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Stability study and uncertainty evaluation of CO_2 certified reference materials for greenhouse gases monitoring

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ABSTRACT

The continuous rising in the concentration of carbon dioxide (CO_2) in the atmosphere is one of the main causes of the increase in the greenhouse effect and global warming. To monitor the alarming scenario and to provide Governments and decision makers with reliable emission data, gaseous certified reference materials (CRMs) at atmospheric CO_2 amount fraction are needed. This paper describes two independent metrological traceability paths established at INRiM for the preparation of this kind of CRMs. The aim of this publication is to show a method for evaluating the uncertainty associated with CRM stability and to demonstrate that there is no significant trend in the results over time. Such CRMs are produced as an intermediate step towards the development of novel generation CRMs certified also for the isotopic composition.

1. Introduction

Economic and population growth, since the pre-industrial era, are the main causes of the continuous increase of anthropogenic activities and, consequently, of greenhouse gases (GHGs) emissions. The associated concentration rise in atmosphere is responsible for the so-called "enhanced greenhouse effect", whose major contributor is carbon dioxide (CO_2) [1–4]. Accurate and sound determinations of the atmospheric concentration of the GHGs, and in particular CO_2, enable the development of models to predict future scenarios and to support the implementation of effective measures to counteract global warming.

To achieve comparability of results over space and time of CO_2 concentration measurements, it is essential to link all the individual measurement results to some common, stable reference or measurement standard [5]. In an increasingly regulated environment, laboratories and agencies formally engaged in the environmental parameters monitoring have to demonstrate that their use of measurement standards and certified reference materials (CRMs) is indeed both appropriate and fit for the purpose. In this context, metrological references represented by gas mixtures at known CO_2 concentration at the atmospheric level are needed to ensure the trustworthiness of the results and to allow their comparability at the international level.

Gas analysis is a sector in which the use of CRMs as measurement standards to calibrate instruments and establish metrological traceability is very wide. Gaseous CRMs are currently used in many fields, like environmental and climate applications [6–8]. Some National Metrology Institutes (NMIs) are already producers of these kind of CRMs [9–14]. CRMs having different characteristics are used in all stages of measurement procedures: the calibration of a measurement system, the value assignment to other materials, the assessment of a measurement procedure, the quality control, etc. [15–17]. Within a single measurement procedure or method, each stage requires different CRMs [5], hence the need of CRMs is constantly growing.

INRiM, the Italian NMI, has a consolidated experience in the preparation of reference gas mixtures, confirmed also by the successful participation in the International Key Comparison CCQM-K120 (Carbon dioxide in synthetic air) [18]. Following the fully implementation of the Quality Management System in compliance with ISO/IEC 17025:2017 [19] and ISO 17034:2016 standards [20] for the certification and production of gaseous CRMs, two new measurement services were recently activated. These CRMs consist of gas mixtures with a certified value of CO_2 amount of substance fraction in the atmospheric range (100–1000) μmol/mol in a matrix of nitrogen (N_2) and/or synthetic air (SA) [21]. Such activity is a necessary starting point towards the development of further CRMs, certified both for CO_2 amount fraction and for isotopic composition, useful to discriminate anthropogenic from natural contributions of CO_2 in the atmosphere, to provide governments and decision makers with reliable emission data.

The stability of a CRM is a critical issue for the assessment of its shelf life, intended as the period of validity of its certificate. The criteria to

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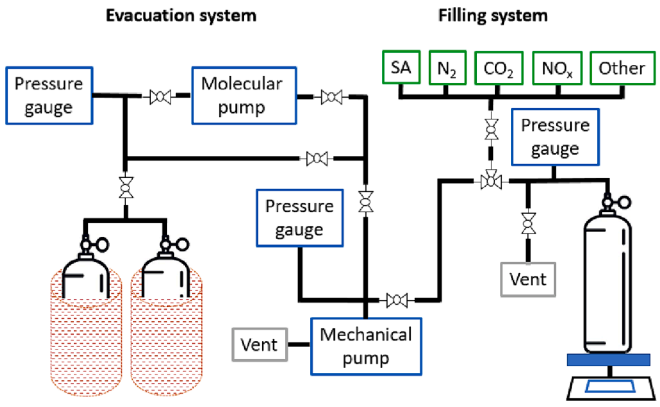

Fig. 1. Scheme of the INRiM emptying/filling station.

carry out stability studies are recalled in the international Standard [20] and described in more detail in ISO Guide 35 [22]. A statistical approach developed at INRiM to estimate the stability of gaseous CRMs and evaluate the associated uncertainty contribution is here presented. To the best of the authors' knowledge, there are few published papers dealing with the evaluation of the stability of gaseous CRMs, related to the amount fraction of gas mixtures, even though CRM producers exist.

