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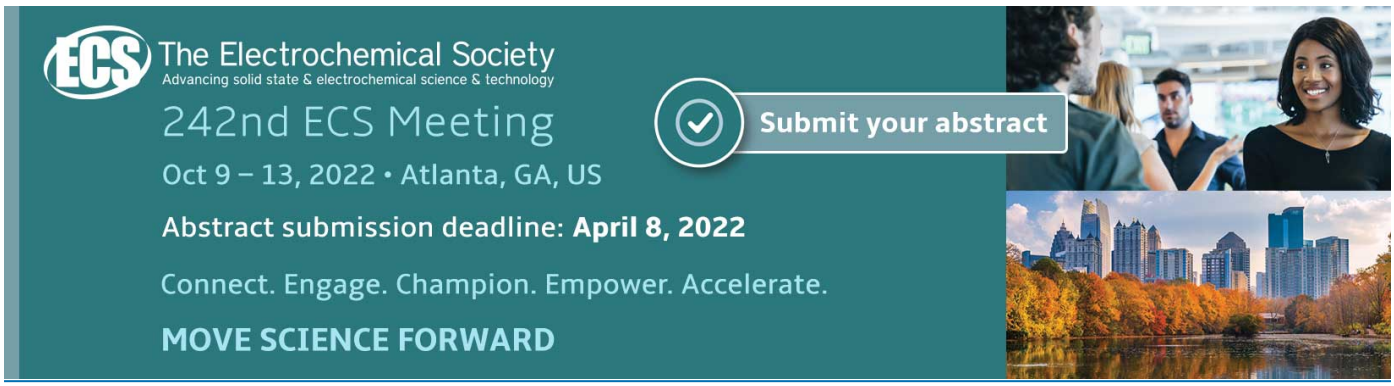

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Reference Materials: gas mixtures to support measurements for climate change studies

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Abstract. This work aims at presenting some activities carried out at INRiM for the development of new reference materials (RMs) of greenhouse gases to support measurements for climate change studies. Since the preindustrial era, greenhouse gases emissions due to human activities have dramatically increased, mostly due to economic and demographic growth and their concentrations in the atmosphere have grown continuously since 2011, reaching highest levels in 2019. The increase of greenhouse gases concentration in atmosphere due to anthropogenic emissions is the main cause of global warming and carbon dioxide (CO_2) is one of the main culprits for this phenomenon. In this context, the capability of discriminating between anthropogenic and natural emissions is of utmost importance. The determination of the isotopic composition of CO_2 can support the assessment of the uptake of CO_2 in the environmental compartments, i.e. atmosphere and hydrosphere, and can help to distinguish natural from anthropogenic carbon in the atmosphere. The possibility to establish metrological traceability of the measurements of CO_2 isotopic composition is a key aspect, and greatly relies on the availability of gaseous reference materials having compositions and uncertainties that are fit for purpose. In the past years, INRiM participated in the EMPIR project 16ENV06 SIRS "Metrology for stable isotope reference standards", and is now taking part in the EMPIR project 19ENV05 STELLAR "Stable isotope metrology to enable climate action and regulation". INRiM has experience in the preparation of gas standards by primary methods, namely gravimetry and dynamic dilution, which can be applied to the realisation of reference materials of CO_2 at known isotopic composition. The present work describes the preliminary results obtained by INRiM in the preparation of pure CO_2 RMs and at atmospheric amount fraction. Examples of uncertainty budgets and identification of the uncertainty sources are also given.

1. Introduction

Atmospheric concentrations of greenhouse gases (GHGs) reflect a balance between emissions from human activities and natural sources, and sinks in biosphere and oceans. Since the pre-industrial era, GHG emissions due to human activities have dramatically increased, mostly due to economic and demographic growth. GHG concentrations in the atmosphere have grown continuously since 2011, reaching new highest levels in 2019 with globally averaged amount fractions of carbon dioxide (CO_2) at 410.5 ± 0.2 parts per million (ppm), methane (CH_4) at 1877 ± 2 parts per billion (ppb) and nitrous oxide (N_2O) at 332.0 ± 0.1 ppb, respectively, that is 148 %, 260 % and 123 % of pre-industrial levels [1]. The increase of GHG concentration in atmosphere due to anthropogenic emissions has been the major driver of climate change since the mid-twentieth century [1], with GHGs warming partly masked by aerosol cooling [2]. CO_2 is one of the most important GHGs in the atmosphere; its growth in the atmosphere is primarily due to emissions from the combustion of fossil fuels and cement production, deforestation and other land-use change. Of the total emissions from human activities during the 2009–2018 period, about 44 % accumulated in the atmosphere, 23 % in the ocean and 29 % on land, with the unattributed budget imbalance being 4 %. The portion of CO_2 emitted by fossil fuel

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combustion that remains in the atmosphere (airborne fraction), varies inter-annually due to the high natural variability of CO_2 sinks without a confirmed global trend. [3].

