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Realisation and preliminary validation of a dilution device for the generation of CO₂ gas mixtures

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ABSTRACT

The present paper describes the activity carried out at Istituto Nazionale di Ricerca Metrologica (INRIM) within the EMPIR Joint Research Project 16ENV06 “Metrology for Stable Isotope Reference Standards - SIRS”, for the realisation of a dilution device for generating dynamic mixtures of CO₂ at ambient mole fractions.

The aim of the activity was to realise a system able to generate mixtures with isotopic composition and target uncertainties as the static gravimetric reference materials realised in the SIRS project. These dynamic reference materials can be used to validate the static reference materials and for stability and fractionation studies.

The dilution system was realised and a preliminary validation was carried out, focusing on the performances of the mixing chamber, which represents the core of the system. The system was tested in terms of amount fraction, by using a Non-Dispersive Infrared analyser.

1. Scope of the work

The reduction of the emissions of the greenhouse gases, such as carbon dioxide (CO₂) is of utmost importance in order to counteract the phenomenon of global warming. The levels of CO₂ in the atmosphere have reached values never observed in the past eras, and this is mainly attributable to human activities. It is thus necessary to reliably measure the amount of CO₂ emitted in atmosphere, discriminating the anthropogenic sources from the natural contributions and also discerning emissions coming from different productive sectors. A method to distinguish the different origins of CO₂ consists in the measurement of its isotopic composition by means of the measurement of the stable isotope ratios of this gas (¹²C and ¹³C, ¹⁶O and ¹⁸O).

An important point is represented by the need to apply the metrological concepts to this kind of measurements and to establish correct traceability chains, by relying on the availability of gaseous reference materials and suitable analytical methods. These activities are of fundamental importance to support the studies and the monitoring of climate changes.

In this framework, some research activities had started at Istituto Nazionale di Ricerca Metrologica (INRIM), within the EMPIR Joint Research Project 16ENV06 “Metrology for Stable Isotope Reference Standards - SIRS” [1], which ended in November 2020, and are continuing within the follow-up European Joint Research Project “Stable isotope metrology to enable climate action and regulation – STELLAR” [2], started in September 2020. One of the activities carried out at INRIM consists in the set-up and validation of a dynamic dilution system, made up of several Mass Flow Controllers (MFCs) in the range 100–2000 SCCM, to realise gas mixtures of CO₂ at atmospheric amount fraction (400–500 μmol mol^{−1}) having isotopic composition in the range (−48 to −8) ‰ vs VPDB for δ¹³C and (−27 to +2) ‰ vs VPDB for δ¹⁸O. This system is intended to combine in a flexible way MFCs having different flow ranges, to realise “ready-to-use” gas mixtures, both for the

calibration of the analytical instrumentation (Non-Dispersive Infrared - NDIR and Fourier Transform Infrared - FTIR spectrometers) and for the verification of the static CO₂ mixtures realised in high pressure cylinders by gravimetry, based on previous experiences in the field [3–6]. The use of dynamically generated reference gases to verify the static gas mixtures is very convenient in terms of flexibility, time and gas consumption, and allows obtaining a wider range of amount fractions and isotopic values with respect to the preparation of the single static mixtures. Due to the wide range of concentrations that can be obtained by mixing two gas mixtures, the dilution system results in a powerful tool for situations that request the use of many gas mixtures. The accuracy of the generated mixtures, and the relative standard uncertainties, are analogous to those of the gravimetric mixtures, being in the range (0.5–0.01) % and decreasing with increasing amount fractions. The uncertainties for the isotopic mixtures generated with the novel dilution system here described will be evaluated at the complete validation of the system and are not subject of the present work.

In the present paper, the preliminary validation of the dilution system is described, which was focused in particular on the performances of the mixing chamber, the core of the system. As a first step, the system was tested in terms of amount fraction, by using a NDIR analyser. The first validation aimed at testing the performance of the system to realise repeatable dynamic mixtures with values close to the nominal ones, which is a fundamental point for all the subsequent applications to isotope ratio measurements. The CO₂ mixtures at ambient amount fraction, produced inside the chamber proved to be repeatable with standard deviation of (0.16–0.20) μmol mol^{−1}.