This paper is devoted to present the two independent metrological traceability paths needed for the preparation and characterization of CRMs useful for GHG monitoring. Some preliminary data were presented in [21]. This work addresses in a more extensive way the stability study carried out on a larger set of gaseous CRMs. Moreover, the data obtained from the stability studies are assessed by performing linear regression, either neglecting or considering the uncertainties in the historical data, to determine whether there is a significant change in measured values over time. For this purpose, the associated uncertainty was evaluated by applying two different approaches, i.e. the ordinary least squares (OLS) regression and the weighted least squares (WLS) regression. The results obtained by the two approaches were compared and WLS was selected. This latter enables to consider the uncertainties associated with the experimental data attributing a higher weight to the more reliable data. Furthermore, an overall uncertainty is determined for the CRMs, encompassing all principal uncertainty components. The stability study confirmed the absence of a degradation over time for all the considered mixtures.

2. Material and methods

2.1. Characterization of a candidate CRM

CRMs can be prepared by a primary direct method that gives traceability to mass. The estimation of the value assigned to the CRM, the amount fraction value of CO_2 χ_{CRM}, is carried out via gravimetry in accordance with the International Standard ISO 6142–1:2015 [23]. Gas mixtures are prepared in high-pressure cylinders usually made of aluminium alloy (Luxfer, UK) with internal volume of 5 L. The first crucial step in the gas mixture preparation consists in the conditioning process of the cylinder: three repetitions of emptying and filling cycles of the cylinders are carried out with the matrix gas. The emptying/filling station, realised at INRiM, is equipped with a vacuum system composed of a mechanical pump for the pre-vacuum and a turbomolecular pump to achieve a high level of vacuum (5.0×10^{-5} mbar). Moreover, it includes five lines devoted to various types of gases: SA matrix gas, N_2 matrix gas, carbon oxides, nitrogen oxides and possible other types of gas. The pipelines are realised in stainless steel. A set of lubricant-free Swagelok valves are positioned in the lines to actively control the gas flow at the entrance and to selectively insulate the various portions of the line. An adequate level of cleanliness of the internal walls of the cylinder is achieved by reaching an adequate vacuum value, heating the cylinder with the aid of heating grids, and conveying the gases into the cylinder. This process ensures the complete removal of all the impurities and consequently contributes to guarantee the stability over time of the gas mixtures introduced in the cylinders. The station, depicted in Fig. 1, is used both to evacuate the cylinder during its conditioning and to fill it with the desired gas.

The gas mixture is prepared by quantitatively transferring pure gases or more concentrated mixtures of known composition into the target cylinder, which will contain the final mixture. For this filling a technical balance (Mettler Toledo, SR 16001, maximum capacity: 16100.0 g; resolution: 0.1 g, Switzerland) is used.

The second crucial step in the gas mixture preparation consists in the high-precision weighing, which is conducted by a high-level mass comparator (Mettler Toledo, PR 10003, maximum capacity: 10100 g; resolution: 1 mg, Switzerland). The mass of the cylinder during each preparation step (before and after each gas introduction) is determined. Two cylinders, one as a target cylinder (A) and the other as a reference (B), are located in a cabinet and hanged to the mass comparator. They are weighed according to an A-B-B-A double substitution scheme to minimize the correction due to the buoyancy effect. A system of two slides, controlled and moved by an external engine, allows the automatic weighing of the cylinders thus avoiding perturbation effects due to the operator or the environment. The measurements are carried out with the system in thermal equilibrium with the environment. Since environmental conditions influence weighing operations in CRM preparation, temperature, pressure and relative humidity are constantly monitored and recorded during the CRM preparation process. After the masses of gases added in the cylinder are determined, the conversion of these masses to amount of substance is calculated following the equation reported in [23]:

