Generation of CO2 gas mixtures by dynamic dilution for the development of gaseous
certified reference materials

(Article begins on next page)

12 August 2023

Measurement: Sensors

Generation of CO_2 gas mixtures by dynamic dilution for the development of gaseous certified reference materials

Francesca Rolle [*], Francesca Durbiano, Francesca Romana Pennecchi, Stefano Pavarelli, Marco Santiano, Pier Giorgio Spazzini, Michela Sega

Istituto Nazionale di Ricerca Metrologica (INRIM), Torino, Italy

ARTICLE INFO

ABSTRACT

The use of Certified Reference Materials (CRMs) is of utmost importance to achieve the comparability and traceability of data, which are essential features of measurement results in environmental and climate fields. The present paper focuses on the generation of gas mixtures at known composition of carbon dioxide at atmospheric amount-of-substance fraction in synthetic air by means of a dynamic dilution system, designed and implemented at the Istituto Nazionale di Ricerca Metrologica (INRiM). The validation of the dynamic system in terms of amount-of-substance fraction is presented. The system was also used to verify the carbon dioxide amount-of-substance fraction of a suite of gas mixtures gravimetrically prepared at INRiM in the framework of the EMPIR Joint Research Project 19ENV05 – STELLAR. Dynamic dilution proved to be an effective tool for the preparation and certification of CRMs for gaseous pollutants (i.e. carbon dioxide, nitrogen oxides) relevant for monitoring environmental pollution and climate changes.

1. Introduction

The increase of greenhouse gases (GHGs) concentration in the atmosphere due to anthropogenic emissions has been the major driver of climate change since the mid-twentieth century [1,2]. Carbon dioxide (CO_2) is one of the most important GHGs and contributes to the so-called enhanced greenhouse effect. Its concentration has grown continuously reaching an annual average of 410 μmol·mol^{-1} in 2019.

The studies on climate change, the development of models to predict future scenarios and to put into action effective measures to counteract the phenomenon of global warming, rely on accurate and sound determination of the atmospheric concentration of GHGs. An important point is represented by the need to treat these measurements by a fully metrological approach and to establish for them appropriate traceability chains. For that purpose, availability of gaseous reference materials (RMs) is an essential requirement. In this framework, INRiM has a consolidated experience in the preparation of reference gas mixtures of CO_2 in air at atmospheric amount-of-substance fraction (amount fraction in the following) by gravimetry as candidate Certified Reference Materials (CRMs) [3–5]. The in-house prepared reference gas mixtures were used to participate in international key comparisons organised under the umbrella of the Consultative Committee for Amount of

Substance: Metrology in Chemistry and Biology (CCQM) of the International Committee for Weights and Measures (CIPM) [6,7].

The gravimetric preparation is the most widely applied method to produce gaseous RMs and CRMs in high pressure cylinders [8]. It is a primary direct method that gives direct traceability to mass, provided that the prepared mixtures are verified against independent reference gas mixtures by means of specific analysers calibrated under metrological traceability conditions and the purity of parent gases is assessed. The crucial steps of the gravimetric method consist in the determination of the masses of gas added in the cylinders and the conversion of these masses to amount of substance. This second step relies on the knowledge of the chemical purity of the gases used and appropriate relative atomic/molecular masses. Gas purity is indeed a crucial step, and the presence of significant impurities in the parent materials should be evaluated and minimised.

