PRODUCTION OF GASEOUS CERTIFIED REFERENCE MATERIALS AT INRiM FOR AMOUNT OF SUBSTANCE FRACTION OF CO2

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PRODUCTION OF GASEOUS CERTIFIED REFERENCE MATERIALS AT INRiM FOR AMOUNT OF SUBSTANCE FRACTION OF CO_2

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Abstract:

Due to the involvement of carbon dioxide (CO_2) in the global warming effects, INRiM is developing certified reference materials (CRMs) of CO_2 in synthetic air. The mixtures are prepared by gravimetry, a primary method, and verified by Non-Dispersive Infrared spectroscopy. The CO_2 amount fraction in the mixtures and its associated uncertainty are the certified properties of the CRMs. A corresponding stability study of the amount fraction of CO_2 is also ongoing.

Further work foresees the development of CRMs for the isotopic composition of CO_2 in air, after the participation in specific international comparisons.

Keywords: certified reference materials, gas mixtures, amount of substance fraction, CO_2

1. INTRODUCTION

The concentration trend of carbon dioxide (CO_2) in the atmosphere is increasing continuously and the average value in 2023 has reached 424.00 μmol/mol [1]. Accurate and sound determinations of the atmospheric concentration of the greenhouse gases (GHGs) enable the development of models to predict future scenarios and to implement effective measures to counteract global warming. For this purpose, it is very useful to have metrological references represented by gas mixtures with CO_2 concentration at the atmospheric level to ensure the reliability of the results and to have the possibility to compare them at the international level.

The use of Certified Reference Materials (CRMs) for the amount of substance fraction (amount fraction) of CO_2 in matrices of synthetic air is of utmost importance to achieve the comparability and traceability of data, which are essential features of measurement results in environmental and climate fields. CRMs can be used for the calibration of instrumentation that monitors the increasing values of CO_2 concentration in the atmosphere, thus contributing to undertake specific actions to mitigate climate change effects.

Moreover, discriminating between the CO_2 in the atmosphere due to anthropogenic activities and the CO_2 derived from natural sources is another pillar in the climate change studies. Stable isotopes of carbon in CO_2 represent effective markers. In this context, developing CRMs for the isotopic composition of CO_2 in air (δ^{13}C-CO_2) enable to calibrate the instrumentation devoted to such determination.

The National Institute of Metrological Research (INRiM) has among its duties the development of CRMs as readily accessible measurement standards to establish the traceability of measurement results to the International System of Units (SI), in accordance with the focal point "Monitoring the environment and supporting the development of clean technologies" of the document "INRIM Metrology towards 2030" [2].

In this manuscript, the work carried out at INRiM for the preparation of reference gas mixtures which should become candidate CRMs for the amount fraction of CO_2 in air is presented. Moreover, a short description of the work in progress and scheduled for the production of CRMs related to the stable isotopic composition is reported.

2. MATERIALS AND METHODS

INRiM has a consolidated experience in the preparation of reference gas mixtures of CO_2 in synthetic air with an amount fraction similar to the concentration levels in the atmosphere. The candidate CRMs consist of reference gas mixtures contained in high-pressure 5 L aluminium alloy cylinders and accompanied by a certificate.

Considering the metrological traceability chain, the gas mixtures are prepared by gravimetry, a primary direct method, in accordance with the International Standard ISO 6142-1:2015 [3].

The gravimetric method used at INRiM consists in the introduction, in a preconditioned cylinder, of a specific mass of the analyte gas, in this case pure CO_2 or a CO_2 gas mixture and, successively, of the matrix gas by means of a proper filling station designed and realised at INRiM [4]. The various stages of gas injection are followed by an accurate weighing to determine the amount of gas actually introduced in each stage. The weighing is carried out using a mass comparator (Mettler Toledo PR 10003, Switzerland), according to the A-B-B-A double substitution scheme, in which A denotes the cylinder in which the mixture is being prepared and B is an identical but empty cylinder used to minimize the correction due to the buoyancy effect. As prescribed in [3], after their preparation the gas mixtures are verified against independent reference gas mixtures by means of a calibrated Non-Dispersive Infrared (NDIR) analyser (ABB URAS 14, Switzerland), following the requirements of the International Standard ISO 6143:2001 [5] to confirm the gravimetric value. A purity assessment of the parent gases is also required for the critical impurities. The International Standard ISO EN 17034:2016 [6] requires that CRMs, i.e., the reference gas mixtures in the present case, undergo stability assessments in order to track and examine how different environmental conditions or chemical reactions inside the cylinders can affect their composition.

