

TOWARDS THE REALISATION OF CERTIFIED REFERENCE MATERIALS OF CO₂ IN AIR AT AMBIENT AMOUNT FRACTION AND KNOWN δ¹³C



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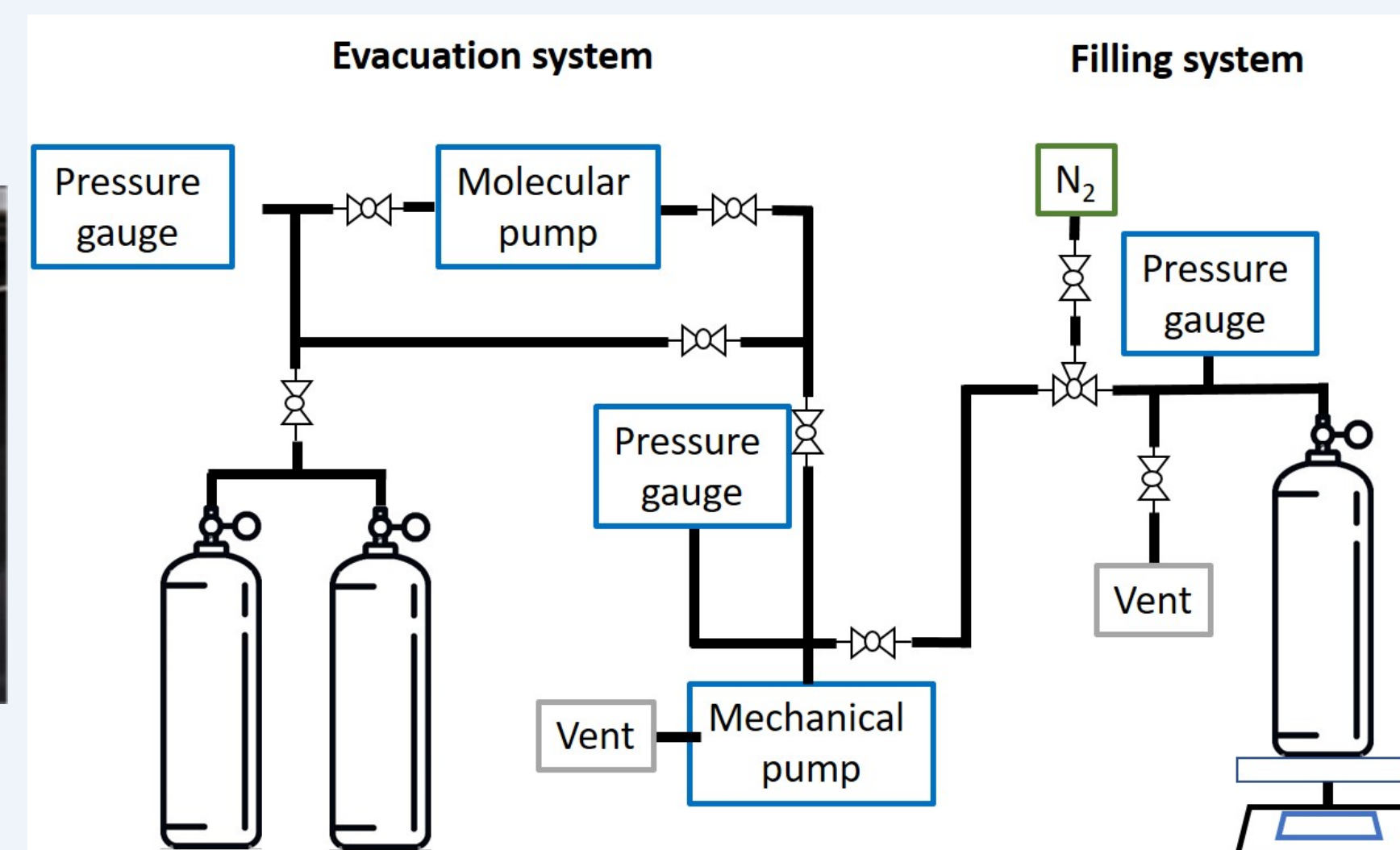


1. INTRODUCTION

- Monitoring the increasing levels of CO₂ in atmosphere and discriminating between the natural and anthropogenic sources of CO₂ are of utmost importance to support climate change studies and to reduce CO₂ emissions from human activities in the close future.
- The availability of sound and affordable **Certified Reference Materials (CRMs)** for the measurement of the isotopic composition of CO₂ at ambient amount fraction is foreseen to support the researchers operating with spectroscopic techniques in the isotope measurement field.