2. Main features of the system

The device is composed of a set of MFCs (MKS Instruments, USA) provided with a corresponding set of valves (Swagelok, USA) and a mixing chamber aimed at maximizing the mixing of gases. The MFCs

used are traceable to the Italian gas flow rate primary standard of INRIM. An important feature of the mixing chamber is the equalization of feed pressures in order to avoid phenomena of counter pressure or variable pressure load, which could lead to irregular mixing and therefore irregular composition of the diluted gas. The MFCs used in the first validation tests have a full-scale range of 500 SCCM and 2000 SCCM. The complete device will be installed on a table provided with all relevant elements stably positioned and with the possibility of calibrating the MFCs while on the table, in order to minimize installation effects. All the components of the dilution device are made of stainless steel type AISI 304L.

Fig. 1 shows the mixing chamber design, Fig. 2 the real mixing chamber. Two couples of inlets were mounted, in order to test two different configurations for the inlet flows: 1) counter-flow configuration and 2) axial configuration.

At an early stage, active pressure controls were proposed, but after a preliminary evaluation, they showed the risk of generating a positive feedback loop with the MFCs, which would have prevented a stable flow condition. It was therefore decided to replace them with a passive pressure control, consisting in grids inserted between the MFCs and the mixing chamber, inside the inlet branches. The resistance introduced by the grid stabilizes the pressure on the exit of the MFCs and consequently the flow. In Fig. 3, a schematic representation of the dilution system is shown. Two parent cylinders, usually a CO₂ “mother cylinder” at higher amount fraction and CO₂-free synthetic air, can be connected to the MFCs. The pressure drops 1 and 2 are located inside the inlet branches.

3. Preliminary validation of the dilution system

The validation of the dilution system was carried out by analysing the prepared dynamic mixtures by means of a NDIR analyser (Advance Optima URAS 14, ABB, Switzerland), operating in the range 1–1000 $\mu\text{mol mol}^{-1}$.

Several tests were performed by diluting different CO₂ parent mixtures prepared by gravimetry and traceable to calibrated mass standards, having nominal amount fractions around 5000 $\mu\text{mol mol}^{-1}$ in nitrogen (N₂) and synthetic air (SA). The dilutions were chosen to reach amount fractions of around 400 $\mu\text{mol mol}^{-1}$, which are summarised in Table 1, together with the relevant working conditions and system configurations.

3.1. Tests on “counter-flow” configuration

The first tests of the performances of the dilutor were carried out on the “counter-flow” configuration by diluting a CO₂ in N₂ parent mixture at 5000.2 $\mu\text{mol mol}^{-1}$ with pure 6.0 N₂ (Nippon Gases). The measurements were carried out continuously (Table 1, line 1). As an example, a



Fig. 1. Design of the mixing chamber of the dilution system (counter-flow inlets not shown).

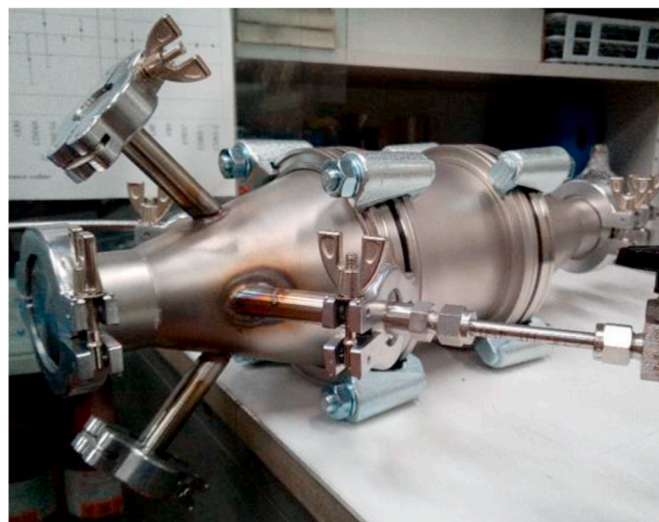


Fig. 2. The mixing chamber of the dilution system.

