

Carbon Dioxide Standards for Accurate and Reliable Greenhouse Gas Emissions Measurement

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INTRODUCTION

Climate change, driven by greenhouse gas (GHG) emissions such as carbon dioxide (CO₂), presents a global challenge that demands precise and reliable measurements for effective control and mitigation. In Uruguay, motor vehicles represent one of the main sources of pollutant gases such as carbon monoxide and carbon dioxide, which have significantly increased the atmospheric concentrations of these gases, particularly CO₂. To ensure that emissions remain within permitted limits, it is essential to develop high-quality reference gas mixtures for calibrating analytical equipment and implementing robust measurement methods.

At LATU, we prepare two types of references gas mixtures Primary Reference Materials (PRMs) and Certified Reference Materials (CRMs). PRMs are produced using primary measurement methods and have direct traceability to a unit of the International System of Units (SI). In the case of gas mixtures, PRMs are prepared by gravimetry, a technique with direct traceability to the mole. CRMs, on the other hand, obtain their traceability through calibration against PRMs. These mixtures contain precisely defined amount fractions of various gases, ensuring metrological traceability for the monitoring of atmospheric pollutants.

PRIMARY REFERENCE MATERIALS

PRMs are prepared gravimetrically using two cylinders of the same material and volume. One is the reference, and the other is filled with pure gases. The amount fraction of each gas is determined based on the combination of the weight difference between the sample and reference cylinders in each weighing cycle, chemical purity, and molar masses.

The accuracy of the reference gas mixtures is ensured by following the guidelines of ISO 6142:2015(E) and ISO 6143:2001, guaranteeing compliance with international standards.

A PRM of 0.35 mol/mol CO₂ in N₂ was prepared as follows:

- Conditioning the cylinder in an evacuation and filling station.
- Weighing the cylinder in three stages: empty, after adding CO₂, and after adding N₂ as the balance gas.
- Homogenize the sample in a cylinder homogenizer.
- The amount fraction (y_k) of each gas was determined using an equation that considers the molar fractions (x), molar masses (M), and added masses (m) of the components.
$$y_k = \frac{\sum_{j=1}^r \left(\frac{x_{k,j} \times m_j}{\sum_{i=1}^q x_{i,j} \times M_i} \right)}{\sum_{j=1}^r \left(\frac{m_j}{\sum_{i=1}^q x_{i,j} \times M_i} \right)}$$
- The certified amount fraction of the PRM was determined using the formula form above. Its associated uncertainty (u_c) derived from the combination of preparation (u_{prep}) and verification (u_{ver}) uncertainties. The preparation uncertainty includes contributions from gravimetric uncertainty and potential instability.

$$u_c(y_k) = \frac{1}{2} \sqrt{u^2(y_{k,prep}) + u^2(y_{k,ver}) + (y_{k,prep} - y_{k,ver})^2}$$

- The final mixture is verified using an independent PRM, in accordance with ISO 6142 and ISO 6143, by applying a calibration curve. The calibration mixture is considered verified if it meets the acceptance criterion.

$$|y_{k,prep} - y_{k,ver}| \leq 2 \sqrt{u^2(y_{k,prep}) + u^2(y_{k,ver})}$$

Once prepared, the PRM serves as a fundamental tool for calibrating gas analyzers, ensuring accurate and traceable measurements. This calibration process is essential for maintaining the precision and reliability of analytical instruments and enabling and accurate quantification of greenhouse gases across different monitoring systems.



Certified value for the PRM of CO₂ in N₂

0.3561 ± 0.0011 mol/mol (k=2)

CONCLUSION

The results confirm the effectiveness of the gravimetric method in producing high-quality reference gas mixtures, essential for calibrating instruments, certifying gas standards, and validating measurement methods. This approach ensures direct traceability to the SI, enabling consistency and comparability of measurements on a global scale. Developing these standards strengthens Uruguay's metrological capabilities, providing key tools for precise GHG monitoring in line with international regulations. By establishing a robust metrological framework, LATU enhances accuracy and traceability, supporting global efforts to reduce emissions and mitigate climate change.



REFERENCES

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