The Challenge of Developing Certified Reference Materials of Carbon Dioxide to Establish Traceability to Greenhouse Gases Monitoring Analysis

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Abstract. In recent years the need for the quality control, reliability and traceability of analytical results has been strongly emphasised. The increase in the concentration of carbon dioxide (CO_2) in the atmosphere has led the scientific community to investigate the adverse effects on humanity and nature, including the greenhouse effect, which contributes to global warming and can lead to climate change, besides the risks associated with human health. Due to the importance of metrological issues in the current scenario, the Laboratory of Gas Analysis (Lanag) of the National Institute of Metrology, Quality and Technology (Inmetro), is involved in improving measurement capabilities to provide confidence level regarding greenhouse gases standards by developing the methodology of preparation of such primary standard gas mixtures through gravimetry. This paper describes the development of certified reference materials of carbon dioxide in atmospheric synthetic air that are used to monitor its concentration in the atmosphere. Considering the contributions from gravimetry preparation and its verification analysis by cavity ringdown spectroscopy (CRDS) the relative expanded uncertainty of the standard mixture of carbon dioxide was lower than 0.5 % for the range studied from 370 to 550 µmol/mol, which is comparable to the average of 0.25% relative uncertainties presented on international standards mixtures.

1. Introduction

Greenhouse gases (GHG), as defined by ISO 14065:2013 [1] Clause 3.1.1, are gaseous constituent of the atmosphere, both natural and anthropogenic, that absorbs and emits radiation at specific wavelengths within the spectrum of infrared radiation emitted by Earth's surface, the atmosphere, and clouds. Include carbon dioxide (CO_2), methane (CH_4), nitrous oxide (N_2O), hydrofluorocarbons (HFCs), perfluorocarbons (PFCs) and sulfur hexafluoride (SF_6). It is well known that improved quality and monitoring points in greenhouse gases (GHG) is needed to better predict climate tendencies and monitor sources and sinks of GHG, but also there is the need to increase certainty in achieved values of the mitigation reduction goals of GHG. Then, building reliable testing of GHG based on new capabilities of traceable measurement results is needed, both for atmospheric measurements and local

measurement of emission factors of GHG. Besides, environmental legislation requires international standards of comparison.
Inmetro, is a locus of knowledge and credibility who plays an indispensable role, mainly towards the development and maintenance of certified reference material (CRM), as well as for carrying and spread the SI units of measurement, and its harmonization on a global level, providing traceability to a large number of users via a metrological chain. The Gas Analysis Laboratory (Lanag) from the Chemistry Metrology Division (Dquim) from Inmetro has the knowledge and facilities on producing certified gas mixtures for atmospheric levels of greenhouse gases, especially carbon dioxide and methane.
Within this framework the assurance of the required traceability of all measurements reflects in the use of reference materials which ensures that the results obtained by different laboratories are comparable and traceable. This reliability is essential in the maintenance of a universal and consistent system of measurements among different laboratories, besides disseminating traceability throughout society.

2. Methodology

2.1 Primary standard gas mixtures of GHG reference material

The use of reference mixtures/materials with matrix compositions and analytes concentrations similar to those found in environmental samples makes it possible to obtain reliable measurement results. Investigations of samples of different types of gas mixtures are being carried out on an ever greater scale, so there is an increasing need for new techniques in preparing primary standard gas mixtures (PSM). Primary Reference Materials (PRM) are prepared gravimetrically as Primary Standard Gas mixtures (PSM) by National Metrology Institutes (NMI) using guideline ISO 6142:2015 - "Gas analysis – Preparation of calibration gas mixtures – Weighing methods". The accuracy level of PRM is the highest commercially available mixture, and therefore, not mended for direct use as working standard calibrating gas analysers, but more as reference standard to which working standards are traceable to.
Certified Reference Materials (CRM) are prepared in compliance with ISO 17034:2016 – "General requirements for the competence of reference materials producers", and are certified by the national standards laboratory using guideline ISO 6143:2001 - "Gas analysis – Determination of composition of calibrating gas mixtures – Comparison methods". In this comparison the method of multipoint calibration is applied, where the analyser is calibrated using PRM.
Standard gas mixtures are used mainly in validating analytical procedures and for assessing the competence of laboratory staff. They are also essential in monitoring air pollution. The increasing need to monitor the degree of air pollution has driven the search for new techniques of preparing PSM containing reliable mixtures with analytes at ever smaller concentrations levels [e.g., ppb and ppt], closely resembling those of environmental samples. However, it challenges analysts to produce such reference gaseous mixtures.
Advance in specific metrological services of providing local CRM mixtures to account GHG based on metrologically traceable measurement results are increasingly being demanded, especially for the three main greenhouse gas contributors: carbon dioxide, methane and nitrous oxide. Improve robustness and accuracy of climate data and uncertainties associated with measurements of GHG in outdoor measurements and in local emission factors of specific GHG are being needed. Thus, making available local CRM and their dissemination to end users in Latin America countries for new services of measurement of GHG based on traceable measurements should be encouraged.
The new certified reference material (CRM) was developed by Inmetro consists in a primary reference mixture (PRM) of carbon dioxide (CO_2) in a matrix of synthetic air at atmospheric levels. The standard mixtures developed by expertise NMI, such as NIST and KRISS, use as matrix whole dry air

