm: one absorption line of <sup>12</sup>C<sup>18</sup>O<sup>16</sup>O, one of <sup>13</sup>C<sup>16</sup>O<sub>2</sub> and a strong as well as a weak absorption line of <sup>12</sup>C<sup>16</sup>O<sub>2</sub>. This choice between those two is made according to the mole fraction of CO<sub>2</sub> in the instrument's gas cell. For the measurements reported here the weak absorption line was selected, as the mole fraction of CO<sub>2</sub> was kept at sufficiently high level (700 μmol mol<sup>-1</sup>). A polynomial fit is implemented in the instrument control programme (Qtegra) to determine the peak areas for each absorption line. From the ratios of the peak areas obtained with the sample ( $R_S^{13}$ ) and reference gases ( $R_{\text{VPDB-CO}_2}^{13}$ ), the software calculates the isotopic ratios in the sample and expresses the result in terms of the relative difference from the reference. The reference gases are expected to be two

Reference Materials with two different certified isotope ratios expressed on the conventional scale VPDB-CO<sub>2</sub>. The isotope ratios of the sample on the same scale are then calculated according to the following equations (from now on, the subscript VPDB-CO<sub>2</sub> for δ<sup>13</sup>C and δ<sup>18</sup>O will be omitted in a simplified notation):

$$\delta^{13}\text{C} = \left( \frac{R_S^{13}}{R_{\text{VPDB-CO}_2}^{13}} - 1 \right) \quad (1)$$

$$\delta^{18}\text{O} = \left( \frac{R_S^{18}}{R_{\text{VPDB-CO}_2}^{18}} - 1 \right) \quad (2)$$

Where  $R_S^{13}$  (respectively  $R_{\text{VPDB-CO}_2}^{13}$ ) is the ratio of <sup>13</sup>C to <sup>12</sup>C in the sample (respectively in the reference gas), and  $R_S^{18}$  (respectively  $R_{\text{VPDB-CO}_2}^{18}$ ) is the ratio of <sup>18</sup>O to <sup>16</sup>O in the sample (respectively in the reference gas). Each isotopic ratio is estimated from the ratio of the relevant peak areas: <sup>13</sup>C<sup>16</sup>O<sub>2</sub> to <sup>12</sup>C<sup>16</sup>O<sub>2</sub> for  $R^{13}$ , and <sup>12</sup>C<sup>18</sup>O<sup>16</sup>O to <sup>12</sup>C<sup>16</sup>O<sub>2</sub> for  $R^{18}$ .

The control software allows users to implement their specific measurement sequence including one or more Reference Material(s). The typical measurement sequence used in this work is described in the following section.

### 3 Measurement process

The measurement sequence described in this section included a series of actions which were all electronically controlled by the IRIS analyser control programme Qtegra. This choice was imposed by the operating principle of Qtegra. It includes a number of features described in details by Braden-Behrens et al.[13], starting with the measurement of the mole fraction dependency during a process called GET READY, and followed by calibration of the mole fraction with the two mole fraction reference gases and the calibration of the delta values with the two delta reference gases during the acquisition of data. The process GET READY was performed with the analyzer several months before this study and was not repeated after this. The features of GET READY were replaced with a control of the mole fraction (described in section 4) and a two-point calibration with drift correction of delta values described below. While the effectiveness of both choices is demonstrated in this paper, this does not mean that similar results cannot be obtained with the default GET READY process.

The measurement sequence always started with evacuating the ports of the 16 position valve by pumping the lines via the 2 position valve. Then the ports were flushed with the sample gas

and evacuated again. This flushing, repeated three times, allowed preparation of the tubing from the sample ports to MPV-2. It was followed by the successive flushing of the sample as well as references lines, from MPV-2 for the sample and from the pressure reducers for the references, up to the IRIS analyser. This was done during 1 minute for each port of the MPV-16 and the two references and repeated 6 times, with the corresponding mass flow controllers set at their maximum flow rate ( $0.6 \text{ mL min}^{-1}$ ). The mole fraction is seen to stabilise rapidly after multiple flushing cycles.

In a second phase, the samples were analysed successively in between the reference gases, following the scheme REF2-REF1-Sample 1-REF2-REF1-Sample 2, noting that each individual gas analysis included a first period of 5 minutes of flushing of tubing after MPV-4 at high flow rate, inducing a high mole fraction, close to  $6000 \mu\text{mol mol}^{-1}$ . This was then followed by the acquisition of the signal at a mole fraction close to  $700 \mu\text{mol mol}^{-1}$  obtained by reducing the flow rate to  $0.07 \text{ mL min}^{-1}$  during another 5 minutes. This acquisition time was driven by an Allan variance analysis, which had demonstrated that Allan deviations smaller than 0.02 ‰ could be obtained on both  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  for this averaging time. The value of the  $\text{CO}_2$  mole fraction after dilution was also chosen based on Allan variance measurements performed at  $380 \mu\text{mol mol}^{-1}$  and  $700 \mu\text{mol mol}^{-1}$ , resulting in Allan variances of 0.014 ‰ for the later instead of 0.02 ‰ for the former (both for five minutes averaging time).

Measurement sequences were implemented via the Delta Ray control programme Qtegra. The (uncalibrated) concentration of  $\text{CO}_2$  inside the analyser gas cell during a typical sequence is displayed in Figure 3, showing the switch between flushing and recording periods.

