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## Comparison of gravimetry and dynamic dilution for the generation of reference gas mixtures of CO<sub>2</sub> at atmospheric amount fraction

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### ABSTRACT

Carbon dioxide (CO<sub>2</sub>) is the most important greenhouse gas generated by human activities. Its concentration has been growing in the atmosphere reaching a current annual average of 410 μmol mol<sup>-1</sup>. Reliable determinations of the atmospheric CO<sub>2</sub> concentration are of great importance for the development of models used in climate change predictions. The production of reference mixtures of known composition is a key step for the achievement of reliable data for the monitoring of greenhouse gases in atmosphere.

The present work deals with a comparison of two methods for gas mixtures preparation, the first based on the gravimetric preparation of gas mixtures in high pressure cylinders and the second based on dynamic dilution, for generating gas mixtures at the desired amount fraction online.

Reference mixtures of CO<sub>2</sub> can be used for the calibration of monitoring sensors, with various applications ranging from environmental monitoring to industrial process control.

### 1. Introduction

The global mean temperature in 2022 was estimated to be 1.15 °C ± 0.13 °C above the pre-industrial average level, thus making 2022 one of the warmest year on record. The increased levels of greenhouse gases (GHGs) in the atmosphere represent the main cause for such an increasing [1]. Available evidence on projected climate risks indicates that opportunities for adaptation will likely have reduced effectiveness should 1.5 °C global warming be exceeded, thus requiring the achievement of mitigation targets [2]. Carbon dioxide (CO<sub>2</sub>) is the single most important anthropogenic GHG in the atmosphere; it is closely linked to anthropogenic activities and interacts strongly with the biosphere and the oceans. The National Oceanic and Atmospheric Administration (NOAA) Annual Greenhouse Gas Index shows that from 1990 to 2021, radiative forcing by long-lived greenhouse gases increased by 49 %, with CO<sub>2</sub> accounting for about 80 % of this increase [3]. The latest analysis of observations from the WMO GAW *in situ* observational network shows that the globally averaged surface amount fraction of CO<sub>2</sub> reached 415.7 ± 0.2 μmol mol<sup>-1</sup>, a new high record. Its increase from 2020 to 2021 was equal to that observed from 2019 to 2020 and larger than the average annual growth rate over the last decade [3]. In this context, predicting the evolution of the atmospheric content of CO<sub>2</sub> and monitoring its actual levels are of utmost importance and require a quantitative

understanding of its many sources and sinks. The use of monitoring sensors, also grouped in distributed networks, allows to collect relevant measurement data. For the achievement of meaningful data, the measurement results need to be comparable and the performance of sensors must be investigated, both in laboratory and in the field. To carry out such verifications and to perform the calibration of sensors, the availability of suitable reference gas standards, such as Certified Reference Materials (CRMs) of CO<sub>2</sub> at proper amount fraction in a matrix of air, is needed. Furthermore, the possibility to have gas measurement standards readily available on site is advisable. This theme is of high importance for its applications and fallouts in many sectors, and the development of methods for the preparation of gaseous RMs and CRMs started many years ago and is continuously growing and updating [4,5]. Two complementary methods, i.e. gravimetry and dynamic dilution, are widely used for the generation of reference gas mixtures and CRMs; the advantages of gravimetry are high accuracy and low uncertainties, whereas dynamic dilution has more versatility in particular for reactive species and low amount fractions [6,7].

The present work describes the activity carried out at INRiM on the preparation of reference gas standards by the above-mentioned methods. Gravimetry allows the preparation of CRMs in high-pressure cylinders having the best associated uncertainty. The dynamic dilution, instead, starting from CRMs and diluting them with pure matrix

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gases, leads to the production of ready-to-use reference gas standards at the desired amount fraction. The latter technique can be further exploited also for *in situ* sensor characterisation.

## 2. Materials and methods

### 2.1. Gravimetry

Gravimetry is a primary method, which allows the preparation of static mixtures of stable gaseous analytes in high-pressure cylinders, and is particularly meant for gases as CO<sub>2</sub>. Several National Metrology Institutes around the world have facilities for the realisation of gravimetric CRMs. The Global Monitoring Division of the National Oceanic and Atmospheric Administration (NOAA) also realises CO<sub>2</sub>-in air standards and contribute to maintain the World Meteorological Organisation Global Atmosphere Watch (WMO-GAW) mole fraction scale for CO<sub>2</sub> in air [8]. CO<sub>2</sub> in air mixtures can be prepared by gravimetry with relatively low uncertainty (~0.04 %, *k* = 2) by measuring the gas masses with high precision and by using well-characterised cylinders [8,9]. Applications of gravimetry to analytes other than CO<sub>2</sub> can be found in literature [10–12].