sampled from clean dry air at specific places. This paper presents the development of a standard using a synthetic matrix of atmospheric air at the same level concentration as the whole air, being defined here as atmospheric synthetic air mixtures or by synthetic clean dry air (SCDA).

2.2 Gravimetric development procedure

The gravimetric preparation, as well as the calculation of the gas composition and associated uncertainty evaluation should be done in accordance with ISO 6142:2015. Before the gravimetric preparation of the mixture, the cylinder is cleaned by evacuation in a Pfeiffer turbo molecular pumping station followed by filling, after a sequence of pressure and vacuum, with high purity nitrogen (N_2) 99.9999% mol/mol. Aluminium gas cylinders of 5L treated with a proprietary process Aculife IV, by Scott Specialty Gases, were used. Afterwards, the empty cylinder is weighed in a mass comparator, Mettler balance, where it is compared against an identical (reference) cylinder. Then the pure gas or a pre-mixture with higher concentration of carbon dioxide in air is transferred via a filling station to the empty cylinder. This process of weighing and filling is repeated for all components of the matrix at the atmospheric air composition, i.e.: 0.9% mol/mol of argon, 21% mol/mol of oxygen and 79% mol/mol of nitrogen. Once the mixture is produced the final composition is calculated according to ISO 6142 by using the added masses of each component that is expressed as mole fraction µmol/mol.
The carbon dioxide in atmospheric synthetic air mixtures (CO_2/SCDA) were prepared in the range of 370 to 550 µmol/mol from the sequence dilution of a 3.0 (pre-mixture PM1) and a 0.5 (pre-mixture PM2) cmol/mol CO_2/SCDA pre-mixtures, preliminary prepared from the following pure gases, all of them from the supplier White Martins: CO_2 99.9995%, Argon 99.9999%, Oxygen 99.9999%, and Nitrogen 99.9999%. The scheme of the gravimetric planning preparation can be observed at Figure 1.

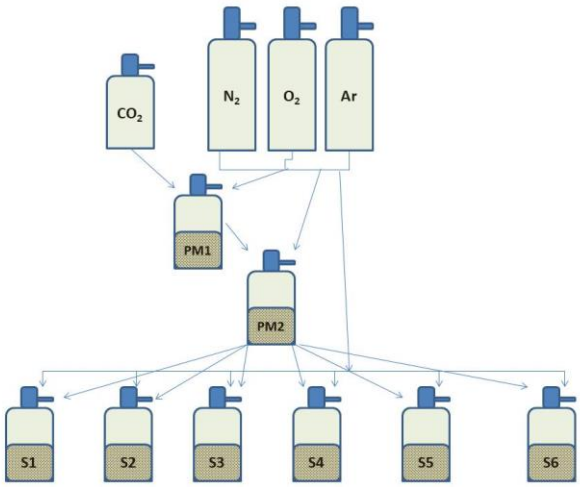

Figure 1

Primary gravimetric gas standards (PSM) are prepared in-house using parent gases with certified purity and contain no species that would affect the certified concentration values or be detrimental to the stability of the mixtures. The purity of the parent gases are checked against the manufacturers specification using high-sensitivity instrumentation, to ensure that no chemical or physical reactions take place during any stages of the preparation and dilution process, and to demonstrate the long term stability of the standards after preparation. For this work, first it was just applied the purity estimation based on ISO 6142, which uses the supplier data from gas industry of the pure gases to estimate the uncertainty of each component detected as impurity that can be interfering at the main component, i.e. trace levels of impurity carbon dioxide in pure nitrogen, for example. Afterwards, a purity analysis

using GC/PDHID is intended to be done in order to confirm the amount of impurities in the pure gases used by the use of new standards of trace level compounds prepared for this specific analysis, such as trace levels of carbon monoxide and argon in pure nitrogen, nitrogen and oxygen in pure oxygen, and nitrogen and oxygen in pure argon.
The primary gas standards prepared are checked soon after the gravimetric preparation to confirm that their concentrations are as expected. The analytical method employed in this paper was cavity ringdown (CRDS) by using a Tiger Optics – Prismatic equipment. The analysis were performed in 03 (three) different days under repeatability conditions with 10 (ten) runs of half an hour for stabilization each day. Based on the calibration curve, analysis values and its respective uncertainties were assigned to the amount of molar fractions of carbon dioxide. The analytical verification takes place to confirm gravimetric molar fraction results which is based on calculation regression presented in accordance with ISO 6143:2001.