#### **4 Post-processing of data**

Qtegra aims at calculating calibrated values of  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  from the absorption peaks of the relevant isotopologues as described in section 2.3, providing that values of the references traceable to VPDB- $\text{CO}_2$  are entered in the software and identified as “standards”. An example of a data file is displayed in Table 2 for  $\delta^{13}\text{C}$  values only. The same calculations were performed on  $\delta^{18}\text{O}$ . For this work Qtegra was instructed to calculate values calibrated with reference 1 only (identified as “STANDARD”), using the first value of a measurement sequence (parameter “bracketing” off, “pre-referencing” on, and “linearity” off). The values obtained by Qtegra were

further processed to correct for drifts and calibrate with the two references. The steps are the following:

- 1) The measured delta values for the references were linearly interpolated in between two measurements at the time of the sample measurement :

$$\delta_{REFi,int} = \delta_{REFi,1} + \frac{k}{3}(\delta_{REFi,2} - \delta_{REFi,1})$$

Where  $k$  equals 1 for REF1 and 2 for REF2 to account for the order of measurements (REF2–REF1–Sample 1–REF2–REF1)

- 2) The slope  $a$  and intercept  $b$  of the (assumed) linear relationship between the references nominal values ( $\delta^{13}\text{C}_{\text{VPDB-CO}_2} = -1.384 \text{ ‰}$  for REF1 and  $\delta^{13}\text{C}_{\text{VPDB-CO}_2} = -42.131 \text{ ‰}$  for REF2) and interpolated values were calculated;
- 3) The sample values were deduced from the measured values  $\delta^{13}\text{C}_m$  and the parameters of the linear regression:  $\delta^{13}\text{C} = (\delta_m^{13} - b)/a$

All isotope ratios reported below are the result of this drift correction and two-point calibration.

## 5 Dependence of delta values on the CO<sub>2</sub> mole fraction

Several groups have reported on the dependency of isotope ratio values measured by IRIS analyzers on the CO<sub>2</sub> mole fractions inside the instrument gas cell, as summarized by Griffith[23]. This effect was also observed in previous work with the instrument used in this study and applied to measurements of CO<sub>2</sub> in air samples[12]. This observation, among others, motivated the proposal of a specific calibration scheme for measurements in air. This same instrument was also studied in detail by Braden-Behrens et al.[13], including the observation of isotope ratios measured with CO<sub>2</sub> in air mole fractions covering a range from 400 μmol mol<sup>-1</sup> to 1600 μmol mol<sup>-1</sup>. The authors noted that the  $\delta^{13}\text{C}$  value of their sample was modified in a non-linear way by as much as 1 ‰ over that range. They explained how to derive a correction function, and how this function is being used by Qtegra to correct raw values (by GET READY process). As mentioned earlier, this feature was not used in this study. The post-calibration explained in the previous section ensured the correction of biases due to possible variations of the CO<sub>2</sub> mole fraction inside the gas cell, after the dilution step.

More importantly for this work, it was observed that this mole fraction dependency had an impact on the repeatability of the measurements, when the CO<sub>2</sub> mole fraction obtained with the sample gas did not match those of the reference gases. This effect was further studied as reported below, and further minimized with the implementation of a feedback loop to ensure minimum variations in the CO<sub>2</sub> mole fractions throughout the measurement cycle.

The sample gas used to demonstrate the mole fraction dependence was a 50 L cylinder of pure CO<sub>2</sub> (99.999%) from Air Liquide with similar characteristics as REF1 gas. The exact value of the isotope ratio on the VPDB-CO<sub>2</sub> scale is not provided here as measurements were performed relatively. The two mass flow controllers on the reference gases lines (MFC2 and MFC3) were set to deliver the same flow rate, and the CO<sub>2</sub> mole fraction in the analyzer cell was around 730 μmol mol<sup>-1</sup>, with no more than 2 μmol mol<sup>-1</sup> difference between the two reference gases. The reference gases dilution factor was kept constant, and the sample gas dilution was varied in between each measurement to span a mole fraction range of ± 74 μmol mol<sup>-1</sup> around the reference gas mole fraction. The isotope ratios were calculated as described previously, using the drift correction and two-point calibration. Results are displayed in Figure 4, and plotted in terms of the difference in ‰ between the measured isotope ratio and its average value when the CO<sub>2</sub> mole fraction was exactly matched, both for δ<sup>13</sup>C (top plot) and δ<sup>18</sup>O (bottom plot).

The dependency of the isotope ratio on the CO<sub>2</sub> mole fraction difference was clearly observed, and followed an almost linear behavior with a negative slope of -0.0033 ‰/(μmol mol<sup>-1</sup>) for δ<sup>13</sup>C and -0.0045 ‰/(μmol mol<sup>-1</sup>) for δ<sup>18</sup>O, demonstrating, for example, that if the sample mole fraction was higher than that of the references, the sample would appear more depleted in <sup>13</sup>C and <sup>18</sup>O. This observation is consistent with the study of Braden-Behrens, who reported a decrease in the raw isotope ratio measured by the analyser when the CO<sub>2</sub> mole fraction increased from 400 μmol mol<sup>-1</sup> to 1500 μmol mol<sup>-1</sup> [13]. In order to overcome this source of potential measurement bias, a feedback loop was implemented in a Labview®-based control programme. This programme reads the mole fraction of the main isotopologue as provided by Qtegra in its output file, calculates the corresponding dilution factor to be applied to keep this constant and adjusts the flow rate of the appropriate mass flow controller. This loop was performed every twenty seconds. Possible variations of the mole fraction were limited to not more than 2 μmol mol<sup>-1</sup>, thereby limiting variations in the isotope

ratio to 0.0066 ‰ for  $\delta^{13}\text{C}$  and to 0.009 ‰ for  $\delta^{18}\text{O}$ . The resulting variations then become negligible compared to the repeatability of the measurements.