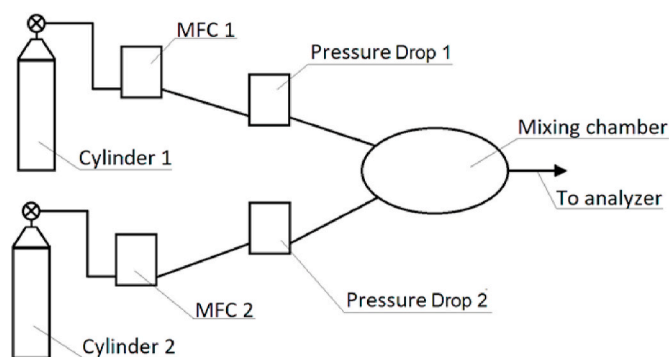


Fig. 3. Schematic representation of the dilution system.

Table 1

Summary of the tests carried out on the dilution system.

| | CO ₂ amount fraction ($\mu\text{mol mol}^{-1}$) | Matrix gas | Working conditions | Configuration of the system |
|---|--|----------------|--|-----------------------------|
| 1 | 399.1 | N ₂ | Continuous flow | Counter-flow |
| 2 | 396.9 | N ₂ | Flushing between subsequent measurements | Counter-flow |
| 3 | 399.9 | SA | Flushing between subsequent measurements | Counter-flow |
| 4 | 398.5 | SA | Flushing between subsequent measurements | Axial |
| 5 | 399.9 | SA | Flushing prior to and between measurements | Counter-flow |
| 6 | 400.0 | SA | Flushing prior to and between measurements | Counter-flow |

measurement sequence is shown in Fig. 4. Relevant statistics are reported in Table 2 (first line).

Further analyses were carried out by alternating each measurement with a pure N₂ flow for 10 seconds (Table 1, line 2) and, in this way, the standard deviation of the measurements improved (see for statistics Table 2, second line).

The performance of the dilution system was also tested by preparing mixtures in a synthetic air matrix, starting from a parent mixture of CO₂ in SA having an amount fraction of 4976 $\mu\text{mol mol}^{-1}$, that was diluted

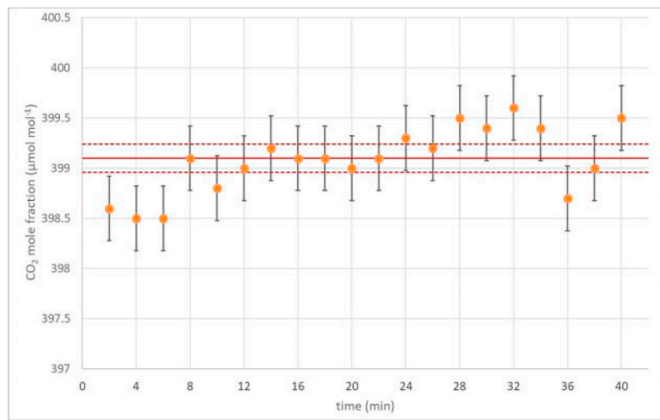


Fig. 4. Measurement results for the dilution of a CO₂ in N₂ mixture. The error bars are the standard deviation ($k = 1$) of the measurement sequence. The solid red line represents the mean value of the measurements and the dotted red lines are the expanded standard deviation of the mean ($k = 2$). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

Table 2

Summary of the results obtained for the “counter-flow” configuration, with a CO₂ in N₂ parent mixture.

| | Mean Value ($\mu\text{mol mol}^{-1}$) | Std Deviation ($\mu\text{mol mol}^{-1}$) | Std Dev of the mean ($\mu\text{mol mol}^{-1}$) | Max-Min Value ($\mu\text{mol mol}^{-1}$) |
|--|--|---|---|--|
| CO ₂ in N ₂ (continuous) | 399.1 | 0.32 | 0.07 | 1.1 |
| CO ₂ in N ₂ (with flushing) | 396.9 | 0.19 | 0.04 | 0.7 |

with N57 grade (99.9997 %) synthetic air, to amount fraction values around 400 $\mu\text{mol mol}^{-1}$ (Table 1, lines 3–6). An example of measurement sequence is shown in Fig. 5. The results are summarised in Table 3.

In the presented cases, all the measurements were consistent with their mean value, considered with its expanded standard deviation, within twice the standard deviation of the sequence, hence showing no evident outlier or anomaly.