2.3 Characterization of the primary standard mixture

Finally, after verification analysis, standard mixtures are then allowed to stand for a defined period before final certification is carried out. Following this period, all standards will be then are certified. This work presents the steps of developing a PSM of CO_2/SCDA with its results for gravimetry and verification analysis, and their respective uncertainties contributions.

3. Results and Discussion

The gravimetric preparation data with the respective uncertainty was obtained by the Gas Metrology software developed by the Dutch NMI – VSL; this software was developed under demand to be used together with the gravimetric facilities based on calculation required by ISO 6142 and validated by all KC that the Gas Analysis Laboratory - Lanag from Inmetro that has participated before under the auspices of BIPM/CCQM. The gravimetric concentration and its uncertainty it's given at Table 1.

Table 1 - Gravimetric results for the batch of PSM CO_2/CDA

Mixture Code	**Concentration$_{grav}$ (*micro*mol/mol)**	**uncertainty$_{grav}$ (%)**
S1	370.55	0.02
S2	390.6	0.02
S3	421.32	0.02
S4	453.33	0.02
S5	479.94	0.02
S6	545.71	0.02

With the method developed for the CRDS technique, calibration curves were drawn for each selected range, using the primary standards produced in-house to compose the curve and as samples, as well as, certified reference materials to verify the adjust of the proposed calibration curve. In this way, the establishment of the calibration curve that represents the set of points (x_i, y_i), which the known concentrations used are x_i, are plotted against the responses of the instrument, y_i, obtained at independent and repetitive conditions. A linear relationship between the concentrations and the measurement results is adjusted, obtained by the mathematical model of correlation: least squares numerical method. It was selected 03 (three) primary standard gaseous mixtures produced by Lanag, which range of concentration adopted was from 370 to 420 μmol mol^{-1}, due to the specifications from the equipment used. Those standards were analyzed to be fitted in a linear model of calibration curve,

and a standard selected as sample at a mole fraction of 380 μmol mol^{-1}. Table 2 presents the primary standard mixtures used at the calibration curve fitted for each method and their respective relative standard deviation or coefficient of variation (CV) obtained by each standard mixture.

Table 2 – PSM from calibration curve from CRDS method validation

Primary standard mole fraction (*micro*mol mol^{-1})	**Gravimetric uncertainty (*micro*mol mol^{-1})**	**Day 1 – CV (%)**	**Day 2 – CV (%)**	**Day 3 – CV (%)**
370.55	0.08	0.21	0.06	0.05
390.61	0.08	0.23	0.60	0.02
421.32	0.08	0.03	0.16	0.08

The linearity was assessed by repeated injections of five primary standards produced at different concentrations englobing the selected range. The linearity is evaluated by the following statistical approach: the coefficient of correlation and the goodness of fit, derived by the part of validation of the response model at ISO 6143. To effectively test the compatibility of a prospective analysis function, calculate the measure of goodness-of-fit (GOF), defined as the maximum value of the weighted differences, $|\hat{x}i - xi|/u(xi)$ and $|\hat{y}i - yi|/u(yi)$, between the coordinates of measured and adjusted calibration points (i=1,2,3…, n). A function is admissible if GOF<2, as well, as r2>0.99.
Results from the primary standards used as samples at the curve of calibration fitted with the responses from the primary standards obtained from each technique can be seen at Table 3. It is presented the relative deviation of the calibrated mole fraction (x_c) obtained by the regression from the gravimetric mole fraction (x_g); the relative expanded uncertainty (U) calculated by the calibration curve fitted; and the number of response repetitions (N) of each day analyzed at each technique evaluated.