## 6 Precision

The precision of the carousel sampling system and the IRIS were characterised first by measuring the repeatability obtained on one single sample, then the reproducibility over all ports of the carousel, and finally the reproducibility over a range of isotope ratio values in samples prepared with the BIPM's blending facility. Results of these three experiments are reported below.

### 6.1 Repeatability

The repeatability of the carousel sampling system was estimated with the REF2 connected directly to one port of the carousel, to also confirm that the carousel was not introducing any bias in the isotope ratios. This was possible without disconnecting the cylinder from the mass flow controller 3 through a tee previously introduced on the line. The measurement sequence described earlier was repeated five times, resulting in a mean value of  $-42.104$  ‰ for  $\delta^{13}\text{C}$  with a standard deviation of 0.024 ‰, and a mean value of  $-27.606$  ‰ for  $\delta^{18}\text{O}$ , with a standard deviation of 0.023 ‰. Those values are in agreement with the values provided by MPI-BGC made on the  $\text{CO}_2$  in air mixtures made with REF2, and demonstrate a good repeatability for both isotope ratios.

### 6.2 Reproducibility over all ports of the carousel

To evaluate the reproducibility of the system over all ports of the carousel, one single source of  $\text{CO}_2$  contained in a 50 L cylinder was connected to all fourteen available ports of the 16 positions valve, using an appropriate tubing setup to split the flow after the pressure regulator in fourteen channels. Each port of the carousel was then analysed successively. Results are displayed in Figure 5 in terms of  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  values obtained on all fourteen ports. The average and  $1\sigma$  standard deviation are also indicated on the same plots with blue dashed and dotted lines. Figure 5 shows that a typical standard deviation of 0.026 ‰ was obtained on  $\delta^{13}\text{C}$ , and of 0.023 ‰ on  $\delta^{18}\text{O}$ , values which are very similar to those obtained when measuring one

sample with the same port. Therefore, it can be concluded that the carousel does not add further variability in the analytical measurements.

### 6.3 Reproducibility over the range of isotope ratios

The facility developed at the BIPM which allows the mixing of two samples (large cylinders of pure CO<sub>2</sub>) with different isotope ratios was used to prepare smaller samples (50 mL aliquots) with adjustable isotope ratios. These smaller samples were used during this study to demonstrate the precision of the analytical part comprised of the carousel and the IRIS analyzer for the measurement of isotope ratios over a large range of values, between  $\delta^{13}\text{C} = -45\text{‰}$  and  $\delta^{13}\text{C} = -1\text{‰}$ . Aliquots were prepared at five different isotope ratios in batches, disconnected from the preparation facility and connected to the carousel ports via MPV-16. Measurements were repeated several times following the process described earlier. Results are displayed in Table 3, in which the total number of measurements  $N_m$  is indicated, as well as the number of different samples  $N_s$ , a sample being either an aliquot of 50 mL or a cylinder of 50 L. When the number of samples  $N_s$  was just one, all measurements were made from the same port of the carousel. Mean values and standard deviations displayed in Table 3 were calculated over the total number of repeated measurements  $N_m$ . It should be emphasized that although all measurements were calibrated, their accuracy is not discussed here, only their repeatability.

Values displayed in Table 3 show an observed standard deviation of 0.022 ‰ on average for  $\delta^{13}\text{C}$ , and of 0.027 ‰ for  $\delta^{18}\text{O}$ , without any clear correlation with the nominal isotope ratio values. A closer look at the measurement data shows that the larger standard deviation was obtained for the second series of measurements at  $\delta^{18}\text{O} = -20.40\text{‰}$ , and this can be explained with some issues encountered with the feedback loop on the mole fraction, leading to up to 10  $\mu\text{mol mol}^{-1}$  difference between the CO<sub>2</sub> mole fractions of the sample and the references.

## 7 Conclusion

An experimental setup was developed to measure samples of pure CO<sub>2</sub> by IRIS with repeatability close to 0.02 ‰ on both  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$ . A measurement sequence was developed to include frequent drift corrections and two-point calibration with two reference gases, as well as a stringent control of the CO<sub>2</sub> mole fraction entering the instrument gas cell for IR absorption measurements. The entire setup was designed to include a carousel sampling system with which

up to fourteen aliquots of gas could be analyzed sequentially with no impact on the repeatability thanks to the almost identical treatment of the sample and reference gases. It was validated on a number of samples prepared by blending two different CO<sub>2</sub> sources and covering a range of  $\delta^{13}\text{C}$  values between  $-43.36\text{‰}$  and  $-1.37\text{‰}$  vs VPDB-CO<sub>2</sub>, and no impact of the isotope ratio was observed. The amount of sample gas used for each measurement was less than 5 ml of CO<sub>2</sub> at standard conditions, making the system easily deployable for isotope ratio value assignment of bulk CO<sub>2</sub> gas, adaptable to atmospheric mole fractions of CO<sub>2</sub> in air, and for value assignments of standards. Using the sampling system described the measurement reproducibility of current IRIS systems approaches the values that can be achieved with some IRMS systems. The system developed at BIPM will be fundamental to validate the homogenous preparation of samples during the international comparison of isotope ratio measurements in samples of pure CO<sub>2</sub> gas which the BIPM will coordinate with the IAEA in 2020-2021. Future replacement of the compressed CO<sub>2</sub> cylinders used as references with certified isotopic reference materials will allow full validation of its calibration potential.

## **Acknowledgments**

The authors would like to acknowledge the Gas Analysis Working Group (GAWG) of the Consultative Committee for Amount of Substance: Metrology in Chemistry and Biology (CCQM) for the useful discussions, and especially W. Brand (MPI-BGC), S. Assonov and M. Groening (IAEA) for advices on samples preparation. Certain commercial equipment, instruments, and materials are identified in order to specify experimental procedures as completely as possible. This does not imply a recommendation or endorsement by the Bureau International des Poids et Mesures nor does it imply that any of the materials, instruments, or equipment identified are necessarily the best available for the purpose.