On the other hand, dynamic dilution is a promising technique to generate ready-to-use reference gas standards, by mixing two gases together in order to reach the desired amount fraction, starting from a more concentrated gas mixture and a matrix gas. It is complementary to gravimetry as it can be applied also to generate gas mixtures with unstable and/or reactive components. Due to its features, it is less demanding and time consuming with respect to gravimetric
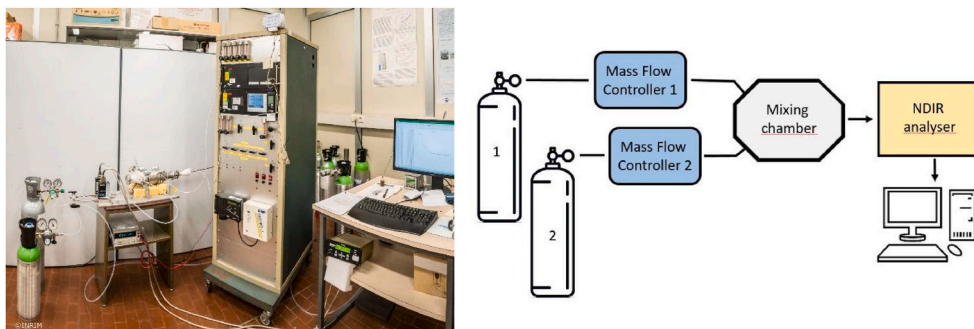
Fig. 1. INRiM measurement system for the preparation of gas mixtures by dynamic dilution: a) left: photo of the real set-up; b) right: schematic representation of the system.

Table 1
Compositions and associated uncertainties of three dynamic mixtures prepared at INRiM.

Mixture	CO_2 amount fraction χ μmol·mol^{-1}	Expanded uncertainty $U(\chi)$ ($k = 2$) μmol·mol^{-1}
1	250.4	1.0
2	411.4	1.0
3	546.8	1.0

preparation, however it might lead to larger uncertainties. The mixtures generated by dynamic dilution can be used for instrumental calibration, hence are also useful to check and verify gas standards prepared by gravimetry [9,10]. 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 to obtain a wider range of amount fractions with respect to the preparation of the single static mixtures. Due to the wide range of amount fractions 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 the ones of the gravimetric mixtures, being in the range (0.5–0.01) % and decreasing with increasing amount fractions.

A dilution system was developed at INRiM in the framework of the EMPIR Joint Research Project 16ENV06 "Metrology for Stable Isotope Reference Standards - SIRS" [11] and preliminarily validated mainly in terms of repeatability [12]. The present work deals with a further validation of the system in terms of CO_2 amount fraction of the generated mixtures. A set of dynamic mixtures was prepared and readily used to calibrate a non-dispersive infrared analyser (NDIR) in the range (250–550) μmol·mol^{-1}. The obtained calibration curve was validated by using an independent mixture purchased from the National Physical Laboratory (NPL, UK). The calibrated analyser was in turn used to check the composition of primary mixtures of CO_2 in synthetic air at nominal amount fraction of 410 μmol·mol^{-1}, gravimetrically prepared at INRiM in the framework of the EMPIR Joint Research Project 19ENV05 "Stable isotope metrology to enable climate action and regulation – STELLAR" [13]. The obtained satisfactory results confirmed the good performance of the dilution system and the reliability of the gravimetric preparation process.

Table 2
Analytical values of the control mixture recalculated on different calibration curves, with the associated expanded uncertainty ($k = 2$).

Calibration curve	CO_2 amount fraction, χ μmol·mol^{-1}	Expanded uncertainty, $U(\chi)$ ($k = 2$) μmol·mol^{-1}
1	399.6	1.3
2	399.3	1.4
3	400.1	1.1

2. Materials and methods

The dilution system is composed of a mixing chamber coupled with a set of Mass Flow Controllers (MFCs) (MKS Instruments, USA) and a set of valves (Swagelok, USA). The chamber, designed at INRiM, is made of stainless steel type AISI 304L and its design aims at maximising the mixing of gases. A full description of the device is available in [12]. A picture and a scheme of the complete measurement system are shown in Fig. 1.

In the present work, two MFCs with full-scale range of 500 standard cubic centimetres (SCCM) and 2000 SCCM, respectively, were used. A parent mixture of CO_2 in synthetic air at the amount fraction of 4987.6 μmol·mol^{-1} (mixture code: INRiM 080, cylinder S/N D206743), gravimetrically prepared at INRiM, was diluted with synthetic air zero grade (Sapio, Italy) to generate three dynamic mixtures of CO_2 in the range (250–550) μmol·mol^{-1}. Their compositions and the associated uncertainties are reported in Table 1.