Table 3 - Results from the sample evaluated at the calibration curve

CRDS						
Day	**x_g (μmol mol^{-1})**	**x_c (μmol mol^{-1})**	**Δ (%)**	**U (%)**	**CV (%)**	**N**
1	380.09	378.82	0.32	0.42	0.14	05
2	380.09	380.12	-0.02	0.48	0.25	05
3	380.09	380.12	-0.02	0.22	0.21	05

The analytical results obtained by cavity ringdown spectroscopy system (CRDS) were applied to get an adjusted fit model where the analytical or verification concentration and its respective uncertainties were obtained through a statistical regression. Appling ISO 6143 calculation for concentration and uncertainties derived by this calibration curve analysis, results of the verification analysis of the primary standards prepared can be observed at Table 4 by means of deviation of gravimetric concentration and analysis value, as well as the relative combined expanded uncertainty for gravimetric and analysis verification.

Table 4 - Verification results for the batch of PSM CO_2/CDA

Mixture Code	Δ (%)[1]	U (%)[2]
S1	0.01	0.18
S2	0.17	0.48
S3	0.21	0.21
S4	0.03	0.09
S5	0.02	0.11
S6	0.01	0.14

[1] Relative deviation between the gravimetric and verification analysis concentration
[2] Relative combined expanded uncertainty (gravimetry and verification analysis)

According to the verification requirement stated by ISO 6142, all gravimetric mixtures results are considered approved when the absolute difference between the gravimetry and verification analysis results are lower than expanded combined uncertainties, as presented at equation 1.

$$|x_g - x_v| \leq k \times \sqrt{{x_g}^2 + {x_v}^2} \quad (1)$$

where,
x_g – gravimetric concentration (μmol/mol)
x_v – verification analysis concentration (μmol/mol)
u_g – gravimetric absolute uncertainty (μmol/mol)
u_v – verification analysis absolute uncertainty (μmol/mol)

The relative uncertainty estimated by the calibration for the selected sample at the inferior limit of the range, 380 μmol/mol, was lower than 0.5%, which is accepted considering that the purity analysis was done only by estimation on supplier data quality. Therefore, all standards of CO_2/SCDA developed were considered approved during this step of verification analysis.
Each analysis uncertainty is then combined with the gravimetry uncertainty to deliver the final expanded uncertainty of the PSM, which can be observed at Table 5 presented.

Table 5 – Certified Value and Expanded Uncertainty of PSM of CO_2/SCDA

PSM	*Certified value (mol/mol)*
S1	$(370.55 \pm 0.68) \times 10^{-6}$
S2	$(380.03 \pm 1.82) \times 10^{-6}$
S3	$(421.32 \pm 0.88) \times 10^{-6}$
S4	$(453.33 \pm 0.40) \times 10^{-6}$
S5	$(479.94 \pm 0.52) \times 10^{-6}$
S6	$(545.71 \pm 0.78) \times 10^{-6}$

The value attribution calculation presents the expanded uncertainty (U), and it is expressed as the product of the combined standard uncertainty (u) and the coverage factor k=2 (approximately 95% of confidence level).
For the final certification of the batch produced, these standard gas mixtures shall go through a short-term and a long-term stability study, to be performed during the period of one year, with periodic analysis to compose the final estimation from this uncertainty contribution of stability of the mixture. It´s important to note that for gas mixtures standards no homogeneous studies are needed, as the batches are prepared individually, besides considering the homogeneous physical-chemistry behaviour of those component in these gas mixtures.

4. Conclusions

Nowadays, the rising concerning on environment regarding global atmospheric air plays an important role in the level of air pollution. So, the analysis of air quality using certified reference material presents reliable and comparable analytical methods in order to reduce the emission of such greenhouse gases. An appropriate CRM can usually be matched to the characteristics of a real sample.
This paper describes several aspects regarding new developments in the gravimetric production of primary standard gas mixtures of carbon dioxide in atmospheric synthetic air in Brazil's Metrology Institute, Inmetro, in order to provide traceability and confidence on GHG monitoring research and analysis.. Carbon dioxide at atmospheric levels primary standards mixtures were gravimetrically produced according ISO 6142:2015, and .the results were analytically verified by cavity ringdown system with a calibration model regression, according to ISO 6143:2001. The materials were prepared obeying all the gravimetric requirements of ISO Standards, and were certified after undergoing the requirements of ISO 17034:2016.
We expect this paper will contribute to scientific community to alert to the importance of reliability and traceability in environmental measurements, especially in such a complex field like the monitoring of atmospheric air of GHG parameters, by the use of this kind of reference materials. So, this works presents as novelty and interest to readership the use of primary methods and achievements made in developing of environmental CRM, in order to support the needs of global society and to disseminate traceability and harmonization among countries all over the world measurements of carbon dioxide traces in the atmosphere.

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