## **AUTHOR INFORMATION**

### **Corresponding Author**

\* E-mail : [vjallon@bipm.org](mailto:vjallon@bipm.org). Tel +33 1 45076270.

### **Author Contributions**

All authors have given approval to the final version of the manuscript.

## **References**



- [1] Coleman D.C. 2012 *Carbon isotope techniques*: Academic Press)
- [2] Brand Willi A., Coplen Tyler B., Vogl J., Rosner M. and Prohaska T. 2014 Assessment of international reference materials for isotope-ratio analysis (IUPAC Technical Report). In: *Pure and Applied Chemistry*, p 425, 10.1515/pac-2013-1023
- [3] INTERNATIONAL ATOMIC ENERGY AGENCY 2016 Reference Sheet for IAEA-603 (Vienna: IAEA), 2016-08-28, p 7
- [4] Verkouteren R.M., 1999, Preparation, Characterization, and Value Assignment of Carbon Dioxide Isotopic Reference Materials: RMs 8562, 8563, and 8564, *Analytical Chemistry*, **71**, 4740-4746, 10.1021/ac990233c
- [5] Coplen T.B. and Kendall C., 1982, Preparation and stable isotope determination of NBS-16 and NBS-17 carbon dioxide reference samples, *Analytical chemistry*, **54**, 2611-2612,
- [6] Srivastava A. and Verkouteren R.M., 2018, Metrology for stable isotope reference materials:  $^{13}\text{C}/^{12}\text{C}$  and  $^{18}\text{O}/^{16}\text{O}$  isotope ratio value assignment of pure carbon dioxide gas samples on the Vienna PeeDee Belemnite- $\text{CO}_2$  scale using dual-inlet mass spectrometry, *Analytical and bioanalytical chemistry*, **410**, 4153-4163,
- [7] Metrology for Stable Isotope Reference Standards, <https://www.vtt.fi/sites/SIRS>, 13.06.2019
- [8] Tans P.P. and Zellweger C. WMO 2016 GAW Report No. 229, 18th WMO/IAEA Meeting of Experts on Carbon Dioxide, Other Greenhouse Gases and Related Measurement Techniques
- [9] Nørgaard J., Valkiers S., Van Nevel L., Vendelbo E., Papadakis I., Bréas O. and Taylor P., 2002, The International Measurement Evaluation Programme, IMEP-8: carbon and oxygen isotope ratios in  $\text{CO}_2$ , *Analytical and bioanalytical chemistry*, **374**, 1147-1154,
- [10] Mukai H. Intercomparison of isotope ratios for  $\text{CO}_2$  using several reference materials. In: *12th IAEA/WMO Meeting of  $\text{CO}_2$  Experts. Vol WMO-GAW Report*, pp 58-63,
- [11] Crotwell A.M. and Steinbacher M. WMO 2019 GAW Report No. 242, 19th WMO/IAEA Meeting of Experts on Carbon Dioxide, Other Greenhouse Gases and Related Measurement Techniques
- [12] Flores E., Viallon J., Moussay P., Griffith D.W.T. and Wielgosz R.I., 2017, Calibration strategies for FTIR and other IRIS instruments for accurate  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  measurements of  $\text{CO}_2$  in air, *Analytical Chemistry*, **89**, 3648-3655, 10.1021/acs.analchem.6b05063
- [13] Braden-Behrens J., Yan Y. and Knohl A., 2017, A new instrument for stable isotope measurements of  $^{13}\text{C}$  and  $^{18}\text{O}$  in  $\text{CO}_2$  – instrument performance and ecological application of the Delta Ray IRIS analyzer, *Atmos. Meas. Tech.*, **10**, 4537-4560, 10.5194/amt-10-4537-2017
- [14] Sturm P., Tuzson B., Henne S. and Emmenegger L., 2013, Tracking isotopic signatures of  $\text{CO}_2$  at the high altitude site Jungfraujoch with laser spectroscopy: analytical improvements and representative results, *Atmos. Meas. Tech.*, **6**, 1659-1671,
- [15] Sakai S., Matsuda S., Hikida T., Shimono A., McManus J.B., Zahniser M., Nelson D., Dettman D.L., Yang D. and Ohkouchi N., 2017, High-Precision Simultaneous  $^{18}\text{O}/^{16}\text{O}$ ,  $^{13}\text{C}/^{12}\text{C}$ , and  $^{17}\text{O}/^{16}\text{O}$  Analyses for Microgram Quantities of  $\text{CaCO}_3$  by Tunable Infrared Laser Absorption Spectroscopy, *Analytical Chemistry*, **89**, 11846-11852, 10.1021/acs.analchem.7b03582

