

Background

Monitoring atmospheric greenhouse gas (GHG) concentrations and isotopic composition is essential for understanding emissions, assessing mitigation efforts, and studying environmental changes. This has led to the need for reliable, affordable instruments providing accurate, real-time data. Over the past decade, laser-based instruments for measuring isotopic ratios of GHGs like carbon dioxide, methane, and nitrous oxide have become commercially available, requiring careful calibration to align with mass spectrometric methods. There is also a growing interest in mid-cost sensors for denser networks in urban areas. The NMIs and BIPM are developing global quality infrastructure to ensure accurate GHG isotope measurements, focusing on comparisons of isotopic standards for CO₂. This work highlights progress in global equivalence of pure CO₂ gas standards (CCQM-P204) and CO₂ in air standards (CCQM-239).

The BIPM IRMS facility

- In 2020, the BIPM Chemistry Department acquired a Thermo Fisher 253+ Isotope Ratio Mass Spectrometer (IRMS) for measuring stable isotopes of gaseous CO₂ samples.
- In 2021, the instrument was used in the CCQM-P204 pilot study to assess laboratories' capabilities in assigning isotope ratios for pure CO₂ gas samples.
- The isotope ratios were expressed as delta values relative to international scales: $\delta^{13}\text{C}_{\text{VPDB}}$ and $\delta^{18}\text{O}_{\text{VPDB-CO}_2}$.
- Participants in the study used either IRMS or IRIS technology to measure $\delta^{13}\text{C}_{\text{VPDB}}$ and $\delta^{18}\text{O}_{\text{VPDB-CO}_2}$ in the gas phase.

The BAT System

The BIPM's IRMS facility has been now equipped with a custom built (BIPM) Air Trapping system (BAT) to extract CO₂ from air mixtures using cryogenic separation for determination of $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ -CO₂, with a correction for the N₂O present in the sample. A procedure for regularly determining the relative ionization efficiency of N₂O in relation to CO₂ has also been developed and is applied as a function of the amount fraction of N₂O in the sample.