In 2020, the confinement measures taken in response to COVID-19 resulted in a temporary reduction in emissions and in changes in the chemical composition of the atmosphere. These changes have been especially pronounced in urban areas and are visible in traditional pollutants as well as in GHGs. However, such a reduction is not expected to have a discernible effect on global mean atmospheric CO_2 in 2020, being comparable to the natural year-to-year variability of atmospheric CO_2 [3]. Future emissions will cause additional warming, with total warming dominated by past and future CO_2 emissions [2].

In this context, the ability to discriminate between anthropic and natural emissions is of utmost importance. The isotopic ratios between stable isotopes of naturally occurring substances are robust indicators and can be used as markers in various scientific sectors. In the case of carbon, three isotopes are found in natural systems: ^{12}C (~ 99 % of all carbon), ^{13}C (~ 1 %) and ^{14}C (~ 1 part per trillion). ^{12}C and ^{13}C are stable isotopes, while ^{14}C is radioactive. All carbon isotopes are present throughout the carbon cycle, but the relative proportion of each isotope in different carbon reservoirs varies, providing unique “fingerprints” for each reservoir. Therefore, measuring the isotopic composition of atmospheric CO_2 helps to identify and quantify its sources and sinks. Organisms preferably use and fix the lightest ^{12}C. For this reason, when burning organic carbon, like the one contained in fossil fuels, more ^{12}C is released in atmosphere with respect to the background level due to natural emissions. As anthropogenic emissions have increased, atmospheric CO_2 has increased also, but the ^{13}C and ^{14}C content of atmospheric CO_2 have declined. Such simultaneous opposite trends can only be explained by the ongoing release of CO_2 from fossil fuel burning [4]. The accurate and reliable determination of CO_2 levels in atmosphere, together with its isotopic composition, is fundamental to monitor the trends of this gas in atmosphere and to support the prediction of its future increase on a global scale. The determination of the isotopic composition of CO_2 can support the assessment of the uptake of CO_2 in the environmental compartments, and can help to distinguish natural from anthropogenic carbon in the atmosphere. In this framework, the possibility to establish metrological traceability of the measurements of CO_2 isotopic composition is a key aspect, and greatly relies on the availability of gaseous reference materials (RMs) fit for the purpose.

Isotope ratios are usually expressed as relative to some accepted standard in the “delta” (δ) notation, for example:

$$\delta^{13}C = [(R^{13}_{sample}/R^{13}_{standard}) - 1] \quad (1)$$

where $R^{13} = {}^{13}C/{}^{12}C$ is the ratio of the abundances of ^{13}C and ^{12}C. The δ values are expressed in the units of ‰ (per mil). For $\delta^{13}C\text{-}CO_2$, the conventional reference standard is the VPDB scale (Vienna Pee Dee Belemnite) maintained by the International Atomic Energy Agency. The $\delta^{13}C_{VPDB}$ value of a material describes how far the isotope ratio in that material differs from the ratio in the standard.

In the past years, INRiM participated in the EMPIR project 16ENV06 “Metrology for stable isotope reference standards (SIRS)” [5], and is now taking part in the EMPIR project 19ENV05 “Stable isotope metrology to enable climate action and regulation (STELLAR)” [6]. INRiM has experience in the preparation of gas standards by primary methods, namely gravimetry and dynamic dilution [7-10], which can be applied to the realisation of RMs of CO_2 in air at atmospheric amount fraction and known isotopic composition. The present paper aims at presenting the latest developments.

2. Materials and methods

At INRiM, reference gas mixtures are prepared by gravimetry, a primary method [11], in cylinders of aluminum alloy (Luxfer, UK), having internal volume of 5 L, by means of a facility designed and realized at INRiM [8]. The precision weighing is carried out by means of a mass comparator having full scale of 10 kg and resolution of 1 mg (mod. PR 10003, Mettler Toledo, Switzerland), following

the double substitution scheme. The weighing facility is equipped with two slides that allow the automatic exchange of the sample cylinder and the reference one. The present work aims at illustrating the results obtained within the gravimetric preparation. In order to fulfill the requirements for RMs related to stability, specific studies are at present ongoing by means of non-dispersive infrared photometry (NDIR) and Fourier transform infrared spectroscopy (FTIR), not reported here. Such studies require the use of proper RMs, in terms of composition and uncertainty, to calibrate the analytical equipment. At this purpose, a device for dynamic mixtures, designed and built at INRiM [12], is used. It is composed of a set of Mass Flow Controllers (MFCs) (MKS Instruments, USA) equipped with a corresponding set of valves (Swagelok, USA) and a mixing chamber aimed at maximizing the mixing of gases. 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 verification of the gravimetric reference mixtures and for the calibration of analytical instrumentation, using a method which is complementary to gravimetry and based on independent principles.