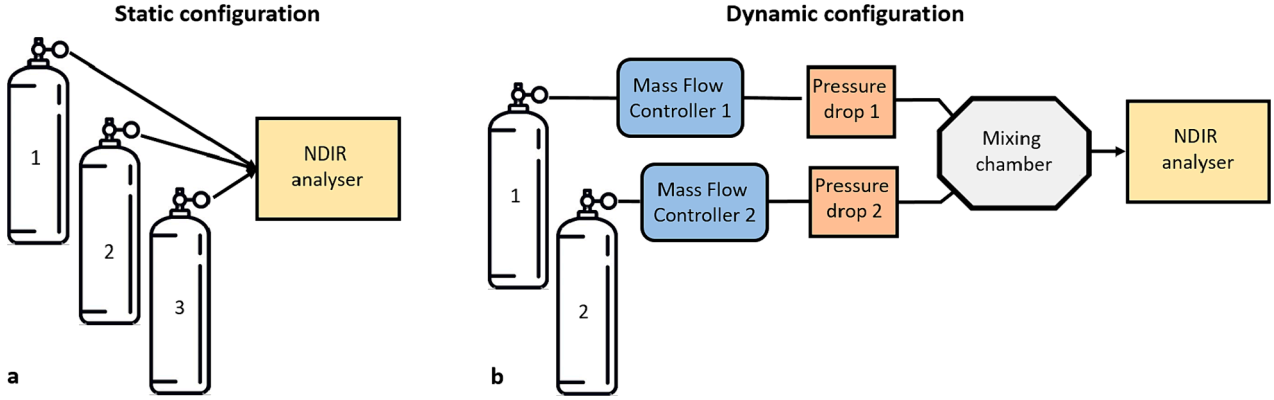

Fig. 2. Schemes of the INRiM measurement system for the verification over time of the gas mixtures in static (a) and dynamic configuration (b).

$$\chi_{\mathrm{Grav}} = \frac{\sum_{j=1}^{r}\left(\frac{\chi_{\mathrm{CO2},j}\bullet m_j}{\sum_{i=1}^{q}\chi_{i,j}\bullet M_i}\right)}{\sum_{j=1}^{r}\left(\frac{m_j}{\sum_{i=1}^{q}\chi_{i,j}\bullet M_i}\right)} \quad (1)$$

where the subscript i refers to the components different from CO_2 in the mixture, the subscript j indicates the different mixtures/pre-mixtures used for the gravimetric preparation, m is the weighed mass of each mixtures/pre-mixtures, M refers to the molar mass of each component, χ is the amount fraction of each component, and χ_{Grav} is the amount fraction of CO_2 assigned to the CRM.

2.2. Analytical verification of a candidate CRM

After the gravimetric preparation, the mixtures are analysed with a calibrated Non-Dispersive Infrared (NDIR) analyser (ABB URAS 14, Switzerland), following the requirements of the International Standard ISO 6143:2001 [24], to confirm the gravimetric value. This verification is performed with a method traceable to the SI units, independent of the gravimetric method. The NDIR is calibrated by using three reference gas mixtures whose amount fraction is determined in three replicates for each concentration, covering a suitable range, that can either be gravimetrically prepared (Static configuration, Fig. 2a) or obtained by dynamic dilution (Dynamic configuration, Fig. 2b). In the latest case, the measurement system is composed of a mixing chamber coupled with a set of calibrated Mass Flow Controllers (MFCs) (MKS Instruments, USA) and valves (Swagelok, USA). The chamber, made of stainless steel type AISI 304L, aimed at maximising the mixing of gases.

After the analysis of the three reference gas mixtures, a calibration curve is obtained and is then validated by analysing an independent primary gas mixture of CO_2 operating as a control mixture.

Eventually the calibrated NDIR analyser is used to verify the composition, χ_{Ver}, of the gas mixtures prepared by gravimetry [25]. Three replicates were also carried out for the latter.

The model equation of the calibration curve used to verify the amount fraction of the candidate CRM is the following:

$$\chi_{\mathrm{Ver}} = y + d(y) \text{ where } d(y) = \alpha_0 + \alpha_1 y \quad (2)$$

where y are the NDIR readings and $d(y)$ is the correction to be applied to the NDIR readings to obtain the χ_{Ver} value of the analysed sample [26].

2.3. Stability and homogeneity assessment of candidate CRMs

One of the important steps for CRM development regards the stability assessment, which consists in the periodical analysis of the material for a suitable period. In the case of the gas mixtures, a possible reason for contamination is typically due to the environmental air (variation in the CO_2 amount fraction) if the cylinder valve does not close appropriately or for back flushing phenomena or due to the internal walls of the cylinder releasing impurities. For these reasons, the stability assessment of the gas mixtures is crucial.