At INRiM, CRMs of CO<sub>2</sub> at atmospheric amount fraction in synthetic air matrix are prepared by gravimetry in high-pressure cylinders [13, 14], usually made of aluminium alloy (Luxfer, UK) and having internal volume of 5 L. According to the gravimetric method described in Ref. [15], the gas mixtures are prepared by transferring pure gases or mixtures of known composition quantitatively into a cylinder that will contain the final mixture. The added masses are precisely determined by weighing the cylinder before and after each introduction, following a double substitution scheme (A-B-B-A). INRiM weighing facility is equipped with a mass comparator (PR 10003, Mettler Toledo, Switzerland) used to determine the mass of the cylinders during each preparation step following the double substitution weighing scheme.

In order to obtain two reference gas mixtures of CO<sub>2</sub> in synthetic air at about the atmospheric amount fraction, the following pure gases were used: CO<sub>2</sub> 4.8 (SIAD, Italy), N<sub>2</sub> 6.0 (Messer Italia, Italy), Ar 5.0 (Air Liquide Italia, Italy), and O<sub>2</sub> 6.0 (Air Liquide Italia, Italy). These pure gases were gravimetrically mixed in accordance with the preparation process reported in Fig. 1, hence obtaining three pre-mixtures (a, b and c), with amount fractions and expanded uncertainties (*k* = 2), reported in Table 1. Pre-mixture b was prepared starting from pre-mixture a. Eventually, two reference gas mixtures, 1<sub>Gr</sub> and 2<sub>Gr</sub>, were prepared by

**Table 1**

Pre-mixtures with their amount fractions and expanded uncertainties (*k* = 2) used for the preparation by gravimetry of two reference gas mixtures.

Pre-mixture	Cylinder identification number	Analyte	Analyte amount fraction, $\chi$ mol/mol	$U(\chi)$ mol/mol	Balance gas
A	D247446	CO <sub>2</sub>	0.080122	$2.5 \cdot 10^{-5}$	N <sub>2</sub>
B	D247441	CO <sub>2</sub>	$5005.4 \cdot 10^{-6}$	$2.1 \cdot 10^{-6}$	N <sub>2</sub>
C	D566424	Ar	0.042703	$1.7 \cdot 10^{-5}$	O <sub>2</sub>

using the pre-mixtures b and c as parent mixtures and using N<sub>2</sub> 6.0 as balance gas to obtain the target CO<sub>2</sub> amount fractions. The CO<sub>2</sub> amount fractions and expanded uncertainties (*k* = 2) of the obtained reference mixtures are reported in Table 2.

### 2.2. Dynamic dilution

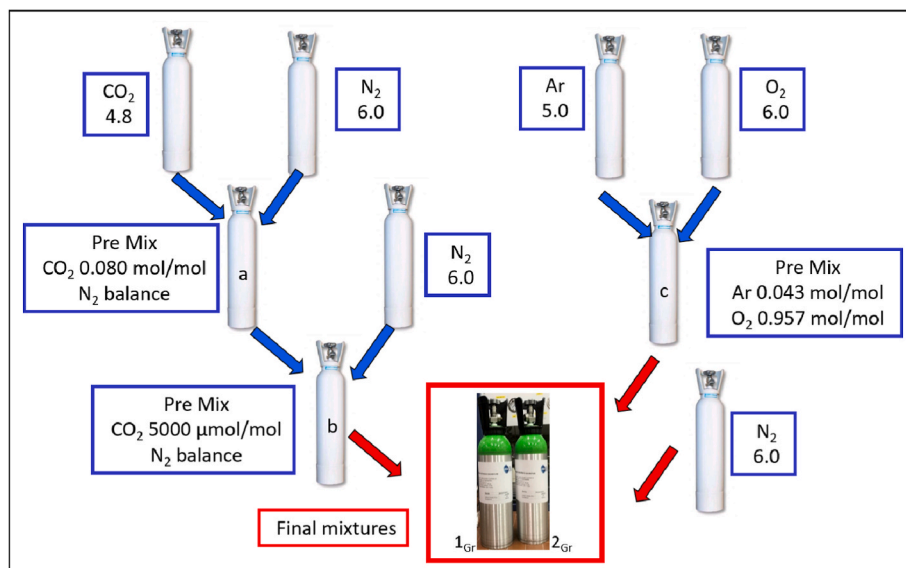
The dynamic dilution method can be carried out by means of different procedures and dilution devices. A widespread approach is based on the use of gas mass-flow meters and mass-flow controllers [16, 17].

