Development of certified reference materials of carbon dioxide in synthetic air for environmental control of greenhouse gases

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1. Inmetro; 2. Nist

Introduction

Global climate change impacted by greenhouse gases (GHG) has been the focus of the scientific community together with society and world authorities. GHG measurements applied in mitigation projects or in the construction of local emission factors must be reliable and accurate in quantification.

In this regard, it is necessary to encourage the use of certified reference materials (CRMs) that ensure that the results are reliable, comparable and under the SI traceability. A suitable CRM can be developed with the characteristics of a real atmospheric sample.

The results presented and the dissemination of the use of these CRMs as quality tools ensure demonstrable metrological traceability on atmospheric research and GHG measurements which will have reliability in the process of compliance with GHG reduction goals, proposals in the mitigation measures of national contributions and in the inventory reports.

Thus, this work aims to be a facilitator in the process of metrological control of GHG monitoring, in order to promote the benefits deriving from its use for sustainable development broadening the accuracy and precision of atmospheric measurements not only on national matters but within SIM.

Objective

This study presents the development of a CRM, also called primary reference gas mixture (PRM), of a carbon dioxide in synthetic air at atmospheric level (CO_2/SCDA) produced for the first time by the Brazilian Metrology Institute, Inmetro.

Materials and Method

- Development of 06 (six) certified reference materials (CRM) of carbon dioxide in synthetic air at atmospheric level.
- Produced range: amount of substance from 380 to 550 μmol/mol.
- Atmospheric synthetic air matrix at the same level concentration as whole air, here defined by synthetic clean dry air (SCDA) following the range proposed by NARA *et al.*, 2012.
- The gravimetric preparation scheme is presented in Figure 1, using 2 (two) pre-mixtures for the PSM of CO_2/SCDA.

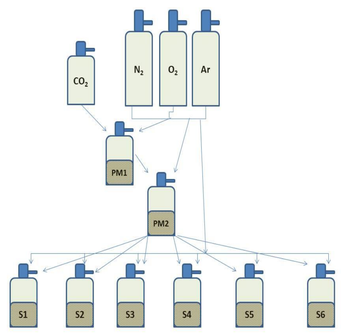

Figure 1 – Gravimetric preparation scheme

- The primary standards development addresses the following steps:

i. gravimetric production under the Standard ISO 6142:2015 of PSM in 5L aluminum cylinders from Scott Specialty gases with Aculife IV internal surface treatment from Luxfer; Pure gases used were: CO_2 5.5, N_2 6.0, O_2 6.0 and Ar 6.0, all from Praxair.
ii. analytical verification under the Standard ISO 6143:2001 (using Xgenline software by NPL), and analysis by cavity ring-down spectroscopy (CRDS) from Tiger Optics, Prismatic (figure 2);
iii. stability study (new PSM107511 production) ; and
iv. Characterization and certification of these CRM of carbon dioxide in synthetic air (CO_2/SCDA).

- This work was supported by the Gas Sensing Metrology Laboratory from NIST, by the use of their CRDS equipment (Picarro) and the analysis of NIST SRM 1720 at atmospheric range composition, as calibration standards, to support traceability in the verification analysis .

Results

The development of the gravimetric production of the new CO_2 in synthetic air batches of PSM begins with the purity analysis of the parent gases (Table 1).