In order to assess the stability for CRMs of CO_2 at atmospheric amount fraction, a verification over time spanning from 7 to 17 years was carried out on the prepared mixtures in the range (100–1000) μmol/mol, which effectively became candidate CRMs. Such assessment involves the application of the measurement method described in Sec 2.2 to the gas mixtures. The moment at which the gas mixture is prepared by gravimetry and the χ_{CRM} value is determined, is considered as the starting time for the stability study. All the analytical verifications carried out over time are considered as independent measurements. Between an analytical verification and the following one, the cylinders containing the gas mixtures are stored in a ventilated environment with a temperature between 15 °C and 30 °C. The conducted study is intended for the assessment of long-term stability of the CRMs, according to the Guide 35 [22, Sec. 8.3.4.2], i.e., "the stability of the material during the period of validity under specified storage conditions". The present study does not deal with the "transportation stability" cited in the Guide 35 [22, Sec. 8.3.4.1], related to chemical reactions possibly caused by rapid changes in temperature or other environmental parameters in the transport. For these kind of gas mixtures, indeed, such changes do not affect the chemical equilibria of the gaseous components; hence, any short-term instability would be rather due to different reasons and its effect would be already encompassed in the long-term instability assessment.

Linear regression is used for fitting the analytical values of the CRMs over time, by application of both the Ordinary Least Squares (OLS) approach, as indicated by Guide 35 [22, Annex B3], and the Weighted Least Squares (WLS) approach, which is able to take into account the uncertainty of the data. When using OLS, the uncertainty contribution due to the stability effect, u_{Stab}, depends only on the dispersion of the analytical values; when WLS are applied, instead, u_{Stab} also accounts for the data uncertainty, related to the performance of the NDIR analyser (the inverse of the squared uncertainties are the weights used in the regression).

A straight line is used to fit the amount fraction values χ provided by the first gravimetrical determination and the subsequent analytical verifications:

$$\chi = a + bt, \quad (3)$$

where b is the degradation rate and t is the time at which subsequent analyses are performed. The statistical analysis is carried out within the R statistical software environment, applying the "lm" function of the "stats" package [27], and enabling the option "weights" for implementation of WLS. Among the output of the elaboration, the estimate of b and its standards error u_b are considered, as well as the corresponding t value (Guide 35 [22, Eq. B19]) and its significance probability. Specifically, the usual Student t-test for a statistically significant slope value is applied, which indicates that b is essentially equal to zero (i.e., there is no degradation in time at a 95 % level of confidence) if the probability of the distribution of the statistic exceeding $|t|$ is higher than 5 %. Moreover, the following variants for the stability uncertainty contribution u_{Stab} are calculated: $u_{\mathrm{Stab,OLS}}$ and $u_{\mathrm{Stab,WLS}}$, given by $u_b \cdot t_{\mathrm{shelflife}}$ (where u_b is either that arising from OLS or from WLS, respectively, and $t_{\mathrm{shelflife}}$ is chosen as an appropriate shelf life for the CRMs) [28,29], and the simple, rough standard deviation of the analytical values of the time series, for comparison purposes.

The evaluation of inter-unit homogeneity (in the case of a batch, it is generally recognised as a prerequisite for the CRM production) is not applicable for gas mixtures as produced at INRiM, because each cylinder (unit) is individually prepared. Furthermore, being these mixtures composed of gases having similar densities and not condensable, consequently intrinsically homogeneous, the intra-unit homogeneity study is also unnecessary. The only operation concerning the homogenisation of gas mixtures consists in the rolling on a specific rotation system of the cylinders after the mixture preparation. In addition, the cylinders are also rolled prior to each analytical verification.

2.4. Uncertainty evaluation of the CRMs

The sources of uncertainty taken into account for the evaluation of the uncertainty associated with the amount fraction value of the CO_2 gaseous mixture prepared by gravimetry, u_{Grav}, reported in Eq. (1) are:

- Uncertainty associated with the concentration of the parent mixture (related to the k^{th} component) and of any impurities of the k^{th} component in the pre-mixtures and in the matrix gas;
- Uncertainty associated with the purity of the matrix gases;
- Precision weighing uncertainty;
- Uncertainty associated with molar masses.