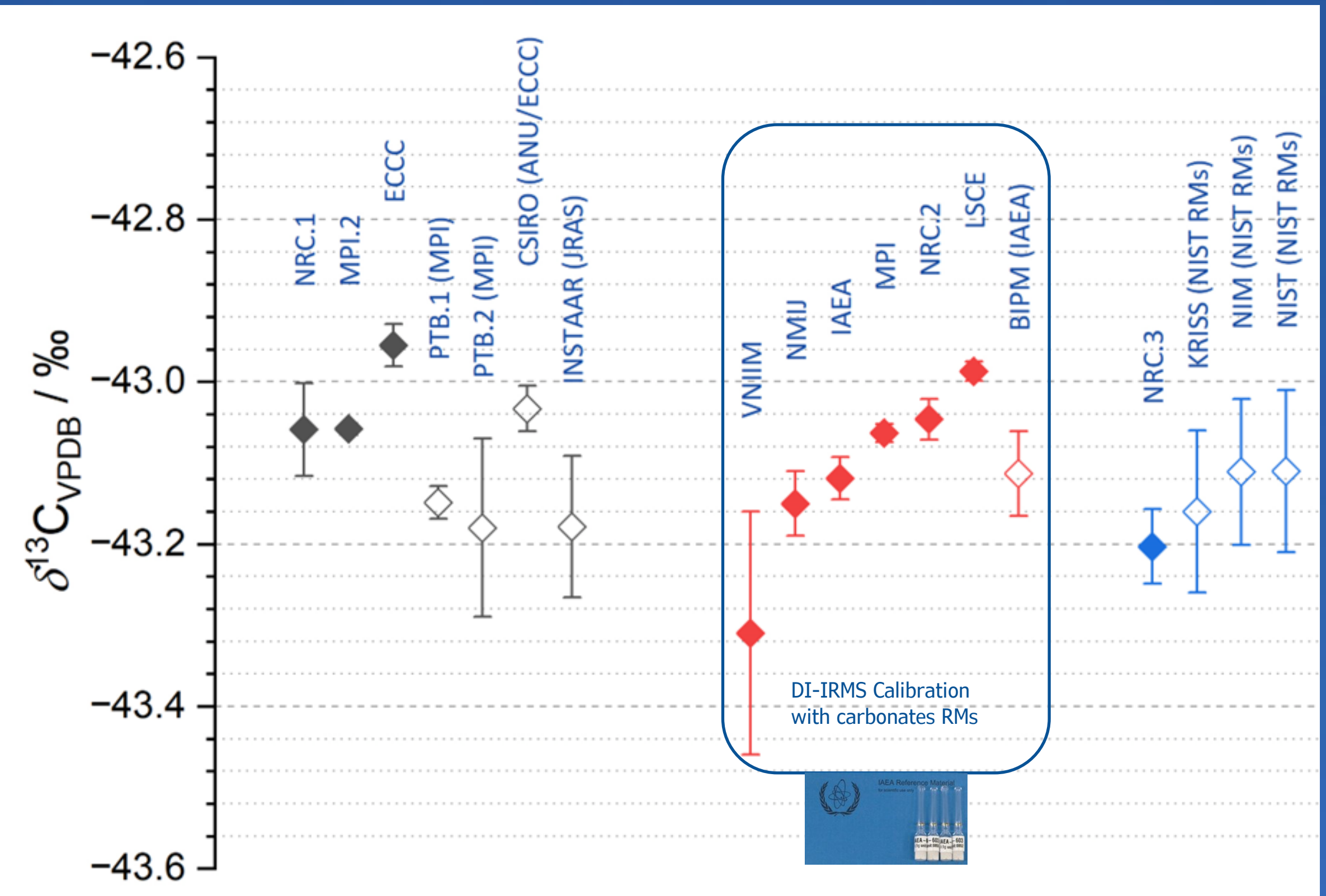
CCQM-P204

Participants included 11 National Metrology Institutes, 5 expert laboratories, and the 2 coordinators BIPM and IAEA.

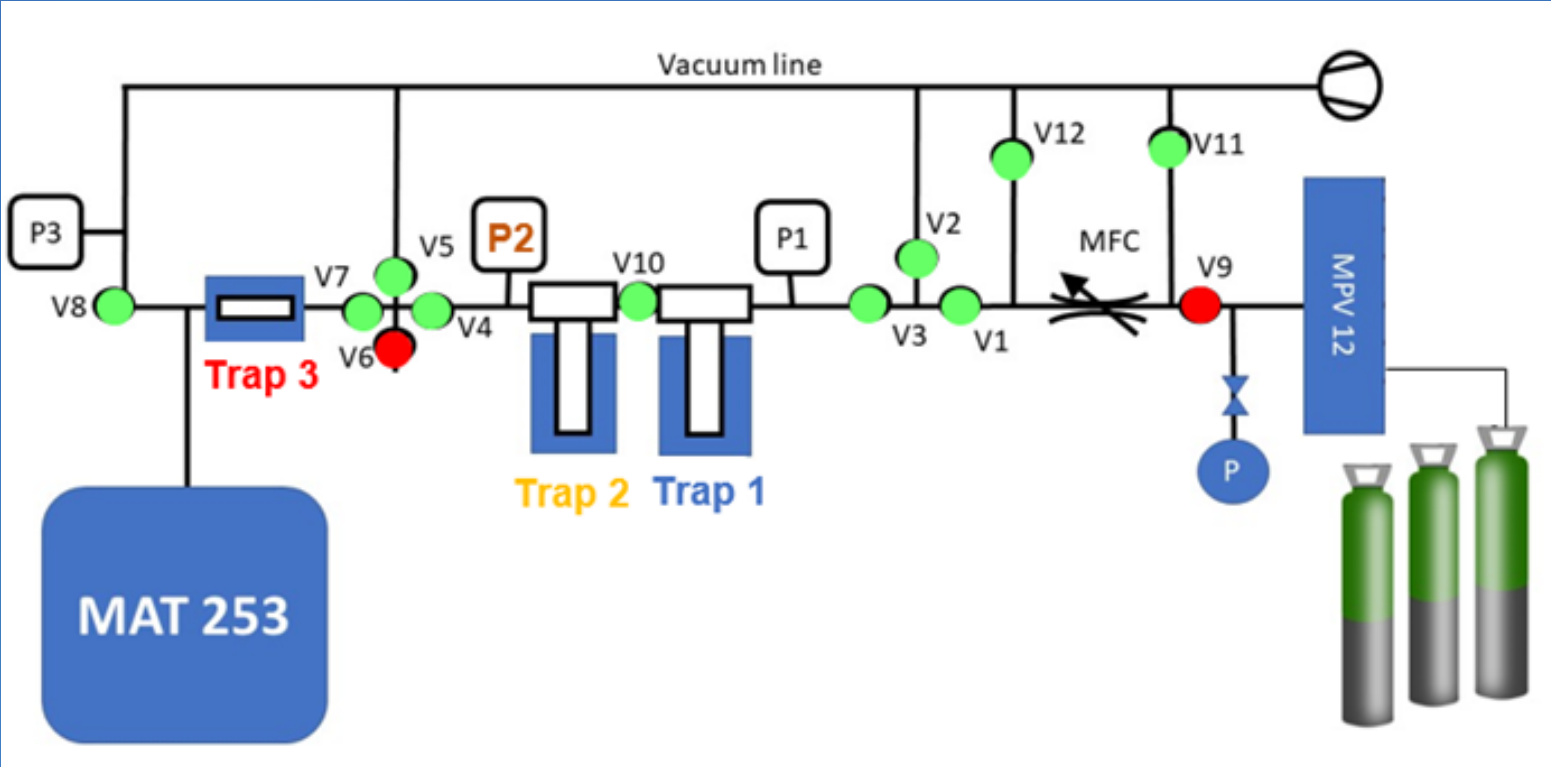
- 6 participants in CCQM-P204 used carbonates RMs which are realization of the VPDB scale as their calibration standards (NBS19 / IAEA-6XXseries). The level of agreement observed on their measurements of the 4 comparison gases was not as good as expected. e.g., standard deviation of 0.06 ‰ on $\delta_{\text{VPDB}}(^{13}\text{C}/^{12}\text{C}, \text{CO}_2)$ measured on gas 4.