A dilution system was developed in the framework of the European EMPIR Projects 16ENV06 SIRS [18] and 19ENV05 STELLAR [19]. This system is composed of a mixing chamber coupled with a set of Mass Flow Controllers (MFCs) (MKS Instruments, USA) and valves (Swagelok, USA). The chamber, made of stainless steel type AISI 304 L, was designed at INRiM and aimed at maximising the mixing of gases. It contains a set of grids, to improve the mixing of the two gas flows. More details on the design and configuration of the chamber are reported in Refs. [20,21]. The mixture is generated inside the chamber from a parent mixture and a pure matrix gas and a typical mixing time of 30 min is chosen, prior to measuring the amount fraction of CO<sub>2</sub> with

**Table 2**

Example of reference gas mixtures prepared at INRiM by gravimetry.

Mixture	Cylinder identification number	CO <sub>2</sub> amount fraction, $\chi_{CO_2}$ $\mu\text{mol/mol}$	$U(\chi_{CO_2})$ $\mu\text{mol/mol}$
1 <sub>Gr</sub>	D247440	479.3	0.2
2 <sub>Gr</sub>	D247445	798.9	0.2



**Fig. 1.** Schematic of the gravimetric preparation process.

dedicated analysers (NDIR, FTIR). A validation of the generated mixtures was previously carried out [21], by using independent static parent mixtures obtained from in-house production and/or purchased from other NMIs.

For the present work, two reference gas mixtures, having composition similar to the gravimetric ones reported in Table 2, were prepared by dynamic dilution. Two MFCs with full-scale range of 500 standard cubic centimetres (sccm) and 2000 sccm, respectively, were used for this purpose. A parent mixture of CO<sub>2</sub> in synthetic air at the amount fraction of 4987.6 μmol mol<sup>-1</sup> (mixture code: INRiM 080, cylinder S/N D206743), gravimetrically prepared at INRiM, was diluted with synthetic air “CO<sub>2</sub>-free” (NPL, UK). The compositions and the associated uncertainties of the two mixtures, 1<sub>Dd</sub> and 2<sub>Dd</sub>, are reported in Table 3. In Fig. 2 the mixing chamber with the MFCs used for the preparation of gas mixtures by dynamic dilution are shown.

### 3. Model equation and uncertainty evaluation

#### 3.1. Gravimetry

The model equation used to calculate the mole fraction of CO<sub>2</sub>,  $\chi_{CO_2}$ , in the final mixtures 1<sub>Gr</sub> and 2<sub>Gr</sub> (Table 2) is taken from Ref. [15]:

$$\chi_{CO_2, prep} = \frac{\sum_{j=1}^r \left( \frac{\chi_{CO_2, j} \cdot m_j}{\sum_{i=1}^q \chi_{i, j} \cdot M_i} \right)}{\sum_{j=1}^r \left( \frac{m_j}{\sum_{i=1}^q \chi_{i, j} \cdot M_i} \right)} \quad (1)$$

where  $j$  refers to the different parent mixtures, while  $i$  refers to the various components in the mixtures,

$\chi_{CO_2, j}$  is the amount fraction of CO<sub>2</sub> in parent gas  $j$ ,

$\chi_{i, j}$  is the amount fraction of component  $i$  in parent gas  $j$ ,

$m_j$  is the added mass of parent gas  $j$ ,

$M_i$  is the molar mass of component  $i$ .

The uncertainty budget for the gravimetric preparation of mixture 1<sub>Gr</sub> at 479.3 μmol mol<sup>-1</sup> of CO<sub>2</sub> is reported in Table 4, as an example. All the relevant uncertainty components are reported. The uncertainty budget is evaluated according to the guidelines prescribed in Ref. [15], taking into account the weighted masses of the parent mixtures, the molar masses of gases and their purity values. The uncertainty of the amount fraction obtained *via* gravimetry is calculated by the application of the law of propagation of uncertainty.