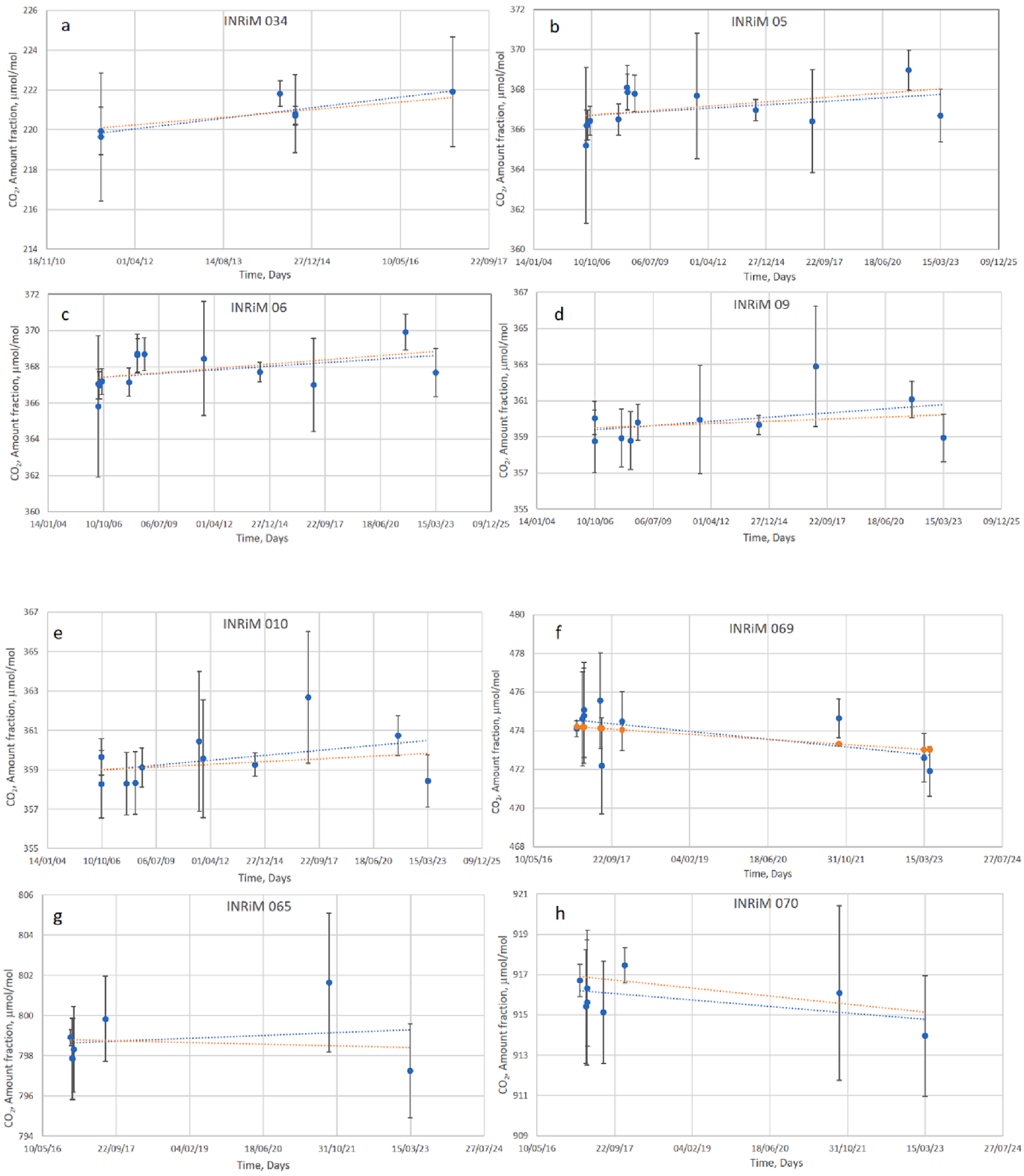

Fig. 3. Eight examples of CO_2 gas mixtures in AS at atmospheric level. Blue dotted line represents the OLS approach, orange dotted line represents the WLS approach. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

The sources of uncertainty taken into account for the evaluation of the uncertainty, u_{Ver}, associated with the verification χ_{Ver} with the calibrated NDIR and reported in Eq. (2) are:

- Uncertainty associated with the concentration of the certified reference mixtures used for calibration of NDIR analyser;
- Uncertainty due to repeatability and resolution of NDIR;
- Uncertainty associated with the model.

The model equation for the estimation of χ_{CRM} is:

$$\chi_{\mathrm{CRM}} = \chi_{\mathrm{Grav}} + \varepsilon_{\mathrm{Ver}} + \varepsilon_{\mathrm{Stab}} \tag{4}$$

Table 1
Data obtained by the application of OLS and WLS methods.