The expanded uncertainties in Table 1 were obtained by taking into account the uncertainty of the parent mixture used for the dilution and the calibration uncertainty of the MFCs used to generate the dynamic mixtures.

The dynamic mixtures were used to calibrate a Non-Dispersive Infrared (NDIR) analyser (Advance Optima URAS 14, ABB, Switzerland), operating in the range (1–1000) μmol·mol^{-1}. The calibration curve was validated by analysing an independent primary gas mixture of CO_2 in synthetic air (S/N 2407, NPL, UK) having CO_2 amount fraction of 399.57 μmol·mol^{-1} and an associated expanded ($k = 2$) uncertainty of 0.40 μmol·mol^{-1}, used as a control mixture. The entire process was repeated three times on different days. The obtained results are reported in Section 3.

The calibrated NDIR analyser was then used to verify the composition of a suite of primary mixtures gravimetrically prepared at INRiM (see par. 3.2), having nominal CO_2 amount fraction of 410 μmol·mol^{-1}. This value was chosen by considering the present concentration levels reached by CO_2 in the atmosphere, as reported in Section 1.

3. Results and discussion

3.1. Validation of calibration curves

Three different calibrations of the NDIR analyser in the range (250–550) μmol·mol^{-1} of CO_2 were carried out on different days by using the dynamic dilution device to generate three CO_2 standard mixtures having the characteristics reported in Table 1. The data were fitted by a straight line using an algorithm based on Weighted Least Squares (WLS) regression [14]. The calibration curves were validated by analysing the independent control mixture, having a CO_2 amount fraction value in the middle of the calibration range. The control mixture was analysed as an unknown sample and its CO_2 amount fraction was estimated starting from the corresponding instrumental reading and using
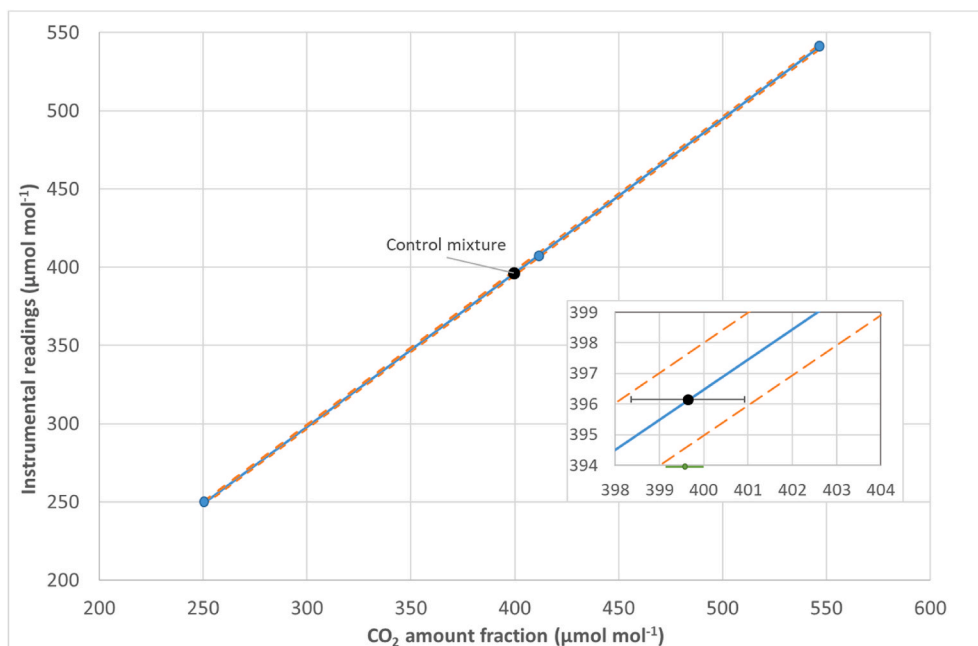
Fig. 2. Example of calibration curve of the NDIR analyser obtained by dynamic dilution in the CO_2 amount fraction range (250–550) $\mu mol \cdot mol^{-1}$. The expanded uncertainty interval ($k = 2$, for a confidence level of approximately 95%) is reported as orange dotted lines. The black dot denotes the control mixture used to validate the calibration curve, while the green dot denotes its certified value. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

Table 3
Values of the normalised error E_n for the three NDIR calibration curves.