- [16] Flores E., Viallon J., Moussay P., Idrees F. and Wielgosz R.I., 2019, An FTIR method for accurate CO<sub>2</sub> mole fraction measurements with correction for differences in isotopic composition of gases, *Metrologia*, **Accepted**.
- [17] Flores E., Viallon J., Choteau T., Moussay P., Idrees F., Wielgosz R.I., Lee J., Zalewska E., Nieuwenkamp G., Veen A.v.d., Konopelko L.A., Kustikov Y.A., Kolobova A.V., Chubchenko Y.K., Efremova O.V., Zhe B.I., Zhou Z., Walter R. Miller J., Rhoderick G.C., Hodge J.T., Shimosaka T., Aoki N., Hall B., Brewer P., Cieciora D., Sega M., Macé T., Fükő J., Szilágyi Z.N., Büki T., Jozela M.I., Ntsasa N.G., Leshabane N., Tshilongo J., Johri P. and Tarhan T., 2019, CCQM-K120 (Carbon dioxide at background and urban level), *Metrologia*, **56**, 08001,
- [18] Wendeberg M., Richter J.M., Rothe M. and Brand W.A., 2013, Jena Reference Air Set (JRAS): a multi-point scale anchor for isotope measurements of CO<sub>2</sub> in air, *Atmos. Meas. Tech.*, **6**, 817-822, 10.5194/amt-6-817-2013
- [19] Werner R.A., Rothe M. and Brand W.A., 2001, Extraction of CO<sub>2</sub> from air samples for isotopic analysis and limits to ultra high precision  $\delta^{18}\text{O}$  determination in CO<sub>2</sub> gas, *Rapid Communications in Mass Spectrometry*, **15**, 2152-2167, 10.1002/rcm.487
- [20] Grootes P.M., Mook W.G. and Vogel J.C., 1969, Isotopic fractionation between gaseous and condensed carbon dioxide, *Zeitschrift für Physik A Hadrons and nuclei*, **221**, 257-273, 10.1007/BF01392177
- [21] Jacksier T., Socki R. and Kumar A. 2018 <sup>13</sup>C and <sup>18</sup>O isotope effects resulting from high pressure regulation and CO<sub>2</sub> cylinder depletion. In: *EGU General Assembly Conference Abstracts*, p 3494,
- [22] van Geldern R., Nowak M.E., Zimmer M., Szizybalski A., Myrntinen A., Barth J.A.C. and Jost H.-J., 2014, Field-Based Stable Isotope Analysis of Carbon Dioxide by Mid-Infrared Laser Spectroscopy for Carbon Capture and Storage Monitoring, *Analytical Chemistry*, **86**, 12191-12198, 10.1021/ac5031732
- [23] W. T. Griffith D. 2018 *Calibration of isotopologue-specific optical trace gas analysers: A practical guide* vol 11

## Figures

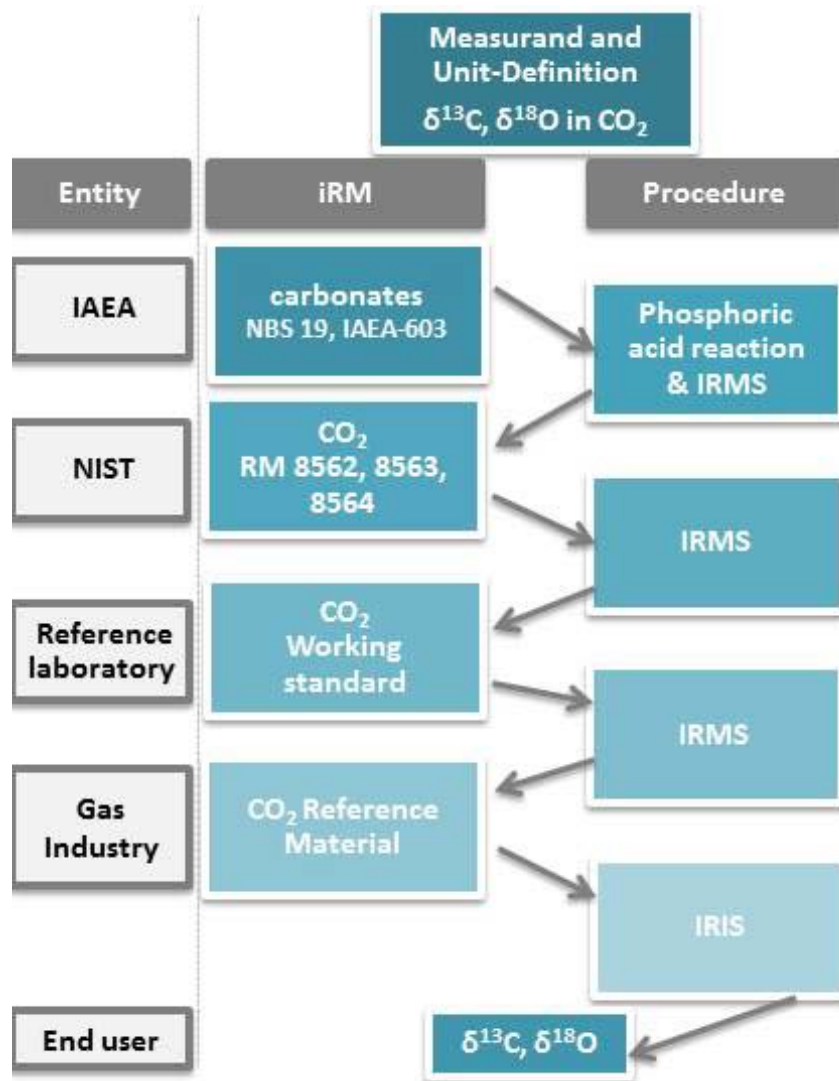


Figure 1: possible calibration hierarchy for the measurement of  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  in  $\text{CO}_2$  using an IRIS system. Entity indicates the institute owning the isotope Reference Materials (iRM) which is used by the next entity applying the “procedure” to implement one calibration step.