The “counter-flow” configuration was tested again, to confirm the results previously obtained. The dilution system was flushed with SA for 20–25 min before starting the measurement sequence. SA was also flushed for 10 seconds between subsequent measurements. Two measurement sequences acquired in different days are shown in Figs. 6 and 7.

As it can be seen from Figs. 6 and 7 and from Table 3, a good repeatability was obtained with the counter-flow configuration and the preliminary flushing of the chamber. A good inter-day repeatability was also obtained, by repeating the same measurement sequence in different days. Most of the values are consistent with the mean value of the relevant measurement sequence, to the extent to which their error bars (at coverage factor $k = 1$) overlap the interval of the expanded standard deviation of the mean. Moreover, they all result to be encompassed in the arithmetic mean plus or minus twice the standard deviation of the sequence.

3.2. Tests on “axial” configuration

The axial configuration of the dilution system was tested only with the parent mixture in SA (4976 $\mu\text{mol mol}^{-1}$), diluted with N57 grade SA, that was flushed for 10 s between subsequent readings. The final mole fraction was 398.5 $\mu\text{mol mol}^{-1}$. It was observed that the axial configuration gave higher values of standard deviation (see Table 3, line 1). An

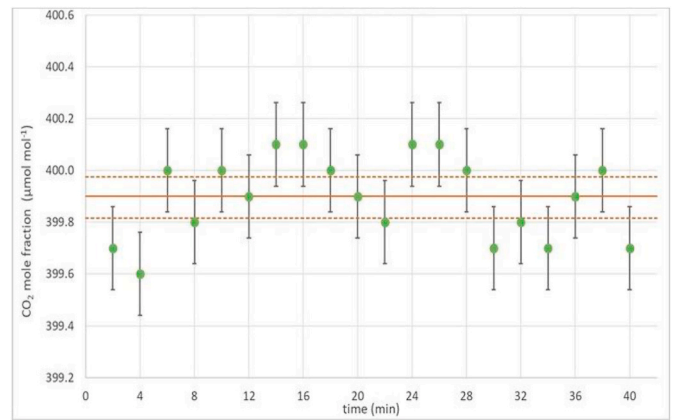


Fig. 5. Measurement results for the dilution of a CO₂ in SA mixture. The error bars are the standard deviation ($k = 1$) of the measurement sequence. The solid red line represents the mean value of the measurements and the dotted red lines are the expanded standard deviation of the mean ($k = 2$). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

Table 3

Summary of the results obtained for the “axial” and “counter-flow” configuration, by diluting a parent mixture of CO₂ in SA (4976 $\mu\text{mol mol}^{-1}$) with N57 grade synthetic air.

| | Mean Value ($\mu\text{mol mol}^{-1}$) | Std Deviation ($\mu\text{mol mol}^{-1}$) | Std Dev of the mean ($\mu\text{mol mol}^{-1}$) | Max-Min Value ($\mu\text{mol mol}^{-1}$) |
|---|--|---|---|--|
| CO ₂ in SA (axial) | 398.5 | 0.38 | 0.10 | 1.5 |
| CO ₂ in SA (counter-flow, with flushing) | 399.9 | 0.16 | 0.04 | 0.5 |
| CO ₂ in SA (counter-flow day 1) | 399.9 | 0.20 | 0.05 | 0.6 |
| CO ₂ in SA (counter-flow day 2) | 400.0 | 0.18 | 0.04 | 0.6 |

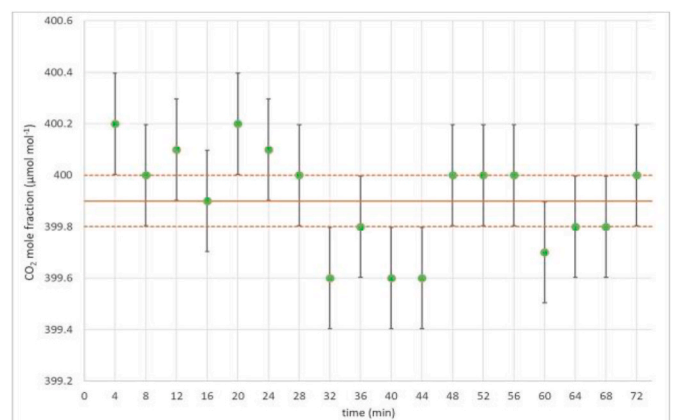


Fig. 6. Measurements carried out with counter-flow configuration. The error bars are the standard deviation ($k = 1$) of the measurement sequence. The solid red line represents the mean value of the measurements and the dotted red lines are the standard deviation of the mean ($k = 2$). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