Conclusion(s)

- Need to better define the scale and how to make measurements traceable to the same scale
- Need to work on uncertainty evaluation for each step: calibration (uncertainty of RMs), chemical transformations if required (eg CO₂ from carbonate RM), precision of instrument (short term), reproducibility, corrections if required (e.g. 17O correction, cross-contamination)
- Need of harmonization: best practices and convention not always followed (e.g. reference values of iR in VPDB)



The BAT System



Schematic Diagram

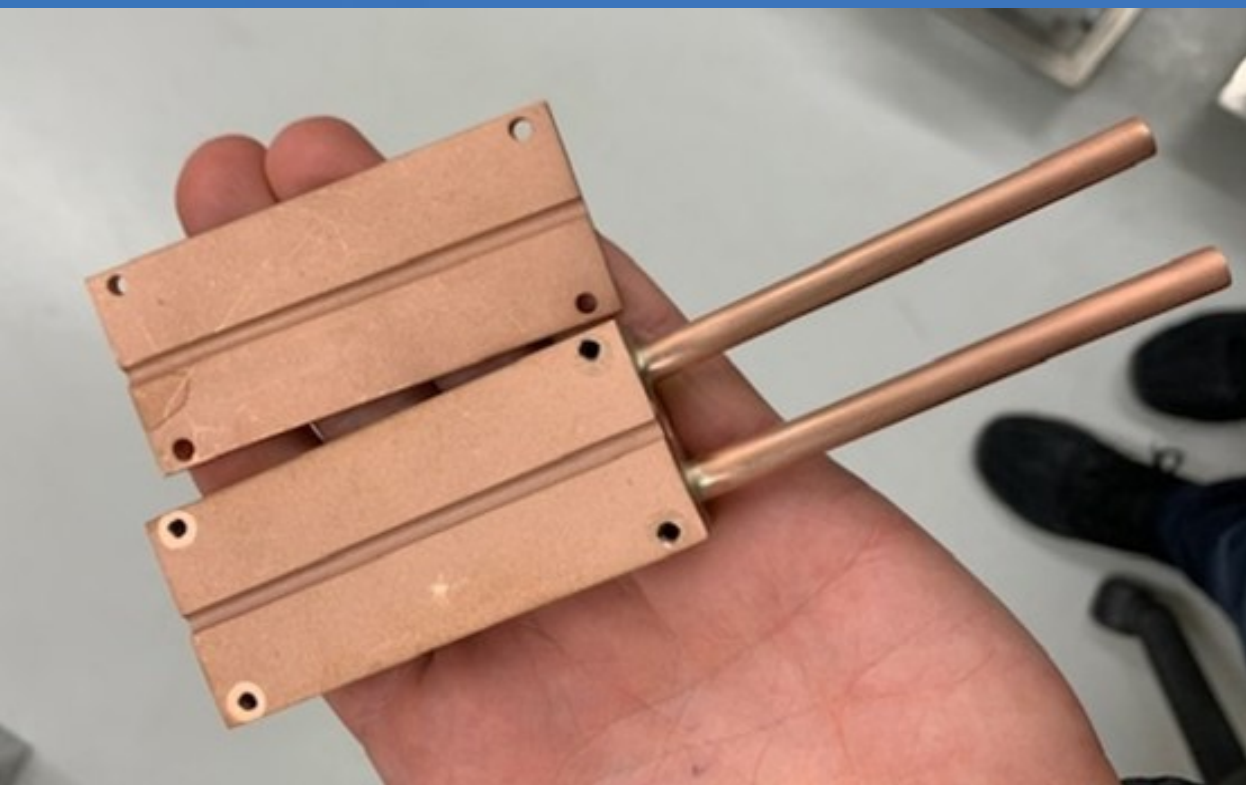
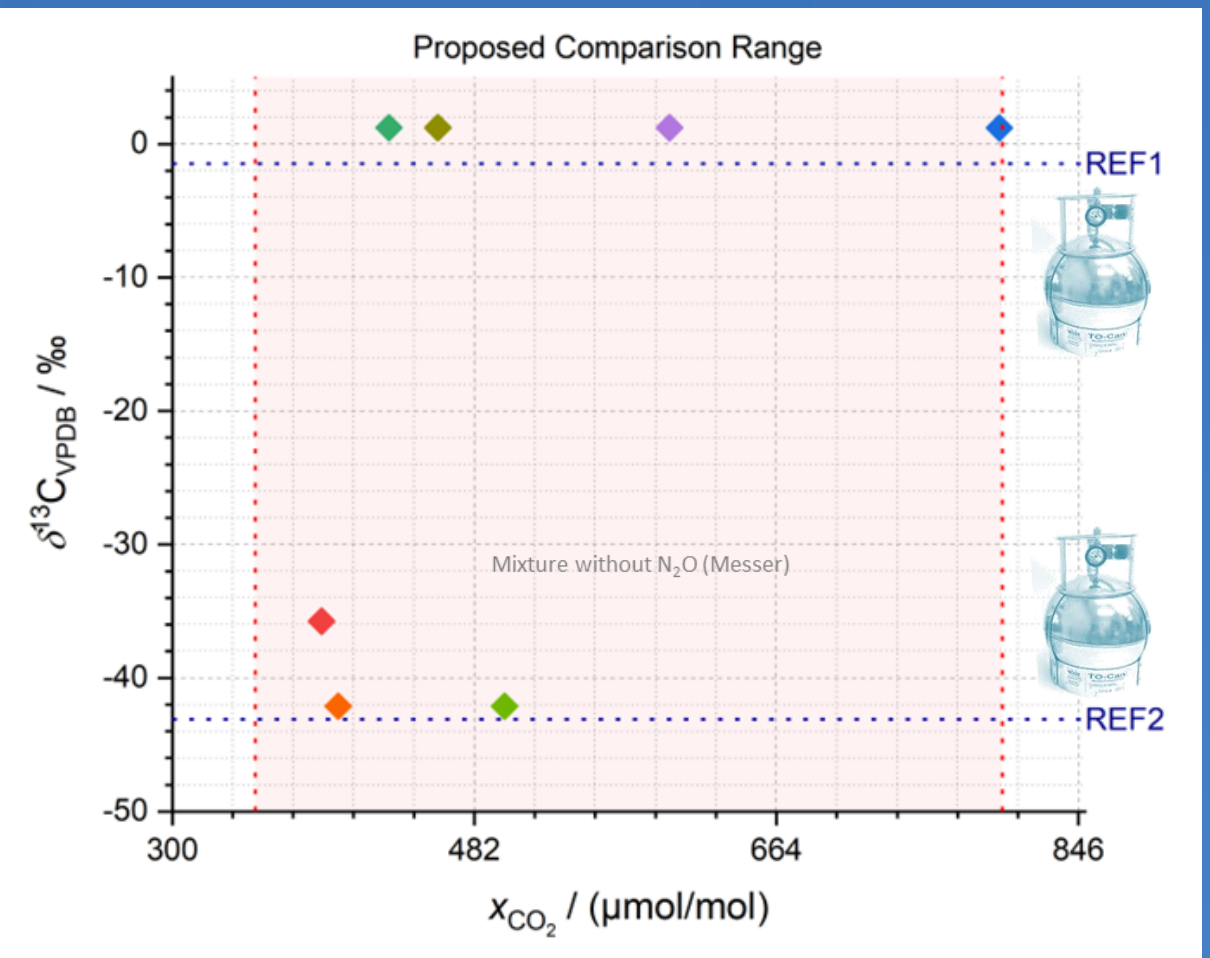