Another requirement of [6] is related to the homogeneity assessments. The inter-units homogeneity assessment is not applicable in this case because every cylinder contains a stand-alone reference gas mixture specifically prepared. Besides, since these mixtures are composed of gases having similar densities and are not condensable, they are intrinsically homogeneous. Therefore, the intra-unit homogeneity study is not necessary.

The uncertainty budget for the value assigned to the amount fraction of CO_2 in synthetic air is described in [7].

From the perspective of the Guide to the Expression of Uncertainty in Measurement (GUM) [8], the uncertainty due to the stability, u_{stab}, is added to the uncertainty of characterization associated with the amount fraction of CO_2, u_{char}, so that the combined uncertainty associated to the CRM, u_{CRM}, results by the application of the law of propagation of uncertainty (Eq. 1):

$$u_{CRM} = \sqrt{u_{char}^2 + u_{stab}^2} \quad (1)$$

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 $k = 2$.

INRiM participated successfully in the international key comparisons CCQM-K52 (Carbon dioxide in synthetic air) [9] and CCQM-K120 (Carbon dioxide at background and urban level) [7], 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). The CIPM Mutual Recognition Arrangement (CIPM MRA) is the framework through which National Metrology Institutes demonstrate the international equivalence of their measurement standards and the calibration and measurement certificates they issue [10]. The outcomes of this Arrangement are the internationally recognized Calibration and Measurement Capabilities (CMCs) of the participating institutes. Approved CMCs are publicly available from the CIPM MRA database (KCDB) [11]. On the basis of a successful participation in the measurement comparisons, it is possible for an institute to propose a CMC.

Further work is in progress at INRiM to establish a metrology traceability chain devoted to the determination of the isotopic composition of CO_2 in air (in terms of δ^{13}C-CO_2), in order to develop the capability to produce CRMs also for this quantity. A stability study is ongoing and the participation in a specific international comparison in this measurement field is expected shortly. In this way, INRiM reference gas mixtures of CO_2 can become CRMs both for the amount fraction of CO_2 and for their isotopic composition, in order to enable the correct determination of the fraction of anthropogenic emissions of CO_2 in the atmosphere with respect to the carbon budget [12].

3. RESULTS AND DISCUSSION

At INRiM the value of the amount fraction associated with the candidate CRMs for CO_2 gas mixture is determined by the gravimetric method. The associated uncertainty, u_{char}, includes the sources due to the weighted masses of the parent gases, their purity and their molar masses.

In general, the average lifetime of a CRM of CO_2 gas mixtures is estimated to be about 5 years [13]. In order to assess the stability of the reference gas mixtures prepared at INRiM, in accordance with the requirements of [6], proper studies are carried out as follows. The gravimetric CO_2 amount fraction is considered as reference value and represents the time-zero value. Immediately after the preparation, the prepared mixture is verified by using the calibrated NDIR analyser to confirm the gravimetric preparation data. The verification is acceptable if the gravimetric value and the analytical value are consistent within their respective expanded uncertainties. Periodically, the mixtures are verified following the same procedure. All these measurements are considered as independent. The uncertainty, u_{stab}, is evaluated as the standard deviation of the analytical values obtained during the study. This approach takes into account the dispersion of the values, which are affected also by the performance of the NDIR analyser.

In the following, an example of stability study carried out on a candidate CRM, identified as INRiM reference gas mixture 010 (cylinder serial number D370674) prepared in 2006, is presented. A graph of the measurement results versus time is reported in Figure 1. Such mixture of CO_2 in synthetic air has a CO_2 amount fraction of 359.65 µmol/mol with an associated combined standard uncertainty, u_{char}, of 0.46 µmol/mol.

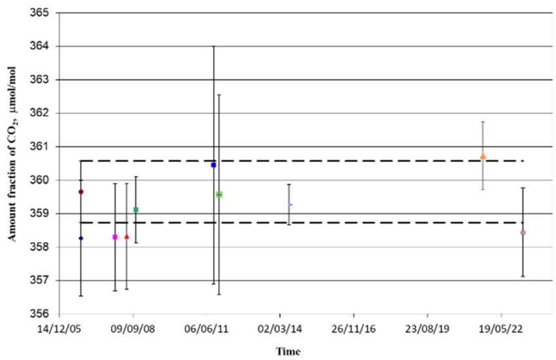

Figure 1. Stability assessment for the candidate CRM CO_2 INRiM reference gas mixture 010. The garnet-coloured circle represents the result obtained by the gravimetric method at time zero. The blue square represents the analytical value at time zero. The other coloured points are the analytical values in time. The black bars denote the associated expanded uncertainty (k = 2). The black dotted lines represent the expanded uncertainty associated with the gravimetric value reported as a reference for visualizing the consistency with the analytical data.