CRM code	Matrix gas	b_{OLS}, (μmol/mol)/d	$u(b)_{OLS}$,(μmol/mol)/d	p-value$_{OLS}$	b_{WLS}, (μmol/mol)/d	$u(b)_{WLS}$(μmol/mol)/d	p-value$_{WLS}$
INRiM 034	AS	$1.1\cdot10^{-3}$	$2.7\cdot10^{-4}$	$1.1\cdot10^{-2}$	$7.6\cdot10^{-4}$	$7.3\cdot10^{-4}$	$3.5\cdot10^{-1}$
INRiM 010	AS	$2.5\cdot10^{-4}$	$1.9\cdot10^{-4}$	$2.3\cdot10^{-1}$	$1.4\cdot10^{-4}$	$1.2\cdot10^{-4}$	$2.8\cdot10^{-1}$
INRiM 09	AS	$2.3\cdot10^{-4}$	$1.8\cdot10^{-4}$	$2.4\cdot10^{-1}$	$1.2\cdot10^{-4}$	$1.2\cdot10^{-4}$	$3.5\cdot10^{-1}$
INRiM 05	AS	$1.7\cdot10^{-4}$	$1.3\cdot10^{-4}$	$2.2\cdot10^{-1}$	$2.2\cdot10^{-4}$	$1.2\cdot10^{-4}$	$8.6\cdot10^{-2}$
INRiM 06	AS	$2.0\cdot10^{-4}$	$1.4\cdot10^{-4}$	$1.8\cdot10^{-1}$	$2.4\cdot10^{-4}$	$1.2\cdot10^{-4}$	$7.2\cdot10^{-2}$
INRiM 069	AS	$-7.9\cdot10^{-4}$	$3.8\cdot10^{-4}$	$7.3\cdot10^{-2}$	$-5.3\cdot10^{-4}$	$2.7\cdot10^{-4}$	$8.3\cdot10^{-2}$
INRiM 065	AS	$2.8\cdot10^{-4}$	$6.7\cdot10^{-4}$	$6.9\cdot10^{-1}$	$-1.7\cdot10^{-4}$	$5.6\cdot10^{-4}$	$7.7\cdot10^{-1}$
INRiM 070	AS	$-6.4\cdot10^{-4}$	$4.3\cdot10^{-4}$	$1.8\cdot10^{-1}$	$-7.9\cdot10^{-4}$	$7.1\cdot10^{-4}$	$3.0\cdot10^{-1}$

Table 2
Uncertainty values obtained by OLS and WLS approaches for a shelf life of 5 years.

CRM code	std μmol/mol	u_{ltsOLS} μmol/mol	u_{ltsWLS} μmol/mol
INRiM 034	0.76	0.49	1.3
INRiM 010	0.85	0.35	0.22
INRiM 09	0.61	0.34	0.22
INRiM 05	1.0	0.24	0.21
INRiM 06	1.0	0.25	0.22
INRiM 069	1.0	0.70	0.49
INRiM 065	1.5	1.2	1.0
INRiM 070	0.81	0.78	1.29

where ε_{Ver} is an error term referring to the effect of the verification, described in Sec. 2.2, and ε_{Stab} is an error term referring to the effect of the stability, described in Sec. 2.3. No correction for the analytical verification with respect to the gravimetric value is carried out because the verification value has always to be consistent with the gravimetric one (compatibility is calculated by the normalized error). Also error ε_{Stab} is considered as equal to zero, on the basis of the studies carried out on the gas mixtures in the years (See Sec. 3). Although both errors ε_{Ver} and ε_{Stab} can be neglected in model (4), their uncertainties are yet taken into account in the combined standard uncertainty, u_{CRM}, associated with the CRM [22]:

$$u_{CRM} = \sqrt{u_{Grav}^2 + u_{Ver}^2 + u_{Stab}^2} \quad (5)$$

The expanded uncertainty is evaluated by considering a normal distribution associated with the measurement result, hence by multiplying the combined standard uncertainty by a coverage factor $k = 2$.

3. Results and discussion

After χ_{CRM} was determined, the stability assessment was carried out for each gas mixture and analytical verification were repeated over time. The CRM supply service was activated for the amount fraction range (100–1000) μmol/mol. The results of stability studies carried out on 8 gas mixtures of CO_2 in SA are reported here, chosen as examples being SA a more complex matrix gas than N_2.

