Detailed description of the proposed research "Development of certified reference materials of CO_2 gas mixtures characterized for the isotopic composition".

Accurate and sound determinations of the atmospheric concentration of the greenhouse gases (GHGs), among which carbon dioxide (CO_2), enable the development of models to predict future scenarios and to implement effective measures to counteract global warming. In particular, the concentration trend of CO_2 in the atmosphere is increasing continuously and require constant monitoring. For this purpose, it is very useful to rely on metrological references represented by gas mixtures with CO_2 concentration at the atmospheric level to ensure the reliability of the results and compare them at the international level. 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 Certified Reference Materials (CRMs) for the isotopic composition of CO_2 in air ($\delta^{13}C\text{-}CO_2$) is of utmost importance to achieve the comparability and traceability of data, which are essential features of measurement results in the environmental and climate fields.

Carbon has two naturally occurring stable isotopes, ^{12}C and ^{13}C, with abundances of 98.89 % and 1.11 %, respectively (with the naturally occurring radioisotope $^{14}C < 10^{-10}$ %). The $\delta^{13}C\text{-}CO_2$ scale refers to a conventional standard, the Vienna Pee Dee Belemnite (VPDB) scale, maintained by the International Atomic Energy Agency. The $\delta^{13}C$ value of a material describes how far the isotope ratio in that material differs from the ratio in the standard. CRMs can be used to calibrate spectroscopic instrumentation for the monitoring of the increase of the $\delta^{13}C\text{-}CO_2$ value in atmospheric air samples, thus contributing to supporting the planning of specific actions aimed at reducing CO_2 emissions.

At INRiM, the realization of CRMs of CO_2 in air at ambient level and known isotopic composition is ongoing, and started from the activities carried out within the European Research Projects 16ENV06 SIRS and 19ENV05 STELLAR. From August 2025, INRiM will be involved in the EPM Project 24GRD03 MetHIR "Metrology for harmonisation of field isotope ratio measurements", which is devoted to support the efforts of the metrological community to achieve the comparability of results and to assure accuracy and metrological traceability to CO_2 stable isotope measurement results. This project seeks to (1) harmonize the field of isotope ratio measurements, (2) improve the traceability and (3) realize compatibility of results targeting World Meteorological Organization (WMO) - Global Atmosphere Watch Programme (GAW) compatibility goals.

At INRiM, the production service for CRMs characterised for the CO_2 amount fraction at atmospheric level in synthetic air is active since 2024. The development of candidate CRMs for the isotopic composition on the same mixtures represents a fundamental and promising activity. The proposed PhD research aims at supporting the INRiM activities conducted in the framework of the MetHIR project. The research activity will focus on the preparation of the gas mixtures by the gravimetric method following the Internationale Standard ISO 6142-1 and on the optimization of the performance of two measurement techniques used to verify the $\delta^{13}C\text{-}CO_2$ value of the gas mixtures: the Fourier transform infrared spectroscopy (FTIR) and the Cavity Ring-Down Spectroscopy (CRDS). Particular attention will also be paid to the evaluation of the uncertainty contributes obtained with the two techniques in order to meet the comparability requirements at WMO level. To improve the measurement uncertainties of the two aforementioned verification techniques and to avoid potential operator errors, the gas uptake system from different cylinders will be automated using solenoid valves, along with the development of software for data acquisition and analysis. The uncertainty contribution related to the stability of the gas mixtures will be deeply investigated to establish their shelf life within the declared uncertainty. Different uncertainty evaluation approaches will be tested (e.g. Ordinary Least Squares and Weighted Least Squares methods). In addition, in order to minimize the uncertainty associated with the CRM value, different uncertainty evaluation approaches will be explored (the uncertainty evaluation according to the Guide to the expression of uncertainty in measurement (GUM) and the propagation of distributions using a Monte Carlo method (JCGM101:2008).

The successful achievement of this research activity will enable INRiM to declare relevant Calibration Measurement Capabilities (CMCs) and to activate a corresponding dissemination service of CRMs for the isotopic composition.