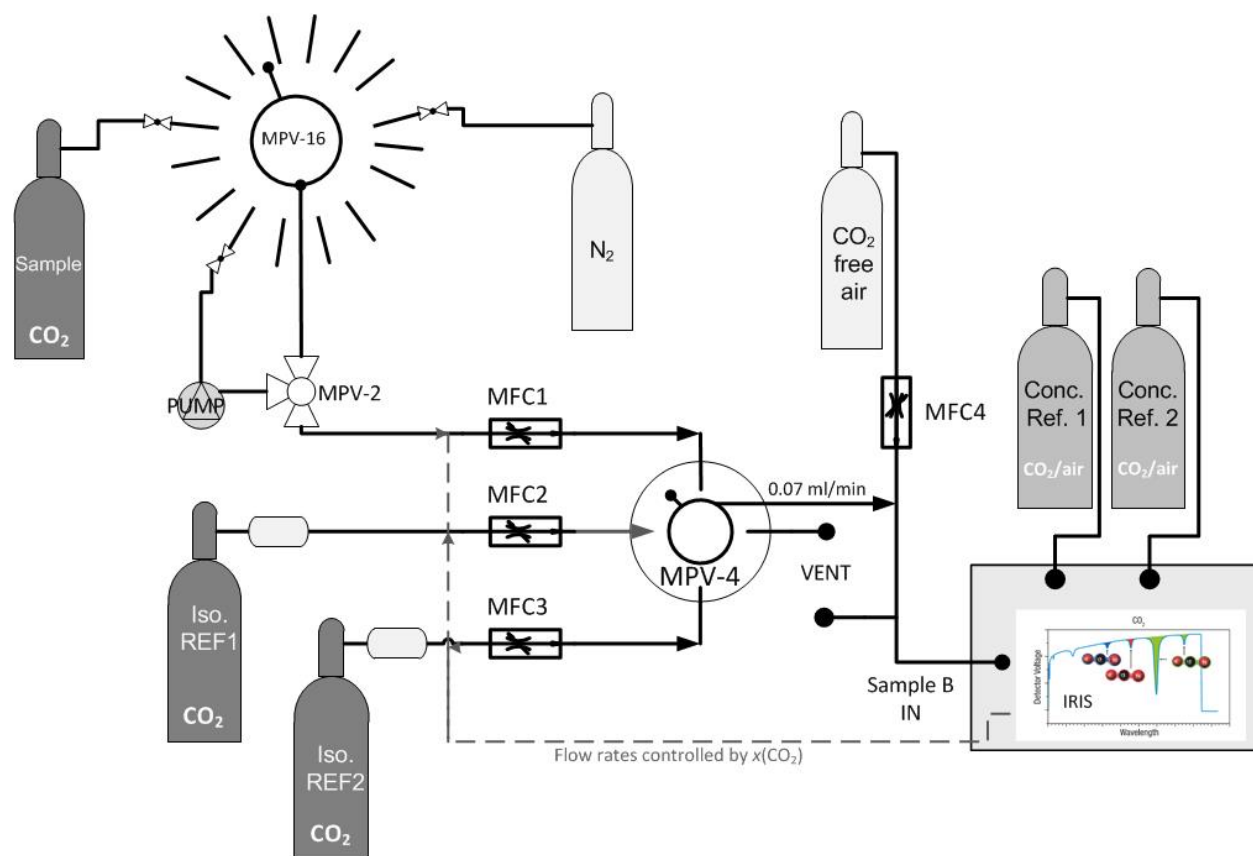


Figure 2. Measurement setup for the analysis of gaseous CO<sub>2</sub> samples with the IRIS instrument.

Abbreviations: MPV-*n*: *n* ports multiple valve; MFC<sub>*i*</sub>: Mass Flow Controller number *i*; Iso. REF<sub>*i*</sub>: reference CO<sub>2</sub> gases for the isotopic ratios; Conc. Ref. *i*: reference CO<sub>2</sub> in air gases for the CO<sub>2</sub> mole fraction; IRIS: Isotope Ratio Infrared Spectroscopy analyser.