The consolidated capabilities in the preparation of gravimetric reference mixtures was used to prepare RMs of pure CO_2 and of CO_2 in air at atmospheric amount fraction in high pressure cylinders with different isotopic compositions. Two different pure CO_2 sources (SIAD S.p.A., Italy) were selected and used as starting materials.

The prepared mixtures were then sampled in glass flasks by using an *ad hoc* system based on calibrated MFCs, and sent to the Max Planck Institute for Biogeochemistry Isolab (MPI-BGC), partner of both SIRS and STELLAR projects, for $\delta^{13}C$-CO_2 and $\delta^{18}O$-CO_2 assignment via Isotope Ratio Mass Spectrometry (IRMS) to provide traceability to the international Vienna Pee Dee Belemnite (VPDB) scale and for the validation of their isotopic composition, obtaining a confirmation of the gravimetric values. The pure CO_2 samples were analysed by IRMS, which is the reference method for the measurement of isotope ratios. The VPDB scale for both $\delta^{13}C$ and $\delta^{18}O$ measurements is defined, and has previously been realised by the primary standard NBS 19. NBS 19 is now exhausted and its replacement IAEA-603 is, at the moment, the metrologically highest available scale anchor for the VPDB scale.

Particular care was given to the conditioning of the flasks, that underwent to three repeats of flushing and evacuation to optimize the removal of residual CO_2 from contaminating laboratory air.

An appropriate uncertainty budget was prepared for the developed reference materials, taking into account the relevant uncertainty sources, such as the contributions pertaining to the parent materials, to possible contaminations from the matrix gas and the uncertainty from sampling.

2.1. Preparation of pure CO_2 RMs

Two RMs (RM1 and RM2) were produced by gravimetrically blending the two pure CO_2 sources A and B, having $\delta^{13}C$-CO_2 and $\delta^{18}O$-CO_2 values reported in Table 1. The cylinders were preconditioned three times by evacuating below $1 \cdot 10^{-5}$ mbar and heating at 60 °C, then filling with 5 bar of pure N_2 (Messer, 6.0), according to the procedure currently in use at INRiM. Each of the pure sources was transferred to the cylinder via a dedicated gas line of the filling station. The mixtures were prepared to approximately 15 bar.

Pure CO_2 source	**$\delta^{13}C$-CO_2 ‰**	**$\delta^{18}O$-CO_2 ‰**
A	1.23	-7.82
B	-42.14	-35.66

Table 1 - $\delta^{13}C$-CO_2 and $\delta^{18}O$-CO_2 values of the pure CO_2 sources

2.2. Preparation of CO_2 RMs at atmospheric amount fraction

Starting from RM1 and RM2, two diluted RMs of CO_2 at atmospheric amount fraction and selected delta values were prepared by gravimetry. Multiple dilutions were necessary to obtain the diluted RMs. RM1 and RM2 were blended with pure nitrogen (Messer, 6.0) to obtain by subsequent dilution

two parent mixtures at nominal amount fractions of 0.08 mol·mol^{-1} and 5000 µmol·mol^{-1} respectively. The atmospheric amount fraction reference materials at CO_2 nominal concentration of 400 µmol·mol^{-1} were finally prepared by further dilution of the parent mixture at 5000 µmol mol^{-1} with nitrogen and a mixture of argon and oxygen to obtain final mixtures in synthetic air.

3. Results and discussions

3.1. Pure CO_2 RMs

Starting from the gravimetric data, the delta values of the RMs, δ_{prep} were calculated from the following model equation (eq. 2):

$$\delta_{prep} = (\delta_A \cdot X_A) + (\delta_B \cdot X_B) \qquad (2)$$

where δ_A and δ_B are the delta values of the pure parent CO_2, and X_A and X_B are the ratios of the parent CO_2 A and B respectively. Table 2 reports the delta values together with their associated expanded uncertainties (k = 2).

RM	δ^{13}C-CO_2 ‰	$U(\delta^{13}$C-$CO_2)$ ‰	δ^{18}O-CO_2 ‰	$U(\delta^{18}$O-$CO_2)$ ‰
RM1	-9.85	0.03	-14.93	0.06
RM2	-19.86	0.03	-21.36	0.06

Table 2 - δ^{13}C-CO_2 and δ^{18}O-CO_2 values in the pure CO_2 RMs, with their associated expanded uncertainties (k = 2).