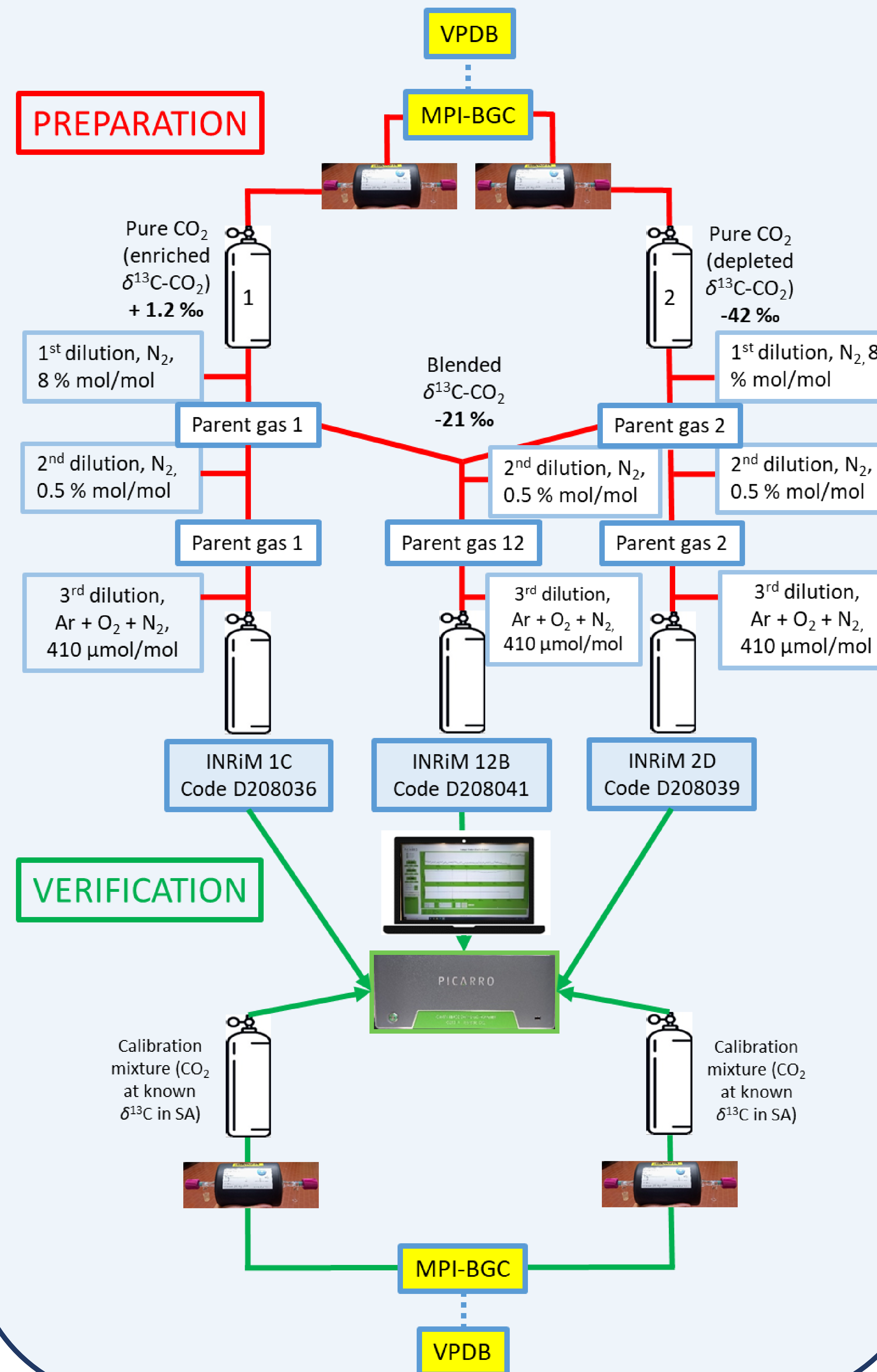
2. REALISATION OF CRMs BY GRAVIMETRY

- At INRiM, the realization of gaseous reference materials of CO₂ in air at known δ¹³C-CO₂ is ongoing.
- CRMs for CO₂ amount fraction are realized by **gravimetry** (ISO standard 6142-1), in high-pressure cylinders of aluminium alloy, with U_{rel} 0.33 %.
- Mixtures are prepared from different pure CO₂ sources (SIAD, Italy), having isotopic composition spanning from +1.3 ‰ to -42 ‰.