Table 1 – Purity analysis of parent gases

	CO_2 99,9995%		CH_4 99,999%		Ar 99,9999%		O_2 99,9999%		N_2 99,9999%	
	C (mol/mol)	Urel (%)	C (mol/mol)	Urel (%)	C (mol/mol)	Urel (%)	C (mol/mol)	Urel (%)	C (mol/mol)	Urel (%)
N_2	---	---	$2{,}0\times10^{-6}$	58	$0{,}05\times10^{-6}$	58	$0{,}275\times10^{-6}$	58	0,9999994	2×10^{-5}
Ar	---	---	---	---	0,9999988	0,00000041	$0{,}15\times10^{-6}$	58	---	---
CO	---	---	0,5x10-6	58	---	---	$0{,}05\times10^{-6}$	58	$0{,}05\times10^{-6}$	58
CO_2	0,999998	$6{,}5\times10^{-5}$			---	---	$0{,}05\times10^{-6}$	58	---	---
O_2	$1{,}0\times10^{-6}$	$5{,}8\times10^{-5}$	---	---	$0{,}10\times10^{-6}$	58	0,99999912	2×10^{-5}	$0{,}25\times10^{-6}$	56
H_2O	$0{,}5\times10^{-6}$	58	---	---	$0{,}05\times10^{-6}$	58	$0{,}25\times10^{-6}$	56	$0{,}25\times10^{-6}$	56
THC	$0{,}01\times10^{-6}$	60	0,9999925	11×10^{-6}	$0{,}05\times10^{-6}$	58	$0{,}05\times10^{-6}$	58	$0{,}05\times10^{-6}$	58

The step of gravimetric production of the PSM batches was done, and the gravimetric composition (amount-of-substance) and its related uncertainty of the PSM defined as sample of the study can be seen at Table 2.

Table 2 – Gravimetric preparation of PSM sample

PSM113637 (sample) Component	Amount-of-substance (mol/mol)	Gravimetric uncertainty (mol/mol)
CO_2	$380{,}03\times10^{-6}$	$0{,}08\times10^{-6}$
Ar	$0{,}8025\times10^{-2}$	$0{,}0005\times10^{-2}$
O_2	$20{,}9014\times10^{-2}$	$0{,}0008\times10^{-2}$
N_2	$78{,}2580\times10^{-2}$	$0{,}0009\times10^{-2}$
CH_4	$0{,}04\times10^{-9}$	$0{,}02\times10^{-9}$
CO	$49{,}58\times10^{-9}$	$21{,}50\times10^{-9}$
H_2	$10{,}45\times10^{-9}$	$5{,}96\times10^{-9}$
THC	$49{,}98\times10^{-9}$	$21{,}50\times10^{-9}$
H_2O	$0{,}25\times10^{-6}$	$0{,}10\times10^{-6}$

The next step was the verification analysis by Picarro CRDS (Figure 2). The calibration curve was well adjusted by a linear GLS regression (GOF <2) with 5 PSM covering the amount-of-substance of the sample selected. The analysis results of all PSM produced can be seen at Table 3. The deviation graph of the verification analysis from the gravimetric composition with the combined uncertainty is presented in Figure 3.

Figure 2 – Verification analysis by CRDS

Table 3 – Verification analysis of CO_2/SCDA PSM

PSM code	C_{grav} (μmol/mol)	u_{grav} (rel, %)	C_{verif} (μmol/mol))	u_{ver} (rel, %)	SSD%	Δ (%)	U (%)	Verification
PSM113637	380,03	0,02	379,37	0,24	0,06	0,17	0,48	Approved
PSM137517	370,55	0,02	370,58	0,09	0,22	0,01	0,18	Approved
PSM107511	390,61	0,02	391,58	0,25	0,26	0,25	0,51	Approved
PSM139443	421,32	0,02	420,45	0,10	0,10	0,21	0,21	Approved
PSM108982	453,33	0,02	453,48	0,04	0,03	0,03	0,09	Approved
PSM107586	479,94	0,02	479,84	0,05	0,04	0,02	0,11	Approved
PSM147516	552,33	0,02	552,30	0,06	0,03	0,00	0,13	Approved

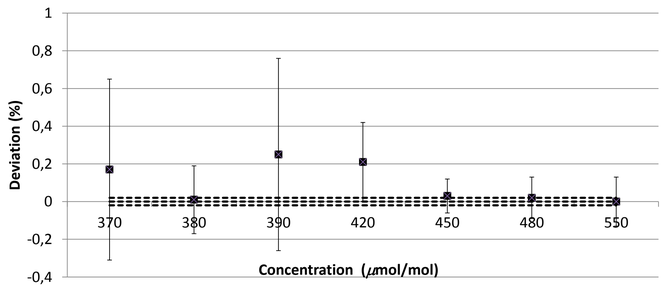

Figure 3 – Verification analysis deviation from gravimetry

Results

The long term stability study of the PSM108982, sample with amount-of-substance of 453 μmol/mol, was evaluated by CRDS analysis (Figure 4). A new PSM sample (PSM107511) was produced. The stability relative uncertainty was of 0,06%, estimated under the intermediate precision method.