Fig. 3 show the time series of the verification values (accompanied with their expanded uncertainties) of the eight gas mixtures, in a time varying between 7 and 17 years, depending on the date of production of each CRM. The plots show, in blue dotted line, the OLS straight line and, in orange, the one for the WLS approach. Table 1 reports the slope, its standard error and the p-value of the corresponding t-test for the significance of the slope (it checks if the true value of the slope coefficient is equal to zero), for both OLS and WLS methods. If the p-value is smaller than 0.05, the test result is considered to be statistically significant, i.e., the slope is likely not to equal zero; if the p-value is greater than 0.05, the result is insignificant, i.e., the slope can be taken as substantially equal to zero, hence proving no degradation in time of the mixture. Concerning the stability uncertainty, it was decided to aim at the evaluation of a stability uncertainty corresponding to a shelf life of 5 years, this stability time being generally accepted for these kind of mixtures [30]. Therefore, Table 2 reports both the uncertainties $u_{Stab,OLS}$ and $u_{Stab,WLS}$, calculated at 5 years from the gravimetric preparation, and the sample standard deviation of the analytical values collected in the first 5 years.

Fig. 3 shows the stability for 8 different gas mixtures, which were repeatedly verified in a temporal range of almost 20 years. Each graph refers to one single mixture (the corresponding cylinder codes are reported in the label of the graph and are related to the codes in the Tables 1–3). The time (expressed in days) on the horizontal axis, gives an indication of the time span in which each mixture was tested for its stability, and the exact date is not reported for each measurement point. In addition, the digits of the amount fractions on the vertical axes have been increased, to ameliorate the verification of the accuracy of the calculations given in the Tables 1–2. The uncertainty bars associated with the results depend on various factors related to both the mixtures used as calibration standards and the instrumentation used. As an example, the use of calibration standards with a higher uncertainty or the concentration range within which the NDIR analyser is calibrated for the analytical verifications can lead to higher uncertainties in the determined analytical value. Furthermore, analytical verifications were conducted either by calibrating the NDIR analyser with gravimetric mixtures or with mixtures prepared by dynamic dilution: the two approaches usually lead to quite different uncertainties (usually higher with dynamic dilution).

For all the mixtures the stability of the equipment was checked by regular calibration carried out every time a stability verification was performed. Proper CO_2 mixtures purchased from other NMIs were used both as calibration standards and as quality control in order to have independent checks.

The gas mixture INRiM 034 ran out in 2017, therefore no verifications could be made after that date. In the case of this mixture, having mole fraction around 220 μmol/mol, the OLS t-test leads to the rejection of the null hypothesis of a zero slope at a significance level of 5 % (nonetheless, the hypothesis might be accepted at a 1 % level of confidence, at least). WLS approach, however, is able to better trust the data with smaller uncertainty, hence decreasing the value of the slope and increasing its p-value to a considerable 35 %. The price to be paid is a substantially larger stability uncertainty $u_{Stab,WLS}$ with respect to $u_{Stab,OLS}$, as well as to the data standard deviation. Therefore, for INRiM 034, a long-term (6-years) stability can be claimed, as far as $u_{Stab,WLS} = 1.3$ μmol/mol is used in the uncertainty budget of Eq. (3).

Examining the four mixtures having nominal amount fraction around 360 μmol/mol, it can be seen that the time behaviour of the mixtures INRiM 05 and 06 is quite close, as well as for mixtures INRiM 09 and 010, as the they were prepared in pairs, at the same time, with the same parent gases. In all cases, the t-test performed on the regression slope supports the null hypothesis of a degradation value practically equal to zero, hence an overall stability can be asserted on the whole time span of 17 years, at a significance level of at least 5 %. For the couple INRiM 05 and 06, the t-test for OLS regression is more conservative than for WLS (the slope is lower and the p-value is higher), whereas for the couple INRiM 09 and 010, the opposite outcome is

Table 3
Values and associated uncertainties of the INRiM CRMs. Both absolute and relative uncertainties associated with the χ_{CRM} values are expressed with two significant figures as required by the internationally recognised and recommended guidelines for calculating and expressing uncertainty [31]. The concentration values are rounded to the first decimal digit to be consistent with the absolute uncertainty values. The variances are deliberately expressed with an extra decimal digit since their square root is taken to get the standard uncertainties.