#### 3.2. Dynamic dilution

The model equation used to calculate the amount fraction of CO<sub>2</sub> in the reference mixtures 1<sub>Dd</sub> and 2<sub>Dd</sub> (Table 3) is the following:

$$\chi_{a, out} = \frac{\chi_{1a} Q_1 + \chi_{2a} Q_2}{Q_1 + Q_2} \quad (2)$$

where:

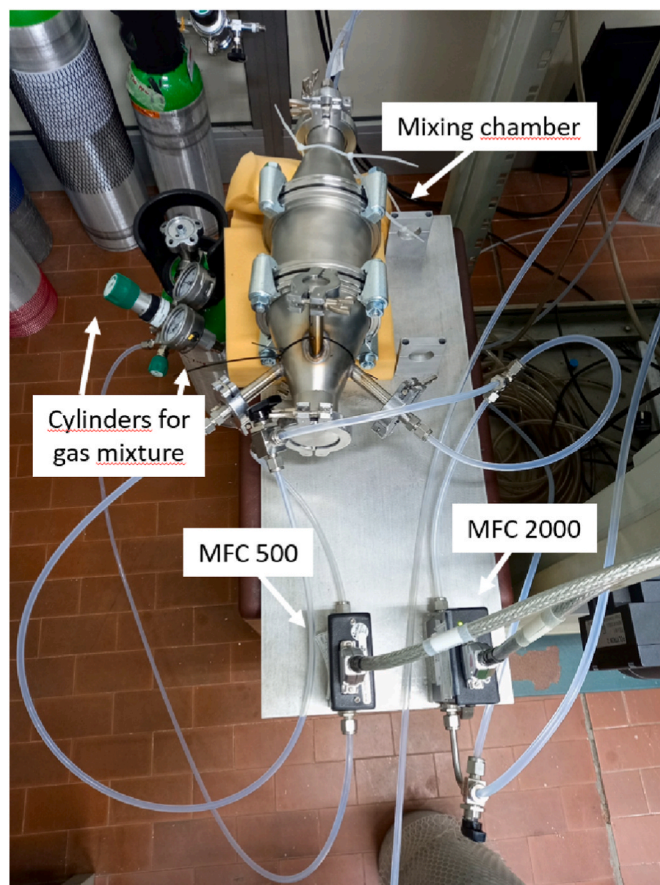
$\chi_{a, out}$  is the amount fraction of the analyte gas in the output mixture (μmol/mol),

$Q_1$  is the flow of the MFC used for the analyte gas, the CO<sub>2</sub> mixture in

**Table 3**

Example of reference gas mixtures prepared at INRiM by dynamic dilution.

Mixture	CO <sub>2</sub> amount fraction, $\chi_{CO_2}$ μmol/mol	$U(\chi_{CO_2})$ μmol/mol
1 <sub>Dd</sub>	477.11	0.93
2 <sub>Dd</sub>	798.93	0.78



**Fig. 2.** Image of the mixing chamber with the MFCs for the preparation of gas mixtures by dynamic dilution.

synthetic air, that has to be diluted (sccm = cm<sup>3</sup>/min),

$Q_2$  is the flow of the MFC used for the diluting matrix gas, synthetic air (sccm = cm<sup>3</sup>/min),

$\chi_{1a}$  is the amount fraction of the analyte gas, 4987.6 μmol mol<sup>-1</sup> of CO<sub>2</sub>, to be diluted (μmol/mol),

$\chi_{2a}$  is the amount fraction of CO<sub>2</sub> in synthetic air (Sapio, Italy) in the diluting matrix gas (μmol/mol).

The uncertainties of  $Q_1$  and  $Q_2$  are evaluated during the calibration of the MFCs, whereas the uncertainties of the concentrations  $\chi_{1a}$  and  $\chi_{2a}$  are certified by the gas mixture producers.

The uncertainty budget for the preparation by dynamic dilution of mixture 1<sub>Dd</sub> at 477.11 μmol/mol of CO<sub>2</sub> takes into account the flow of the two MFCs used to prepare the mixture and the amount fraction of CO<sub>2</sub> in the parent mixture. The uncertainty budget is reported in Table 5.

The input quantities in model 2 providing the amount fraction of CO<sub>2</sub> in the final mixture are considered as essentially uncorrelated.

The uncertainty associated with the amount fraction of the analyte in the diluting gas matrix  $u(\chi_{2a})$  is considered, as a first approximation, negligible and hence is set equal to zero. This is because the CO<sub>2</sub> in the synthetic air is assumed as a non-significant impurity (being below 0.1 μmol/mol from the specifications of the producer), thus supporting this assumption on the associated measurement uncertainty.