Table 1 shows how different lifetime values affect the u_{stab} value, and hence the combined standard uncertainties u_{CRM}. The corresponding expanded uncertainties are also reported considering a normal distribution and a coverage factor $k = 2$.

Table 1

Lifetime, year	u_{stab}, µmol/mol	u_{CRM}, µmol/mol	U_{CRM}, µmol/mol
1.5	0.79	0.91	1.8
5	0.85	0.97	1.9
8	0.78	0.91	1.8
17	0.90	1.01	2.0

The uncertainty associated with the analytical values is not explicitly considered for the evaluation of u_{stab}, as their dispersion is affected by the analytical method. Furthermore, the uncertainty associated with the analytical values may vary with time due to fluctuations and modifications of the experimental setup. About the latter, Figure 1 clearly shows that the values obtained from 2014 onwards present a reduced associated uncertainty. The study outcomes reported in Table 1 prove that gas mixtures of CO_2 at the atmospheric amount fraction show a long-in-time stability. An analogous study, carried out on similar mixtures, confirmed the same results. Currently, a 5-year stability assessment for the INRiM gas mixtures can be considered a suitable compromise, as in the case reported in [13], taking into account a conservative approach.

A second case refers to a more recent reference gas mixture, identified as STELLAR 022 (cylinder serial number 15914), prepared on April 2022 in the framework of the EMPIR Joint Research Project 19ENV05 "Stable isotope metrology to enable climate action and regulation – STELLAR". The stability study is ongoing and the data are shown in Figure 2. The mixture, prepared in a synthetic air matrix, has a CO_2 amount fraction of 404.72 µmol/mol with u_{char} of 0.20 µmol/mol. In this case, u_{stab}, calculated over one year, is 0.15 µmol/mol; u_{CRM} results of 0.25 µmol/mol. The corresponding U_{CRM} is 0.50 µmol/mol.

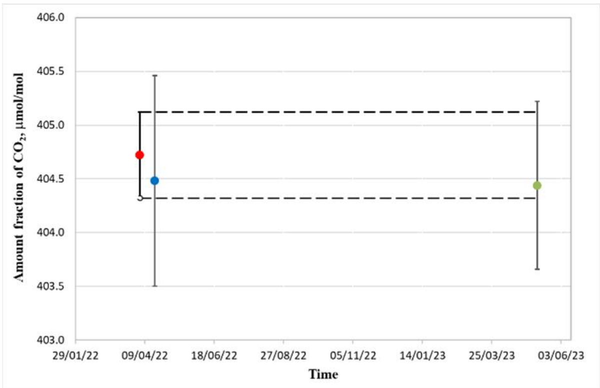

Figure 2. Stability assessment for the candidate CRM CO_2 reference gas mixture STELLAR 022. The red circle represents the result obtained by the gravimetric method at time zero. The blue circle represents the analytical value at time zero. The green circle denotes the analytical value of about one year later. The black bars denote the associated expanded uncertainty (k = 2). The black dotted lines represent the expanded uncertainty associated with the gravimetric value reported as a reference for visualizing the consistency with the analytical data.

For the reference gas mixture STELLAR 022, the isotopic composition was also determined. It has a $\delta^{13}C$ value of -41.87 ‰ with an associated expanded uncertainty (k = 2) of 0.30 ‰. The measurements were carried out by a Fourier-

Transform Infrared Spectrometer - FTIR (Nicolet iS50, ThermoFisher Scientific, USA) equipped with a mercury cadmium telluride (MCT) detector and a 2 m White type gas cell. This reference gas mixture was sent to the Max Planck Institute for Biogeochemistry (MPI-BGC) for the verification of the isotopic composition by isotope-ratio mass spectrometry (IRMS) and the value was consistent with the one reported by INRiM, within the declared uncertainty. Figure 3 shows some of the cylinders which were analysed at MPI-BGC for the validation of their isotopic composition.

Figure 3: Examples of INRiM reference gas mixtures for CO_2 amount fraction and isotopic composition.

4. SUMMARY

INRiM is working to become an official producer of CRMs for the amount fraction of CO_2 in synthetic air. Stability assessments have been carried out for the production of CRMs. Following the stability studies, a 5-year stability assessment for INRiM gas mixtures can be considered a suitable compromise taking into account a conservative approach. The submission of a specific CMC in the KCDB web resource is the next step. The outcome will be the activation of an internationally recognised service available to customers for the distribution of CRMs for this quantity within the CIPM MRA.

Moreover, INRiM started to study the stability of the isotopic composition value for some of the prepared reference gas mixtures. INRiM plans to take part in a programmed international comparison and, on the basis of a successful participation, a new CMC will be proposed also for isotopic composition.

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