Calibration curve	E_n
1	0.06
2	−0.19
3	0.50

Table 4
Compositions and associated uncertainties of the suite of gravimetric CO_2 mixtures prepared at INRiM in the framework of the STELLAR project.

Mixture code	CO_2 gravimetric amount fraction, χ $\mu mol \cdot mol^{-1}$	Expanded uncertainty, $U(\chi)$ ($k = 2$) $\mu mol \cdot mol^{-1}$
INRiM STELLAR 005 (S/N 12882)	409.49	0.40
INRiM STELLAR 006 (S/N 12997)	409.46	0.40
INRiM STELLAR 007 (S/N 12999)	410.00	0.40
INRiM STELLAR 010 (S/N 12998)	410.85	0.40
INRiM STELLAR 011 (S/N 16992)	411.39	0.40

the inverse of the calibration curve [[15] §2.39], thus obtaining its analytical value. This value was compared with the certified value of the control mixture and its associated uncertainty. The analytical values of the control mixture recalculated on different calibration curves are reported in Table 2 and an example of a calibration curve is presented in Fig. 2.

The zoomed-in square of Fig. 2 shows the analytical value of the control mixture (black dot) and the certified value (green dot), both with their associated expanded uncertainties (the green bar reported on the *x*-axis is for comparison purposes, its *y*-value having no physical relevance). A very good consistency between the two results within their expanded uncertainties can be observed, thus indicating the validation of the calibration curve. Similar results were obtained for all the three calibration curves.

In order to further demonstrate the validation of the calibration curves the normalised error E_n was calculated for each curve by applying the following equation (eq. (1)):

$$E_n = d/U(d) \tag{1}$$

where $d = (\chi_{\text{Analytical}} - \chi_{\text{Certified}})$ is the difference between the amount fraction value recalculated by applying the calibration curve ($\chi_{\text{Analytical}}$) and the value certified by NPL ($\chi_{\text{Certified}}$), and $U(d) = U(\chi_{\text{Analytical}} - \chi_{\text{Certified}})$ indicates the expanded uncertainty of the difference d at a 95 % confidence ($k = 2$).

The calibration curve is considered validated if the value of E_n falls between ±1 ($-1 \leq E_n \leq 1$). Table 3 reports the values of E_n for the three different calibration curves.

The results reported in Table 3 show that satisfactory values of E_n were obtained for the three cases, highlighting an excellent agreement between the certified value of the control mixture and its analytical value. Such agreement demonstrates the capability of the dilution

system to generate reliable dynamic mixtures in the amount fraction range under consideration. Furthermore, since the E_n values are in some cases positive and in some cases negative, the absence of a systematic error in the analytical verification with respect to the certified value was demonstrated. The validation of calibration curves with an independent mixture is a fundamental step to guarantee the reliability of the subsequent verifications of the gravimetric mixtures produced in-house, as discussed in Section 3.2.

3.2. Verification of gravimetric gas mixtures

Considering the satisfactory results in the assessment of the dynamic dilution system as reported in Section 3.1, the calibrated NDIR analyser was used to verify a suite of primary reference gas mixtures of CO_2 in synthetic air gravimetrically prepared at INRiM, having the composition reported in Table 4. Such an approach is very effective as it relies on the use of two different and independent methods for mixture preparation. These gravimetric mixtures were prepared in the framework of the STELLAR project [13]. Their validation aimed at verifying their CO_2 amount fraction and confirming the gravimetric process.

The verification was carried out on three different days, by generating three calibration curves with the dynamic mixtures reported in Table 1. The values of the gravimetric preparation and the corresponding analytical verification by NDIR for each mixture were

Table 5
Values of the analytical verification, $\chi_{\text{Analytical}}$, and normalised error, E_n, for the suite of INRiM gravimetric mixtures.