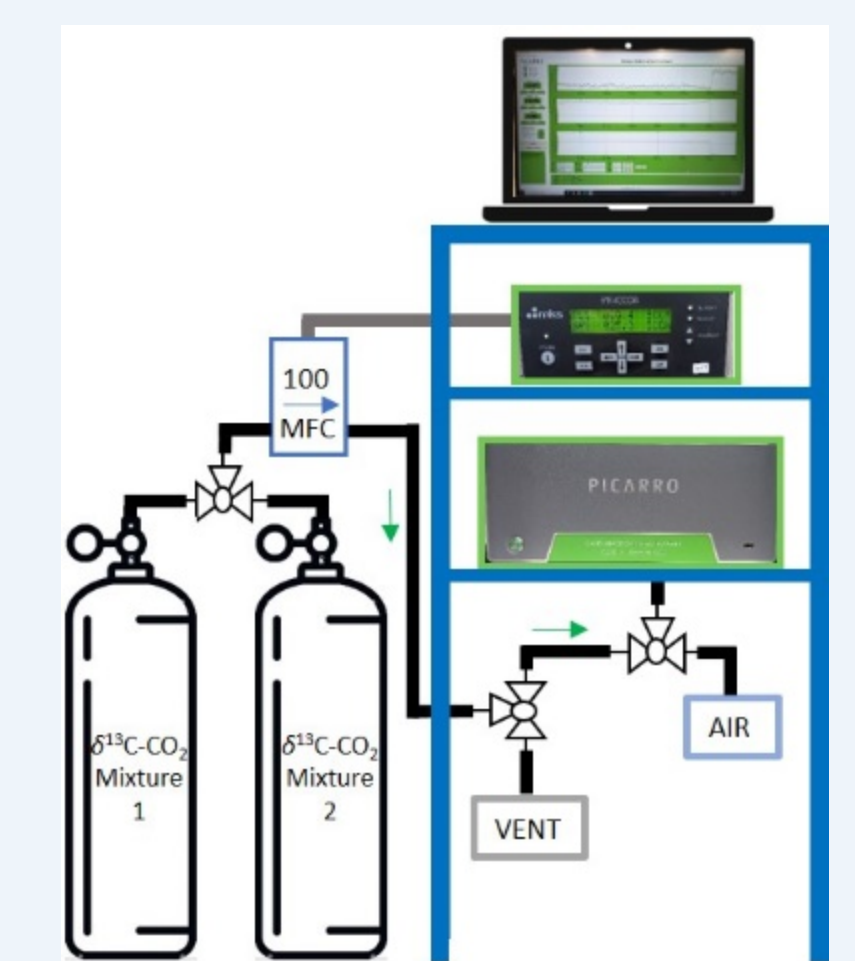
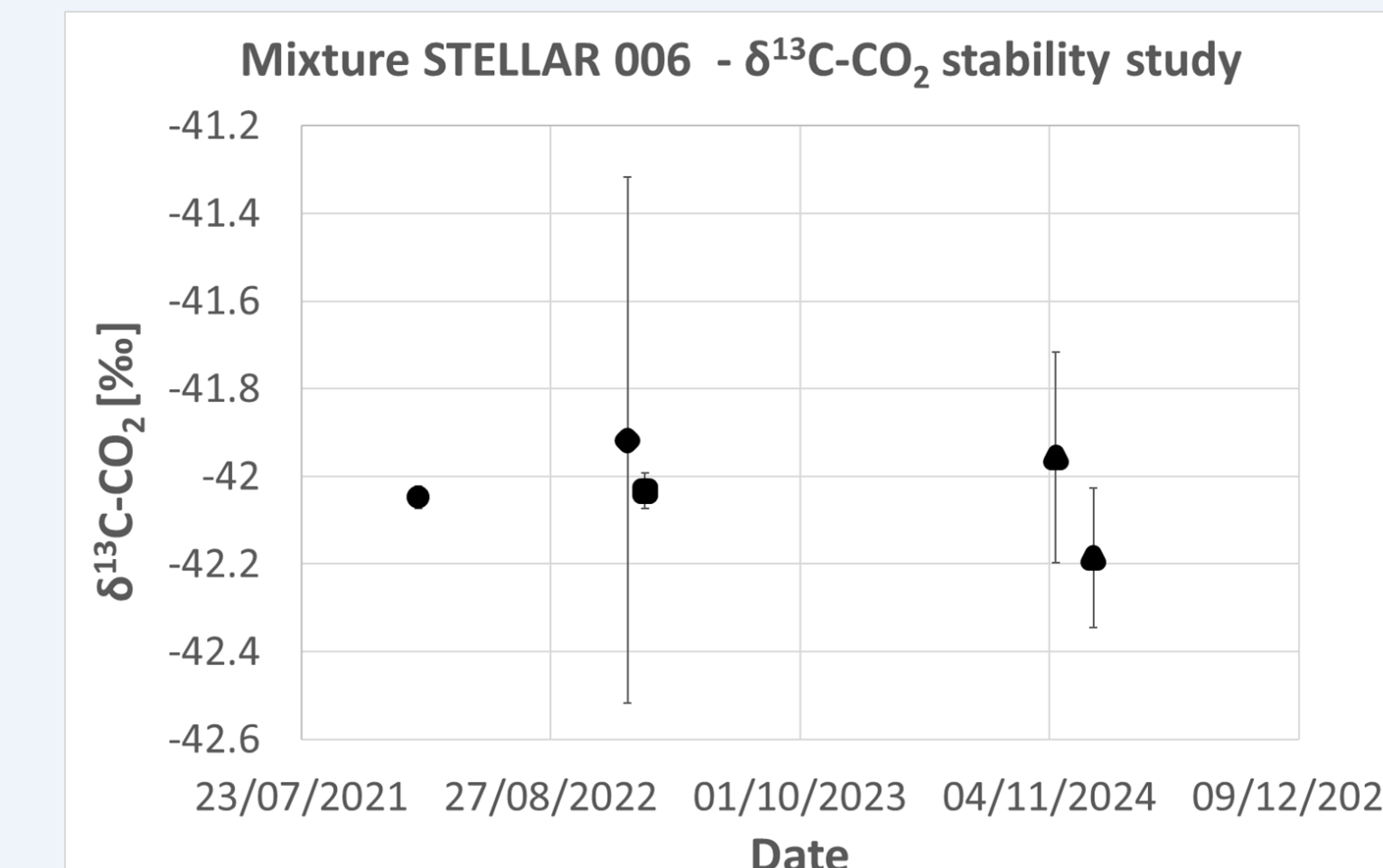
Precision weighing of a reference gas mixture, with calibrated mass standards (left); Scheme of the gravimetric preparation facility (right).