The Law of Propagation of Uncertainties was applied to the model equation (2) according to the Guide to the Expression of Uncertainty in Measurement [13], hence obtaining eq. (3):

$$u^2(\delta_{prep}) = \left(\frac{\partial \delta_{prep}}{\partial \delta_A}\right)^2 u^2(\delta_A) + \left(\frac{\partial \delta_{prep}}{\partial X_A}\right)^2 u^2(X_A) + \left(\frac{\partial \delta_{prep}}{\partial \delta_B}\right)^2 u^2(\delta_B) + \left(\frac{\partial \delta_{prep}}{\partial X_B}\right)^2 u^2(X_B) \qquad (3)$$

As the pure parent CO_2 A and B have different origins, no correlation was taken into account. The uncertainty budget for δ^{13}C-CO_2 in RM2 is reported in table 3, as an example, for an estimate $\delta^{13}C_{prep}$ equal to -19.856 ‰. For RM1 a similar uncertainty budget was obtained.

Uncertainty component $u(x_i)$	Uncertainty source x_i	Uncertainty contribution	Sensitivity coefficient $\partial\delta^{13}C_{prep}/\partial x_i$	Contribution to $u(\delta^{13}C_{prep})$ $\lvert\partial\delta^{13}C_{prep}/\partial x_i\rvert \cdot u(x_i)$
$u_{\delta A}$	Delta value of parent CO_2 A	0.02 ‰	0.486	0.0097 ‰
$u_{\delta B}$	Delta value of parent CO_2 B	0.02 ‰	0.514	0.010 ‰
u_{XA}	Ratio of A	$3.6 \cdot 10^{-6}$	-42.148 ‰	$-1.54 \cdot 10^{-4}$ ‰
u_{XB}	Ratio of B	$3.8 \cdot 10^{-6}$	1.223 ‰	$4.7 \cdot 10^{-6}$ ‰
$u_c(\delta^{13}C_{prep})$				0.014 ‰
$U(\delta^{13}C_{prep})$ (k=2)				0.028 ‰

Table 3 – Uncertainty budget for δ^{13}C-CO_2 in RM2 (measurand estimate $\delta^{13}C_{prep}$ = -19.856 ‰).

Samples from the blended reference materials were prepared in glass flasks and sent to BGC-Isolab for measurement by IRMS, in order to link them to the VPDB scale. A good agreement was obtained

between the gravimetric and the measured results, in particular for δ^{13}C-CO_2, with a normalized error (E_n) of 0.5 for both the RMs.

3.2. CO_2 RMs at atmospheric amount fraction

Two atmospheric amount fraction reference materials at CO_2 nominal concentration of 400 µmol·mol^{-1} were prepared, having nominal values of -10 ‰VPDB and -20 ‰VPDB for δ^{13}C, obtaining an expanded uncertainty of 0.029 ‰ for δ^{13}C-CO_2.

The uncertainty budget was calculated according to [13]. Due to the multiple dilution, the preparation uncertainty on CO_2 amount fraction combines gravimetric uncertainty from the mass and amount fractions of component in each addition with the uncertainty in the purity of matrix gases and the uncertainty in the molar mass of each component. The combined expanded gravimetric uncertainty obtained for a nominally 400 µmol·mol^{-1} CO_2 mixture is 0.021 % (k = 2), corresponding to 0.086 µmol·mol^{-1}. Figure 1 reports the contribution of the various uncertainty sources.

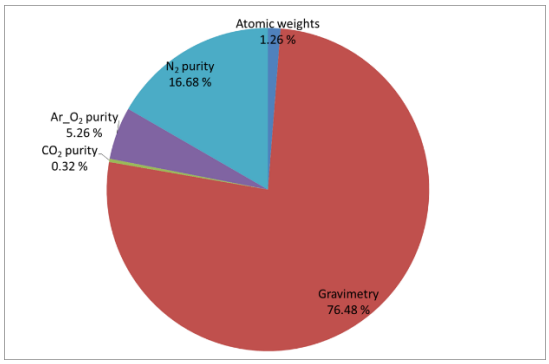

Figure 1 – Uncertainty sources in amount fraction of ambient CO_2 RMs

4. Conclusions

The present works describes the preliminary results obtained by INRiM in the preparation of RMs of CO_2 at known isotopic composition. The activity, started within the EMPIR project SIRS and is now continuing within the EMPIR project STELLAR. In order to investigate the stability of the produced mixtures, proper studies are ongoing by using NDIR and FTIR analysers, calibrated by means of dynamic mixtures.

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