Mixture code	CO_2 amount fraction, $\chi_{\text{Analytical}}$ µmol·mol^{-1}	Expanded uncertainty, U ($\chi_{\text{Analytical}}$) ($k = 2$) µmol·mol^{-1}	E_n
INRiM STELLAR 005 (S/N 12,882)	409.5	1.3	0.00
INRiM STELLAR 006 (S/N 12,997)	409.4	1.3	−0.04
INRiM STELLAR 007 (S/N 12,999)	409.4	1.4	−0.41
INRiM STELLAR 010 (S/N 12,998)	411.1	1.1	0.21
INRiM STELLAR 011 (S/N 16,992)	411.3	1.1	−0.08

compared by applying Eq. (1). The analytical values obtained from the verification and the E_n values are reported in Table 5.

According to Table 5, the analytical verifications gave satisfactory E_n values for all the mixtures, thus confirming the rightness of the gravimetric preparation. In addition, it is demonstrated that there is no evidence of bias between the dilution method and the gravimetric one, as the E_n showed some positive and some negative values. These achievements are promising in the perspective of the use of the dynamic system to carry out periodic verifications of the gravimetric mixtures produced at INRiM, in order to check their medium and long term stability, which is a fundamental requirement to support the production of gaseous CRMs.

4. Conclusions

The use of the dynamic dilution for the generation of reference gas mixtures represents a useful tool due to its high flexibility in terms of amount fractions of the prepared mixtures. This flexibility can be exploited for the calibration of analytical instrumentation, as shown in the present paper, in particular being the gravimetric process more demanding and time consuming. Satisfactory results were obtained for the NDIR calibration and the validation of the calibration curves, showing good performances of the dilution system realised at INRiM. In addition, the NDIR analyser calibrated via dynamic dilution was used to verify a suite of primary reference gas mixtures of CO_2 in synthetic air gravimetrically prepared at INRiM within the framework of the STELLAR project, demonstrating a very good agreement between the analytical and gravimetric values.

Further activity will concern the use of the dynamic system for checking the medium and long term stability of the gravimetric mixtures produced at INRiM. This requirement is fundamental to support the production of gaseous CRMs. Future applications of the system are also foreseen in the generation of gas mixtures of CO_2 at ambient amount fractions in air at known isotopic composition within the STELLAR project. The developed dilution system will allow the generation of ready-to-use CO_2 mixtures at different isotopic composition, in the $\delta^{13}C$ range (+1 to −42) ‰ $_{\text{VPDB}}$, by mixing different CO_2 sources in a versatile and flexible way.

CRediT authorship contribution statement

Francesca Rolle: Writing – original draft, Writing – review & editing, Validation. **Francesca Durbiano:** Writing – original draft, Writing –

review & editing. **Francesca Romana Pennecchi:** Formal analysis, Writing – review & editing. **Stefano Pavarelli:** Software. **Marco Santiano:** Methodology. **Pier Giorgio Spazzini:** Methodology, Writing – review & editing. **Michela Sega:** Writing – original draft, Writing – review & editing, Supervision.

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.