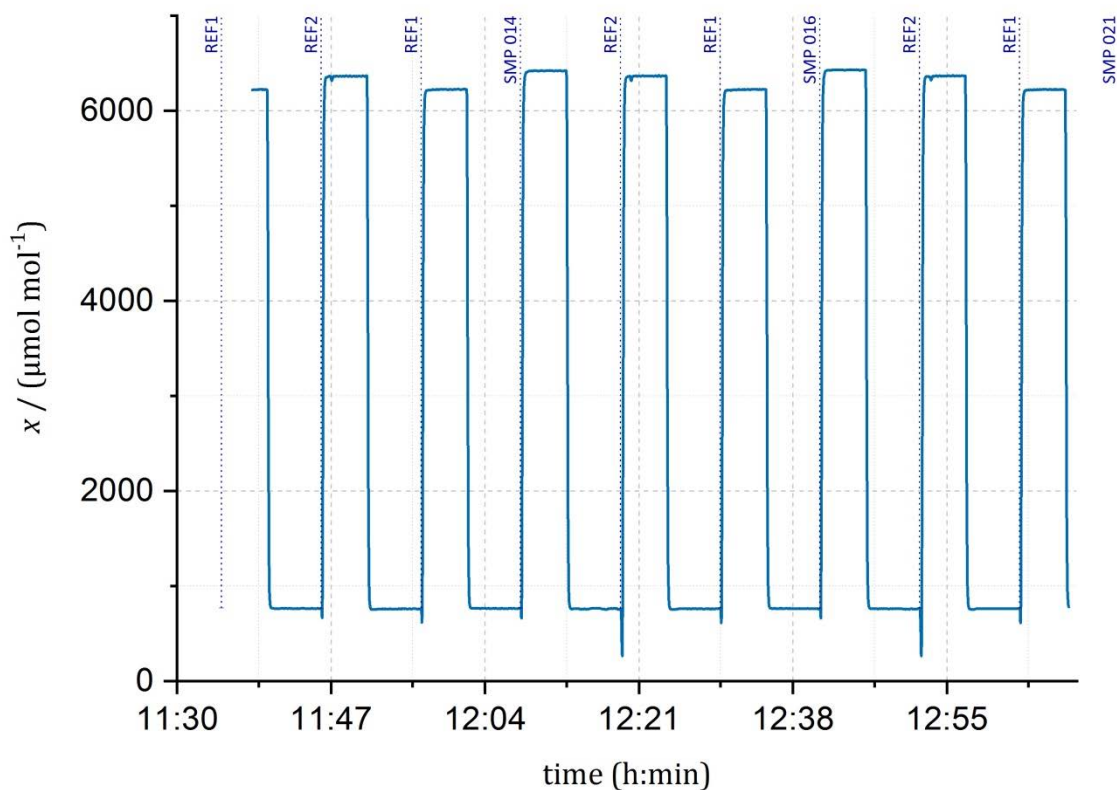


Figure 3: CO<sub>2</sub> mole fraction (uncalibrated) inside the analyzer gas cell during a typical sequence of measurement. Dotted blue vertical lines indicate the time at which a new mixture is introduced, and the associated labels identify the nature of the mixture: REF1 for reference 1, REF2 for reference 2, SMPXXX for sample number XXX contained in an aliquot and connected to the carousel.

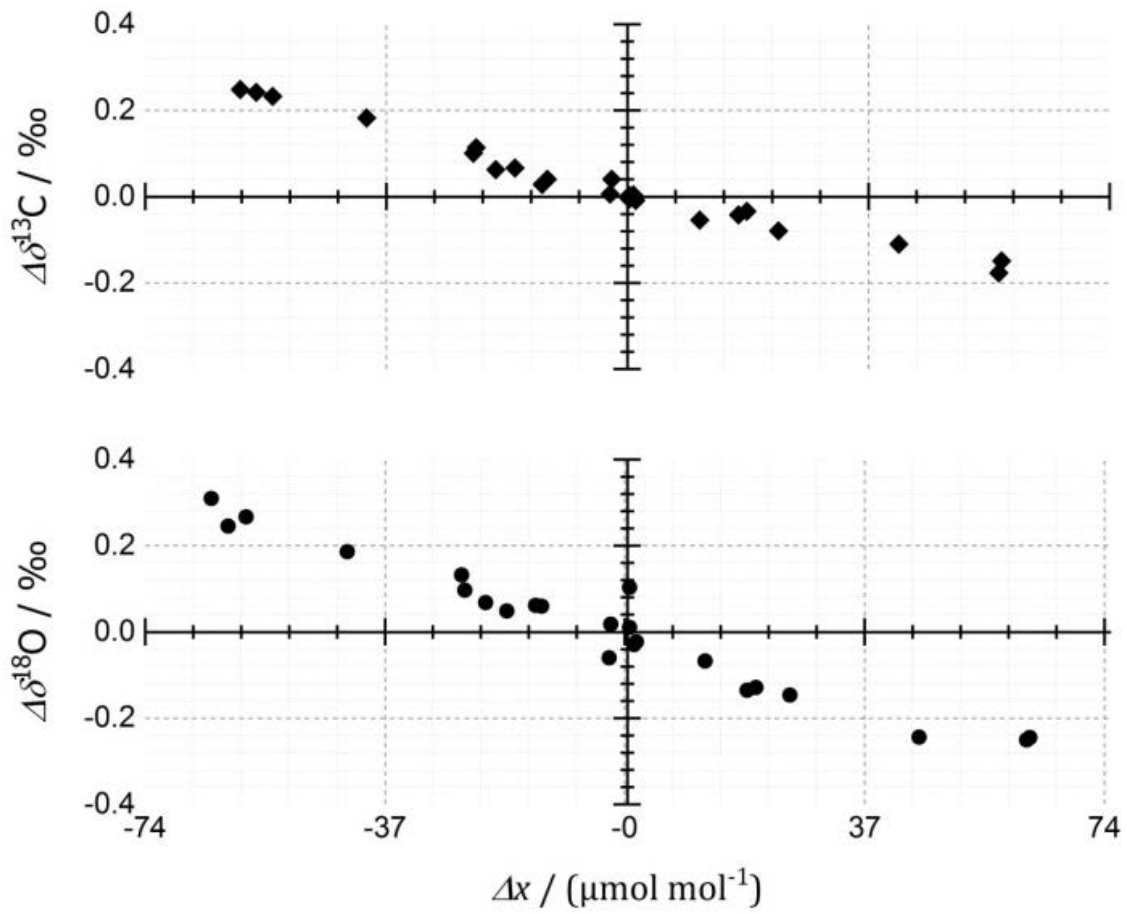


Figure 4: Bias in  $\delta^{13}\text{C}$  (top plot with diamonds) and  $\delta^{18}\text{O}$  (bottom plot with circles) measurements as a function of the difference in  $\text{CO}_2$  mole fractions between the sample and the reference gases ( $\Delta x = x_s - x_{ref}$ ), measured with a nominal mole fraction of  $730 \mu\text{mol mol}^{-1}$ .