The combined standard uncertainty associated to the 1<sub>Dd</sub> gas mixture resulted of 0.46 μmol mol<sup>-1</sup>.

### 4. Results and discussion

From the comparison of the two presented uncertainty budgets, it can be highlighted that the combined standard uncertainty of the preparation by dynamic dilution results to be about four times larger

**Table 4**Uncertainty budget for the gravimetric preparation of mixture 1<sub>Gr</sub> at 479.3 μmol/mol of CO<sub>2</sub> in synthetic air.

Uncertainty component $u(x_i)$	Uncertainty source	Standard uncertainty, $u(x_i)$	$\delta\chi_{\text{CO}_2, \text{prep}}/\delta x_i$	Contribution to $u(\chi_{\text{CO}_2, \text{prep}})$ $ \delta\chi_{\text{CO}_2, \text{prep}}/\delta x_i  \cdot u(x_i)$
$u(m_{\text{CO}_2})$	Weighed mass of the parent mixture of CO <sub>2</sub>	$8.2 \cdot 10^{-4}$ g	$7.20 \cdot 10^{-6}$ mol mol <sup>-1</sup> g <sup>-1</sup>	$5.9 \cdot 10^{-9}$ mol mol <sup>-1</sup>
$u(m_{\text{N}_2})$	Weighed mass of the balance gas N <sub>2</sub>	$8.2 \cdot 10^{-4}$ g	$-7.64 \cdot 10^{-7}$ mol mol <sup>-1</sup> g <sup>-1</sup>	$6.3 \cdot 10^{-10}$ mol mol <sup>-1</sup>
$u(m_{\text{Ar}, \text{O}_2})$	Weighed mass of the parent mixture of Ar in O <sub>2</sub>	$8.2 \cdot 10^{-4}$ g	$-6.62 \cdot 10^{-7}$ mol mol <sup>-1</sup> g <sup>-1</sup>	$5.4 \cdot 10^{-10}$ mol mol <sup>-1</sup>
$u(M_{\text{CO}_2})$	Molar mass of CO <sub>2</sub>	$1.0 \cdot 10^{-3}$ g mol <sup>-1</sup>	$-7.72 \cdot 10^{-8}$ mol <sup>2</sup> mol <sup>-1</sup> g <sup>-1</sup>	$7.7 \cdot 10^{-11}$ mol mol <sup>-1</sup>
$u(M_{\text{N}_2})$	Molar mass of N <sub>2</sub>	$2.0 \cdot 10^{-4}$ g mol <sup>-1</sup>	$-3.61 \cdot 10^{-6}$ mol <sup>2</sup> mol <sup>-1</sup> g <sup>-1</sup>	$7.2 \cdot 10^{-10}$ mol mol <sup>-1</sup>
$u(M_{\text{Ar}})$	Molar mass of Ar	$5.8 \cdot 10^{-4}$ g mol <sup>-1</sup>	$1.38 \cdot 10^{-7}$ mol <sup>2</sup> mol <sup>-1</sup> g <sup>-1</sup>	$8.0 \cdot 10^{-11}$ mol mol <sup>-1</sup>
$u(M_{\text{O}_2})$	Molar mass of O <sub>2</sub>	$2.8 \cdot 10^{-4}$ g mol <sup>-1</sup>	$3.10 \cdot 10^{-6}$ mol <sup>2</sup> mol <sup>-1</sup> g <sup>-1</sup>	$8.7 \cdot 10^{-10}$ mol mol <sup>-1</sup>
$u(\chi_{\text{N}_2 \text{ in CO}_2})$	Amount fraction of N <sub>2</sub> in the parent mixture of CO <sub>2</sub>	$1.0 \cdot 10^{-6}$ mol mol <sup>-1</sup>	$-4.32 \cdot 10^{-4}$	$4.3 \cdot 10^{-10}$ mol mol <sup>-1</sup>
$u(\chi_{\text{N}_2 \text{ in N}_2})$	Amount fraction of N <sub>2</sub> in balance gas (purity)	$8.7 \cdot 10^{-7}$ mol mol <sup>-1</sup>	$3.29 \cdot 10^{-4}$	$2.9 \cdot 10^{-10}$ mol mol <sup>-1</sup>
$u(\chi_{\text{Ar in Ar}, \text{O}_2})$	Amount fraction of Ar in the parent mixture of Ar in O <sub>2</sub>	$8.7 \cdot 10^{-6}$ mol mol <sup>-1</sup>	$1.29 \cdot 10^{-4}$	$1.1 \cdot 10^{-9}$ mol mol <sup>-1</sup>
$u(\chi_{\text{O}_2 \text{ in N}_2})$	Amount fraction of O <sub>2</sub> in balance gas (impurity)	$1.4 \cdot 10^{-7}$ mol mol <sup>-1</sup>	$3.75 \cdot 10^{-4}$	$5.3 \cdot 10^{-11}$ mol mol <sup>-1</sup>
$u(\chi_{\text{O}_2 \text{ in Ar}, \text{O}_2})$	Amount fraction of O <sub>2</sub> in the parent mixture of Ar in O <sub>2</sub>	$8.7 \cdot 10^{-6}$ mol mol <sup>-1</sup>	$1.04 \cdot 10^{-4}$	$9.0 \cdot 10^{-10}$ mol mol <sup>-1</sup>
$u(\chi_{\text{CO}_2 \text{ in CO}_2})$	Amount fraction of CO <sub>2</sub> in the parent mixture of CO <sub>2</sub>	$1.0 \cdot 10^{-6}$ mol mol <sup>-1</sup>	$9.51 \cdot 10^{-2}$	$9.5 \cdot 10^{-8}$ mol mol <sup>-1</sup>
$u(\chi_{\text{CO}_2 \text{ in N}_2})$	Amount fraction of CO <sub>2</sub> in balance gas (impurity)	$2.9 \cdot 10^{-8}$ mol mol <sup>-1</sup>	$6.86 \cdot 10^{-1}$	$2.0 \cdot 10^{-8}$ mol mol <sup>-1</sup>
$u(\chi_{\text{CO}_2 \text{ in Ar}, \text{O}_2})$	Amount fraction of CO <sub>2</sub> in the parent mixture of Ar in O <sub>2</sub>	$8.7 \cdot 10^{-8}$ mol mol <sup>-1</sup>	$2.19 \cdot 10^{-1}$	$1.9 \cdot 10^{-8}$ mol mol <sup>-1</sup>