Acknowledgements

References

[1] WMO-No. 1264, State of the Global Climate 2020" World Meteorological Organization, WMO), Geneva, Switzerland), 2021.
[2] Climate Change 2021, in: V. Masson-Delmotte, P. Zhai, A. Pirani, S.L. Connors, C. Péan, S. Berger, N. Caud, Y. Chen, L. Goldfarb, M.I. Gomis, M. Huang, K. Leitzell, E. Lonnoy, J.B.R. Matthews, T.K. Maycock, T. Waterfield, O. Yelekçi, R. Yu, B. Zhou (Eds.), The Physical Science Basis – Summary for Policymakers. Working Group I Contribution to the Sixth Assessment Report of the Intergovernmental Panel on Climate Change, IPCC, Switzerland, 2021. October.
[3] E. Amico di Meane, M. Plassa, F. Rolle, M. Sega, Metrological traceability in gas analysis at I.N.Ri.M.: gravimetric primary gas mixtures, Accred Qual. Assur. 14 (n° 11) (2009) 607–611.
[4] F. Durbiano, E. Amico di Meane, L. Bergamaschi, C. Boveri, L. Giordani, M. Sega, INRiM contributions in the characterization and certification of reference materials, Measurement 44 (2011) 1381–1388.
[5] F. Rolle, F. Pennecchi, E. Pessana, M. Sega, Production and validation of primary carbon dioxide reference standards at INRIM, in: Proceedings of 18e Congrès International de Métrologie, 2017. Paris, France, 19-22 September.
[6] E. Flores, J. Viallon, T. Choteau, P. Moussay, F. Idrees, R.I. Wielgosz, J. Lee, E. Zalewska, G. Nieuwenkamp, A. van der Veen, L.A. Konopelko, Y.A. Kustikov, A. V. Kolobova, Y.K. Chubchenko, O.V. Efremova, B.I. Zhe, Z. Zhou, W.R. Miller Jr., G. C. Rhoderick, J.T. Hodge, T. Shimosaka, N. Aoki, B. Hall, P. Brewer, D. Cieciora, M. Sega, T. Macé, J. Fükő, Z. Nagyné Szilágyi, T. Büki, M.I. Jozela, N.G. Ntsasa, N. Leshabane, J. Tshilongo, P. Johri, T. Tarhan, CCQM-K120 (Carbon dioxide at background and urban level), Metrologia 56 (1A) (2019).
[7] R.M. Wessel, A.M.H. van der Veen, P.R. Ziel, P. Steele, R. Langenfelds, M. van der Schoot, D. Smeulders, L. Besley, V.S. da Cunha, Z. Zhou, H. Qiao, H.J. Heine, B. Martin, T. Macé, P.K. Gupta, E. Amico di Meane, M. Sega, F. Rolle, M. Maruyama, K. Kato, N. Matsumoto, J.S. Kim, D.M. Moon, J.B. Lee, F.R. Murillo, C.R. Nambo, M.d.J. Avila Salas, A.P. Castorena, L.A. Konopelko, Y.A. Kustikov, A. V. Kolobova, V.V. Pankratov, O.V. Efremova, S. Musil, F. Chromek, M. Valkova, M. J.T. Milton, G. Vargha, F.R. Guenther, W.R. Miller, A. Botha, J. Tshilongo, I. S. Mokgoro, N. Leshabane, International Comparison CCQM-K52 carbon dioxide in synthetic air, Metrologia 45 (1 A) (2008), 08011.
[8] International Standard ISO 6142-1, Gas Analysis — Preparation of Calibration Gas Mixtures — Part 1: Gravimetric Method for Class I Mixtures, International Organization for Standardization, 2015.
[9] M. Sega, F. Pennecchi, F. Rolle, P.G. Spazzini, The use of dynamic dilution by Mass Flow Controllers in the environmental monitoring of CO_2: calibration issues and strategies, J. Phys. Conf. 1065 (8) (2018), 082011.
[10] F. Pennecchi, F. Rolle, M. Sega, P.G. Spazzini, I. de Krom, A.M.H. van der Veen, EMUE-D3-3-CalibrationGasMixtures (Version 1.0) [Data Set] Zenodo, 2020.
[11] https://projectsites.vtt.fi/sites/SIRS/. (Accessed 24 March 2022).
[12] F. Rolle, M. Sega, F.R. Pennecchi, P.G. Spazzini, S. Pavarelli, M. Santiano, Realisation and preliminary validation of a dilution device for the generation of CO_2 gas mixtures, Measurement: Sensors 18 (2021), 100242.
[13] http://empir.npl.co.uk/stellarproject/. (Accessed 24 March 2022).
[14] M. Plassa, M. Mosca, M. Sega, Carbon dioxide determination for high accuracy weighings, in: Myung Sai Chung (Ed.), Proceedings of the 16th International Conference IMEKO TC3/APMF '98, Ed., Taejon, Korea, 1998, pp. 183–191.
[15] VIM JCGM 200, in: International Vocabulary of Metrology – Basic and General Concepts and Associated Terms (VIM), third ed., 2012, 2008 version with minor corrections.