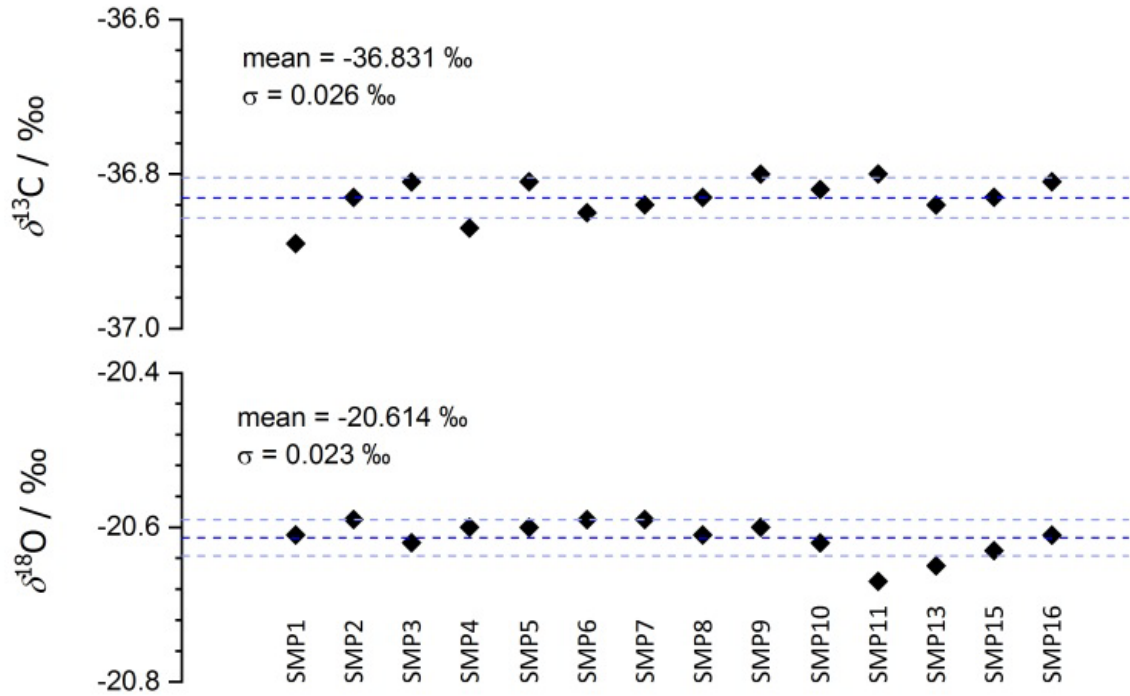


Figure 5: measurements of  $\delta^{13}\text{C}$  (top plot) and  $\delta^{18}\text{O}$  (bottom plot) on the same  $\text{CO}_2$  source sampled via all 14 ports of the carousel. Each individual point represents the measurements via one port. The dashed and dotted lines represent the mean and standard deviation respectively.

## Tables

Table 1: description of cylinders connected to the system

Name	Function	Provider	Cylinder size/ L	Purity / %	$\delta^{13}\text{C} / \text{‰}$	$U(\delta^{13}\text{C}) / \text{‰}$	$\delta^{18}\text{O} / \text{‰}$	$U(\delta^{18}\text{O}) / \text{‰}$
REF1	Isotope reference	Air Liquide	50	99.999	-1.384	0.019	-7.148	0.040
REF2	Isotope reference	Messer	5	99.998	-42.131	0.013	-27.631	0.024
SMP	Sample	Messer	50	99.998	-36.72	NA	-20.40	NA
					$x_{\text{CO}_2} / \mu\text{mol mol}^{-1}$	$U(x_{\text{CO}_2}) / \mu\text{mol mol}^{-1}$		
CREF1	Concentration reference	Scott–Marin	50	NA	791.12	1.0		
CREF2	Concentration reference	Scott–Marin	50		651.44	0.8		
AIR	CO <sub>2</sub> free dilution air <sup>1</sup>	Messer	50		<0.1 $\mu\text{mol mol}^{-1}$			

<sup>1</sup> Synthetic air composed of N<sub>2</sub> at 79.5 % and O<sub>2</sub> at 20.5 %, as reported by the company with 2.5 % tolerance.

Table 2: example of the post-treatment of data recorded by the control programme Qtegra: *n* is an index incremented at each switch of gas mixture, *type* indicate the nature of the mixture for Qtegra first calculation; *Label* is a user-defined label to indicate the nature of the mixture for the data treatment (REF<sub>*i*</sub> for reference material *i* and SMP<sub>*i*</sub> for the samples);  $\delta^{13}\text{C}_m$  is the isotope ratio delta value as calculated by Qtegra,  $\delta^{13}\text{C}_{\text{REF}i, \text{int}}$  is the isotope ratio delta value of reference *i* interpolated at the time of the sample measurement; and  $\delta^{13}\text{C}$  is the isotope ratio delta value in the sample obtained by linear regression of the references interpolated values.

<i>n</i>	<i>type</i>	<i>Label</i>	$\delta^{13}\text{C}_m / \text{‰}$	$\delta^{13}\text{C}_{\text{REF}1, \text{int}} / \text{‰}$	$\delta^{13}\text{C}_{\text{REF}2, \text{int}} / \text{‰}$	$\delta^{13}\text{C} / \text{‰}$
1	STANDARD	REF1	-1.384			
2	UNKNOWN	REF2	-42.429			
3	UNKNOWN	REF1	-1.951			
4	UNKNOWN	SMP1	-37.264	-2.012	-42.517	-36.85
5	UNKNOWN	REF2	-42.561			
6	UNKNOWN	REF1	-2.135			
7	UNKNOWN	SMP2	-37.43	-2.116	-42.648	-36.89



8	UNKNOWN	REF2	-42.692
9	UNKNOWN	REF1	-2.078

Table 3: mean and standard deviation of isotope ratio measurements performed on a number of samples obtained with the preparation facility.

$N_m$	$N_s$	$\delta^{13}\text{C} / \text{‰}$		$\delta^{18}\text{O} / \text{‰}$	
		Mean	$s$	Mean	$s$
6	1	-43.362	0.023	-35.350	0.021
12	8	-36.717	0.020	-20.400	0.052
12	3	-29.884	0.021	-27.341	0.020
10	3	-19.937	0.031	-21.216	0.027
12	3	-10.741	0.019	-15.225	0.023
9	3	-1.375	0.019	-9.290	0.020