The combined standard uncertainty associated with the 1<sub>Gr</sub> gas mixture resulted of 0.1 μmol mol<sup>-1</sup>.

**Table 5**Uncertainty budget for the preparation of mixture 1<sub>Dd</sub> at 477.11 μmol/mol of CO<sub>2</sub> in synthetic air by dynamic dilution.

Uncertainty component $u(x_i)$	Uncertainty source	Standard uncertainty, $u(x_i)$	$\delta\chi_{a, \text{out}}/\delta x_i$	Contribution to $u(\chi_{a, \text{out}})$ $ \delta\chi_{a, \text{out}}/\delta x_i  \cdot u(x_i)$
$u(Q_1)$	Flow of the MFC used for the analyte gas that has to be diluted	$1.23 \cdot 10^{-1}$ sccm	$3.74 \cdot 10^{-6}$ mol mol <sup>-1</sup> sccm <sup>-1</sup>	$4.60 \cdot 10^{-7}$ mol mol <sup>-1</sup>
$u(Q_2)$	Flow of the MFC used for the diluting matrix gas	$1.23 \cdot 10^{-1}$ sccm	$-3.96 \cdot 10^{-7}$ mol mol <sup>-1</sup> sccm <sup>-1</sup>	$4.87 \cdot 10^{-8}$ mol mol <sup>-1</sup>
$u(\chi_{1a})$	Amount fraction of the analyte gas to be diluted	$0.20 \cdot 10^{-6}$ mol mol <sup>-1</sup>	$9.57 \cdot 10^{-2}$	$1.91 \cdot 10^{-8}$ mol mol <sup>-1</sup>
$u(\chi_{2a})$	Amount fraction of the analyte in the diluting gas matrix	$0.0 \cdot 10^{-6}$ mol mol <sup>-1</sup>	$9.04 \cdot 10^{-1}$	0 mol mol <sup>-1</sup>

than that obtained by the gravimetric method, as also reported in Tables 2 and 3 (in terms of expanded uncertainties).