CRM code	χ_{CRM} μmol/mol	$u^2_{Grav} + u^2_{Ver}$ (μmol/mol)^2	$u^2_{Stab,OLS}$ (μmol/mol)^2	$u^2_{Stab,WLS}$ (μmol/mol)^2	$u_{CRM,OLS}$ μmol/mol	$u_{CRM,WLS}$ μmol/mol	$u_{CRM,OLS,rel}$ %	$u_{CRM,WLS,rel}$ %
INRiM 034	219.9	2.92	0.24	1.79	1.8	2.2	0.81	0.99
INRiM 010	359.6	0.95	0.12	0.05	1.0	1.0	0.29	0.28
INRiM 09	360.0	0.95	0.11	0.05	1.0	1.0	0.29	0.28
INRiM 05	365.2	3.95	0.06	0.04	2.0	2.0	0.55	0.55
INRiM 06	365.8	3.97	0.06	0.05	2.0	2.0	0.55	0.55
INRiM 069	474.1	1.50	0.49	0.24	1.4	1.3	0.30	0.28
INRiM 065	798.9	1.04	1.51	1.05	1.6	1.4	0.20	0.18
INRiM 070	916.7	2.15	0.60	1.51	1.7	1.9	0.18	0.21

observed. In all the four cases, however, $u_{Stab,WLS}$ is slightly smaller than $u_{Stab,OLS}$, and both uncertainties are substantially smaller than the standard deviation of analytical data. Moreover, for all the mixtures, it is clear that the WLS straight line is less sensitive than OLS to less reliable data (e.g., values acquired in 2017 accompanied by high analytical uncertainties), whereas it gives more importance to more precise results (e.g., values acquired in 2014).

In the case of INRiM 069 graph, it is particularly marked that the uncertainty associated with the gravimetric preparation (first value plotted) is much smaller than the uncertainty due to the verification. This is also observable in the two bottom plots in Fig. 3 referring to CO_2 gas mixtures in AS with nominal amount fraction between 750 and 950 μmol/mol. These latest mixtures were prepared more recently, with a more consolidated measurement procedure and a proven operator expertise. Also in these cases, the null hypothesis of no significant trend can be safely accepted in the considered time span (according to both OLS and WLS).

Table 3 reports the amount fraction values for the CRMs, the variance contribution due to the independent metrological traceability paths established for the preparation of these CRMs, the variance contribution due to the stability considering the two linear regression approaches, and the corresponding combined standard uncertainty values associated with the CRM amount fraction, in absolute and relative terms.

From the data reported in Table 3, the uncertainty contribution for each CRM associated with stability, assigned both via OLS and WLS, is lower than the one deriving from the value assignment. Comparing the two approaches, usually $u_{Stab,WLS}$ results smaller than $u_{Stab,OLS}$. However, the combined standard uncertainties associated to the CRM property values results very similar. In addition, the $u_{CRM,rel}$ is generally constant within the entire amount fraction range.

From the outcomes of the study, the CO_2 amount fraction value of these CRMs can be reasonably considered reliable for a 5-year period, within the uncertainties reported in Table 3, since no significant trend is observed, as proven by the statistical approaches described in this paper.

4. Conclusions

At INRiM two new measurement services to produce CRMs in accordance with the International Standard ISO 17034:2016 were recently activated. CRMs consist of CO_2 gas mixtures with amount fraction values that cover the atmospheric range (100–1000) μmol/mol in a matrix of N_2 and/or SA.

The assignment of the value is performed based on two independent metrological traceability paths, whose details are described in the paper. While the homogeneity study is not considered relevant for this type of gases, the stability study is necessary to verify whether there is a drift in the values over time.

The manuscript innovative contribution is represented by the development of an innovative approach for the uncertainty evaluation of the CRM stability based on the Weighted Least Squares method. Generally, an Ordinary Least Squares approach is simply used. As a comparison, the two different linear regression approaches were applied to the stability data. The results highlight that no instability of the CO_2 amount fraction was detected over a five-year period, which was established as the shelf life of the INRiM CRMs.

Further activities are ongoing towards the production of CO_2 CRMs having certified property values not only for the amount fraction but also for the isotopic composition.

CRediT authorship contribution statement

F. Durbiano: Writing – original draft, Conceptualization. **F. Pennecchi:** Writing – review & editing, Formal analysis, Conceptualization. **F. Rolle:** Writing – review & editing, Validation, Methodology. **S. Pavarelli:** Software, Investigation. **M. Sega:** Writing – review & editing, Supervision, Project administration.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.measurement.2024.114653.

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