3. TRACEABILITY CHAIN FOR δ¹³C-CO₂



4. MEASUREMENT TECHNIQUES

- Non-dispersive infrared spectroscopy (NDIR ABB URAS 14, Switzerland) is used to verify the mixtures for their amount fraction values.
- Fourier transform infrared spectroscopy (FTIR Thermo Scientific Nicolet iS50, USA) is used for the δ¹³C-CO₂ value assignment.
- A Cavity Ring-Down Spectrometer (CRDS G2131i Picarro, USA) is used to verify the isotopic composition of the prepared mixtures.



The stability of the calibration mixtures was tested over a period of 4 years, by periodically repeating the verification of their isotopic composition.

Set-up of the CRDS spectrometer

Mixture number	Gravimetry	$U(x)$ k=2	FTIR	$U(x)$ k=2	IRMS (MPI)	$U(x)$ k=2	CRDS	$U(x)$ k=2
	‰	‰	‰	‰	‰	‰	‰	‰
SIRS 010 (D580461) CO ₂ 390.04 μmol mol ⁻¹	-19.76	0.06	-19.54	0.60	-19.74	0.04	-19.96	0.35
STELLAR 022 (15914) CO ₂ 404.72 μmol mol ⁻¹	-42.05	0.03	-41.87	0.30	-41.94	0.12	-42.24	0.20
STELLAR 006 (12997) CO ₂ 409.46 μmol mol ⁻¹	-42.05	0.03	-41.92	0.30	-42.03	0.04	-42.19	0.16

Comparison of the values obtained with different techniques for 3 INRiM mixtures, with the reference IRMS value

REFERENCES:

- F. Durbiano, F.R. Pennechi, F. Rolle, S. Pavarelli, M. Segà, Stability study and uncertainty evaluation of CO₂ certified reference materials for greenhouse gases monitoring, *Measurement*, 232, (2024), 114653, doi.org/10.1016/j.measurement.2024.114653
- M. Segà, F. Durbiano, S. Pavarelli, F. R. Pennechi, F. Rolle, Comparison of cavity ring-down spectroscopy and Fourier transform infrared spectroscopy for the isotopic composition determination of CRMs of CO₂ in air - *International Congress of Metrology (CIM2025)*, (2025)

5. CONCLUSIONS AND FUTURE DEVELOPMENTS

- Participation in the European Joint Research Project "Metrology for harmonisation of field isotope ratio measurements – MethIR
- Improvement in the analytical equipment to enhance sensitivity (e.g. autosampler)
- Stability studies on the RMs
- Submission of CMCs for the production of CO₂ in synthetic air CRMs characterised for both CO₂ amount fraction and isotopic composition.