Practically, all the uncertainty contributions of the gravimetric preparation (detailed in Table 4) are smaller than those of the dynamic dilution, showed in Table 5. The largest uncertainty contributions in the gravimetric preparation are related to the amount fractions of CO<sub>2</sub> in the various mixture components and are of the same order of magnitude as the uncertainty contributions of  $\chi_{1a}$  and  $Q_2$  in the dynamic dilution.

The major contribution in the uncertainty budget of dynamic dilution, which causes a considerable difference between the gravimetric and the dynamic dilution final uncertainty, is the uncertainty contribution due to the  $Q_1$  flow. Hence, to improve the preparation by dynamic dilution,  $Q_1$  is the contribution that needs to be kept well under control.

Given two MFCs with approximately the same capabilities and instrumental uncertainties, the sensitivity coefficient in component  $u(Q_1)$  (i.e., the derivative of  $\chi_{a, \text{out}}$  with respect to  $Q_1$ ) depends also on the flow of the other MFC ( $Q_2$ ). Thus, the difference between the two uncertainty contributions  $u(Q_1)$  and  $u(Q_2)$  cannot be decreased. This difference can be kept small if the used flux values of the two gases are

similar.

In addition, the amount fraction of CO<sub>2</sub> in the matrix gas used to dilute the mixture should be preferably close to zero. INRiM operates in this way, i.e. using “CO<sub>2</sub>-free” air matrix. Otherwise, the uncertainty contribution  $u(\chi_{2a})$  would become the most important, due to the value of its sensitivity coefficient.

In case CO<sub>2</sub>-free matrix gases are not available, it is important to use high purity gases, in order to have a negligible CO<sub>2</sub> amount fraction in the matrix gas used for the dilution of the parent mixture. Purity analysis of the matrix gases used for mixtures preparation is underway at INRiM, to improve the uncertainty budget of the mixture preparations.

In Fig. 3, a graphical comparison of the uncertainty budgets for gravimetry (Table 4) and dynamic dilution preparation (Table 5) is presented. All the uncertainty contributions are expressed in percentage with respect to the final value of the combined standard uncertainty.

As for the accuracy in the preparation of the mixtures by means of the two methods, an example can be taken from INRiM results in the participation in the International Key Comparison CCQM-K120 [22]. The goal of this comparison was the preparation of different mixtures by gravimetry, one of which at the nominal amount fractions of 480 μmol/mol with a tolerance of 10 μmol/mol. The mixtures were produced in a dry synthetic air matrix, blended from pure gases that are the main constituents of air. In Fig. 4, it can be seen that the gravimetric mixture prepared for this comparison is well within the requirements of the comparison protocol, and the obtained value differs of less than 1 μmol/mol from the nominal amount fraction. A similar comparison is shown for the mixture prepared by dynamic dilution as an example for this work. Even if there is a higher bias between the nominal and the obtained amount fractions (2.9 μmol/mol), due to set of MFCs used to generate this mixture, the dynamic dilution value is comprised within the tolerance requested by the protocol of the Key Comparison.

## 5. Conclusions and further developments

Gravimetry and dynamic dilution can be used alternatively, or in combination, for the preparation of CO<sub>2</sub> reference mixtures and for their periodical verification, to check the stability of their composition over time.

The versatility of the dynamic dilution makes this technique useful in particular cases, as with reactive or unstable species, despite the larger preparation uncertainties. The dynamic dilution can be employed to calibrate CO<sub>2</sub> analysers and sensors, to validate calibration curves and to assign analytical values in the stability study of CO<sub>2</sub> gas mixtures prepared by gravimetry in high-pressure cylinders.

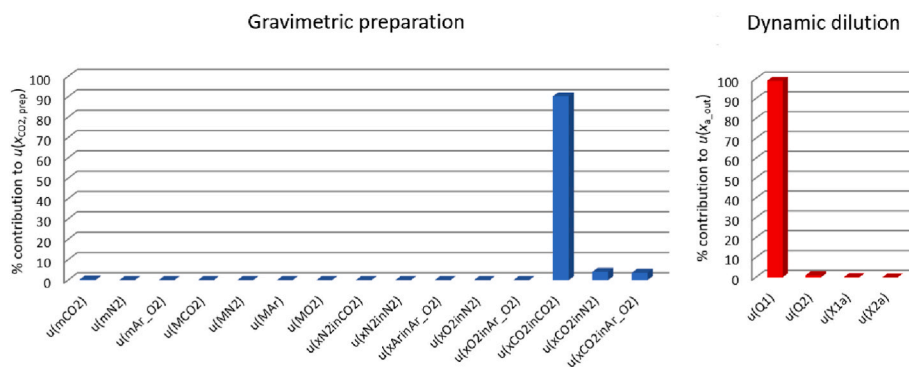


Fig. 3. Squared uncertainty contributions in percent, with respect to the squared combined standard uncertainty for the preparation of reference gas mixtures by gravimetry and dynamic dilution.