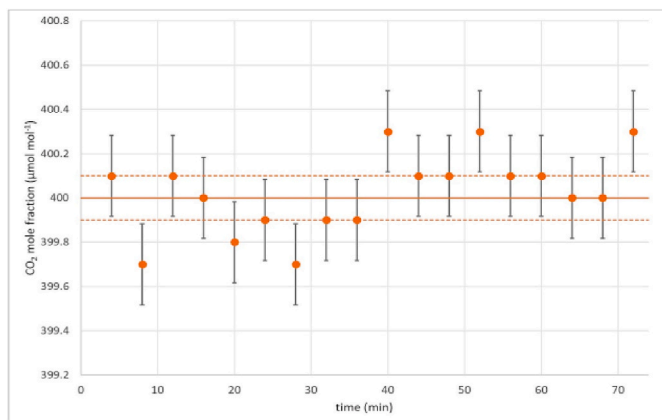


Fig. 7. Sequence of measurements carried out in the same conditions of the sequence in Fig. 6, but on a different day.

example of measurements with the axial configuration is shown in Fig. 8. A comparison of the results obtained with the two different configurations for the CO₂ in SA is shown in Table 3.

4. Conclusions

The preliminary validation of the new dilution system developed at INRIM was focused on the performances of the mixing chamber, which represents the core of the system. The CO₂ mixtures at ambient amount fraction, produced inside the chamber, proved to be repeatable with standard deviations of (0.16–0.20) μmol mol^{−1} by using the “counter-flow” configuration and a flushing step prior to the measurement sequence.

As a general comment concerning Figs. 4–8, it is worth noting that most of the values are consistent with the mean value of the relevant measurement sequence, to the extent to which their error bars (at coverage factor $k = 1$) overlap the interval of the expanded standard deviation of the mean. Moreover, they all result to be encompassed in the arithmetic mean plus or minus twice the standard deviation of the sequence, hence indicating a good repeatability.

Further work will be aimed to test the capabilities of the system with

different MFCs and to improve the standard deviation of the mixtures produced by using the “axial” configuration, by introducing a different passive pressure control (thicker grids between the MFCs and the mixing chamber) so to increase the stabilisation of the parent flows.

Due to the encouraging results obtained, further developments will be the application of the dynamic dilution system to the generation of CO₂ mixtures with the desired isotopic composition, by mixing two CO₂ in air parent mixtures at known isotopic composition. The dynamic mixtures could be used to validate the static reference materials prepared in the SIRS and STELLAR projects, and for stability and fractionation studies. This particular application is fundamental to distinguish the different origins of CO₂ by measuring its isotopic composition.

Acknowledgments

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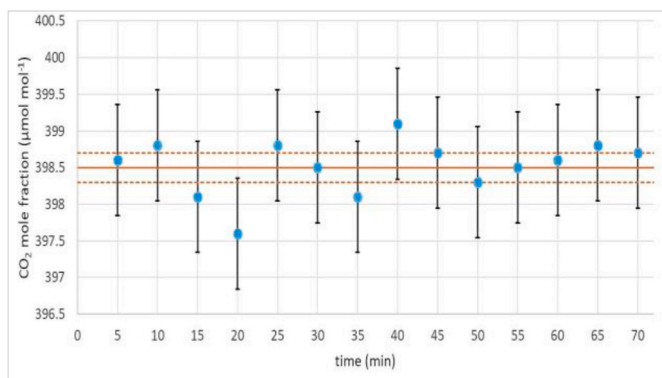


Fig. 8. Measurement results for the dilution of a CO₂ in SA mixture with “axial” configuration. The error bars are the standard deviation ($k = 1$) of the measurement sequence. The solid red line represents the mean value of the measurements and the dotted red lines are the expanded standard deviation of the mean ($k = 2$). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)