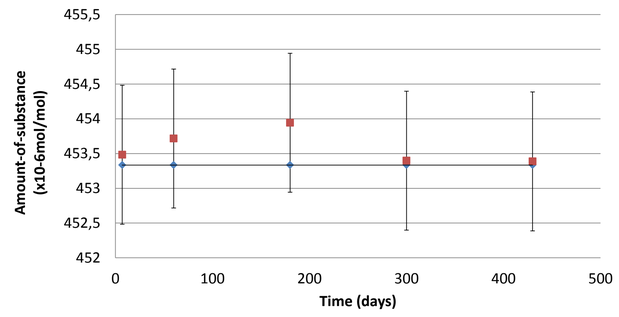

Figure 4 – Stability study of the PSM sample

From the control chart above of the evaluated sample, it is possible to observe that there is no tendency to instability of the sample mixtures over the evaluated period, which can be concluded that this type of CO_2/SCDA PSM for the studied concentration range is valid for at least over one year.

The characterization and certification of the CRM is given by assigning the final combined uncertainty that accompanies the amount-of-substance of the mixture derived from gravimetry. This combination is the gravimetric uncertainty, the analytical uncertainty by CRDS and the uncertainty of stability. The uncertainty presented is the expanded uncertainty, with a coverage factor of *k*=2, for a probability level of 95%. The uncertainty contribution from each CRM production step is given in Figure 5.

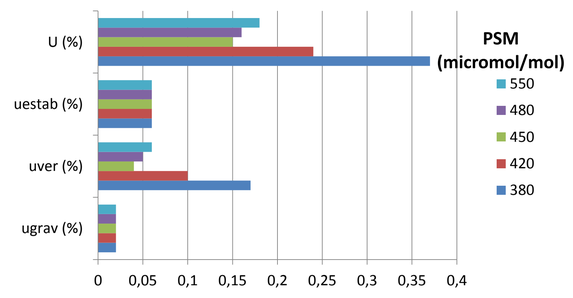

Figure 5 – Uncertainty contribution on CO_2/SCDA CRM

The SRM1720 batches from NIST were also analyzed at NIST (Picarro CRDS) and compared to Inmetro analysis (Tiger Optics CRDS). The results on amount-of-substance and the respective uncertainties between NMIs are equivalent, as presented in Table 4 and Figure 6.

Table 4 – CO2/SCDA analysis

Cilindro	Inmetro_CRDS		NIST_CRDS	
	CO_2		CO_2	
	µmol/mol	U (%)	µmol/mol	U (%)
CC499110	384,26	0,14%	384,52	0,04%
CC499088	390,90	0,06%	391,02	0,04%
CC499093	417,77	0,04%	417,79	0,03%
CC498967	419,57	0,10%	419,46	0,03%
CC499027	449,75	0,04%	449,53	0,03%
CC498929	448,68	0,08%	448,83	0,03%
CC498968	543,92	0,05%	544,02	0,02%

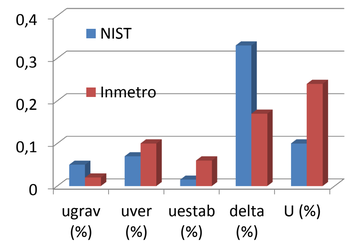

Figure 6 – Inmetro vs Nist

Conclusions

This study describes the development of a batch of primary standard mixtures of carbon dioxide in synthetic clean dry air at atmospheric level range certified by the Brazilian Metrology Institute (Inmetro). They were produced according ISO6142:2015 and ISO6143:2001, and certified after undergoing the requirements of ISO17034:2016.

The characterization of the CRM of CO_2/SCDA has an average expanded uncertainty (*k*=2) of 0.2%.

The use of CRM ensures that results obtained by different laboratories are comparable and traceable.

Acknowledgments

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