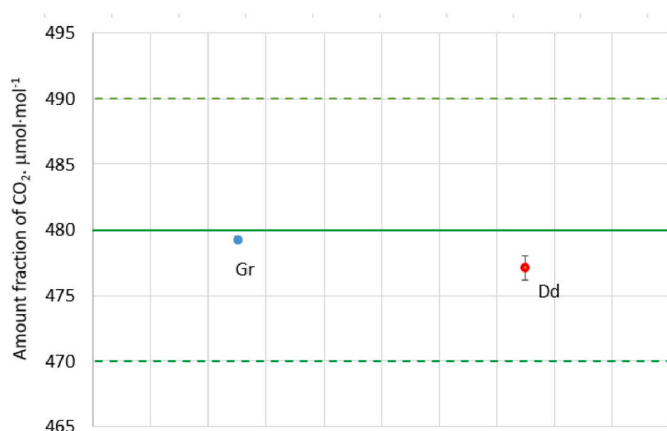


Fig. 4. Values of the reference gas mixtures prepared by gravimetry and by dynamic dilution, compared with the nominal amount fraction (green line), requested by the protocol of the International Key Comparison CCQM-K120 [22]. In blue, the gravimetric value of the mixture prepared for the comparison; in red, the value obtained for a mixture generated by dynamic dilution, here reported as an example. Both values are comprised within the tolerance requested by the protocol of the Key Comparison [22]. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

In particular, gravimetry can assure preparation uncertainties close to the ones necessary to support the network compatibility goals of WMO/GAW for  $\text{CO}_2$  ( $\pm 0.1 \mu\text{mol}/\text{mol}$  in the Northern Hemisphere and  $\pm 0.05 \mu\text{mol}/\text{mol}$  in the Southern Hemisphere) [23]. At the European level, a new monitoring system of emissions is under development in the framework of the Copernicus Atmosphere Monitoring Service (CAMS) [24]. This monitoring system, the “Copernicus anthropogenic  $\text{CO}_2$  emissions monitoring & verification support capacity”, will link the changes in observed atmospheric  $\text{CO}_2$  to the ones in emissions near the surface.

In addition, this system will also benefit from the monitoring of other pollutants emitted from the same source (e.g.  $\text{NO}_x$  and CO from fossil fuel combustion), to help discriminate between man-made and natural  $\text{CO}_2$  sources and sinks. In this framework, it is of paramount importance the availability of fit-for-purpose reference gas mixtures and CRMs produced by primary methods.

Apart from these typical applications, reference gas mixtures can be used for the calibration of semiconductor sensors, metal oxide-based sensors, whose applications are diverse, ranging from environmental monitoring to industrial process control. In the area of air pollution control and industrial hygiene, there has been a new significant impetus for optimised methods to produce reference gas mixtures, particularly at low concentration levels of various components [25].

Another possible exploitation of  $\text{CO}_2$  reference mixtures is in the marine research field, for  $p\text{CO}_2$  monitoring.  $p\text{CO}_2$  is an essential ocean variable and indicates the fractional pressure of  $\text{CO}_2$  as a function of its concentration in gas or dissolved phases. Together with the measurement of pH, dissolved inorganic carbon, and alkalinity, it is used to describe the inorganic carbon system of oceans. Also in the case of seawater  $p\text{CO}_2$  sensors, reference gas mixtures are required for the measurements of the absorbance of a specific infrared wavelength by  $\text{CO}_2$  molecules in the gaseous headspace, where liquid and gas are at equilibration.

The availability of methods for the preparation and certification of reference gas mixtures is essential to guarantee the reliability of data acquisition in many fields, also when dealing with sensors and sensors networks. Gravimetry and dynamic dilution, with their different features, represents two complementary approaches to support the establishment of metrological traceability and the quality of measurement results.

#### Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

Francesca Rolle reports financial support was provided by EURAMET European Metrology Programme for Innovation and Research. Francesca Rolle reports a relationship with EURAMET European Metrology Programme for Innovation and Research that includes: funding grants.

#### Data availability

Data will be made available on request.

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