Photo of advanced trap system.

BAT Key features

- Automated operation with inhouse LabVIEW control software, including communication with IRMS software ISODAT.
- Series of 3 automated traps with temperature control to better separate CO₂ and H₂O
- Self-operating liquid nitrogen supply system with the capacity for 6-10 CO₂ in air cylinder analyses.
- IRMS measurement sequences include Quality Control measurements, calibration with CO₂ canisters traceable to IAEA, and CO₂ in air cylinder analyses. Aliquots of pure CO₂ can be included as well (samples in CCQM-P204).

BAT - Further validation with mixtures from another source

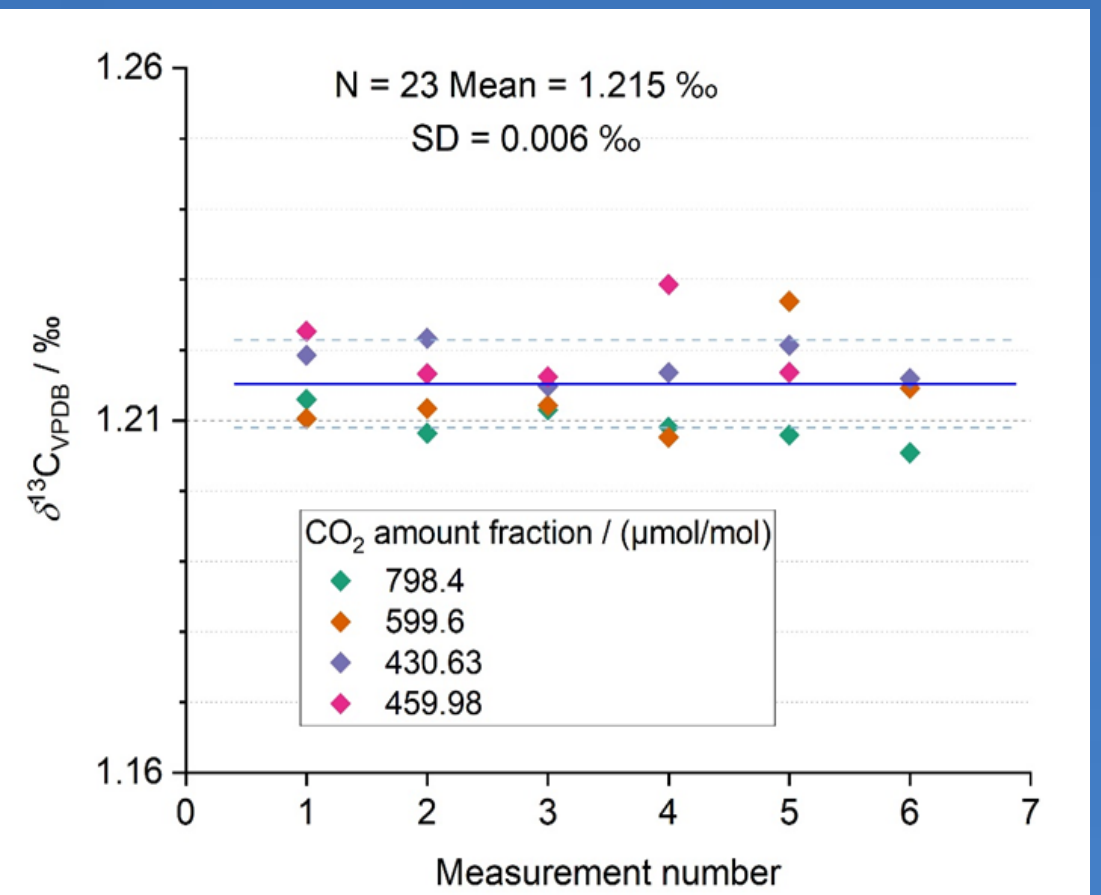


Joint Technical Project with NPL:

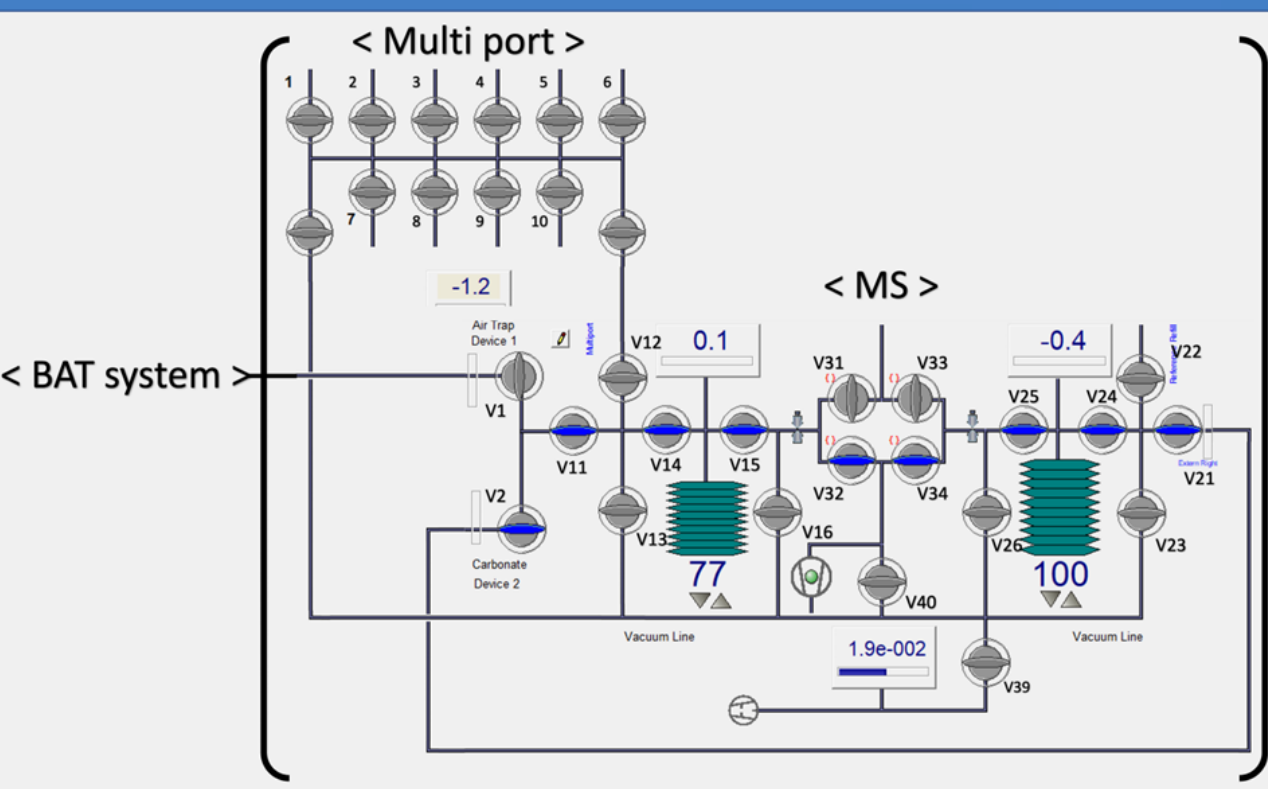
- Total of 6 gravimetric mixtures with different CO₂ amount fraction prepared from 2 different CO₂ parent cylinders
- IRMS measurements with BIPM reference standards traceable to VPDB via IAEA show similar results.
- REF1 $\delta^{13}\text{C}_{\text{VPDB}} = -1.473$ ‰
- REF2 $\delta^{13}\text{C}_{\text{VPDB}} = -43.103$ ‰

Validation of the BIPM Air Trapping system (BAT)

Set of 4 NPL gravimetric mixtures with different CO₂ amount fraction prepared from same CO₂ parent cylinder
IRMS measurements show standard deviation similar than analytical capability (0.005 ‰)



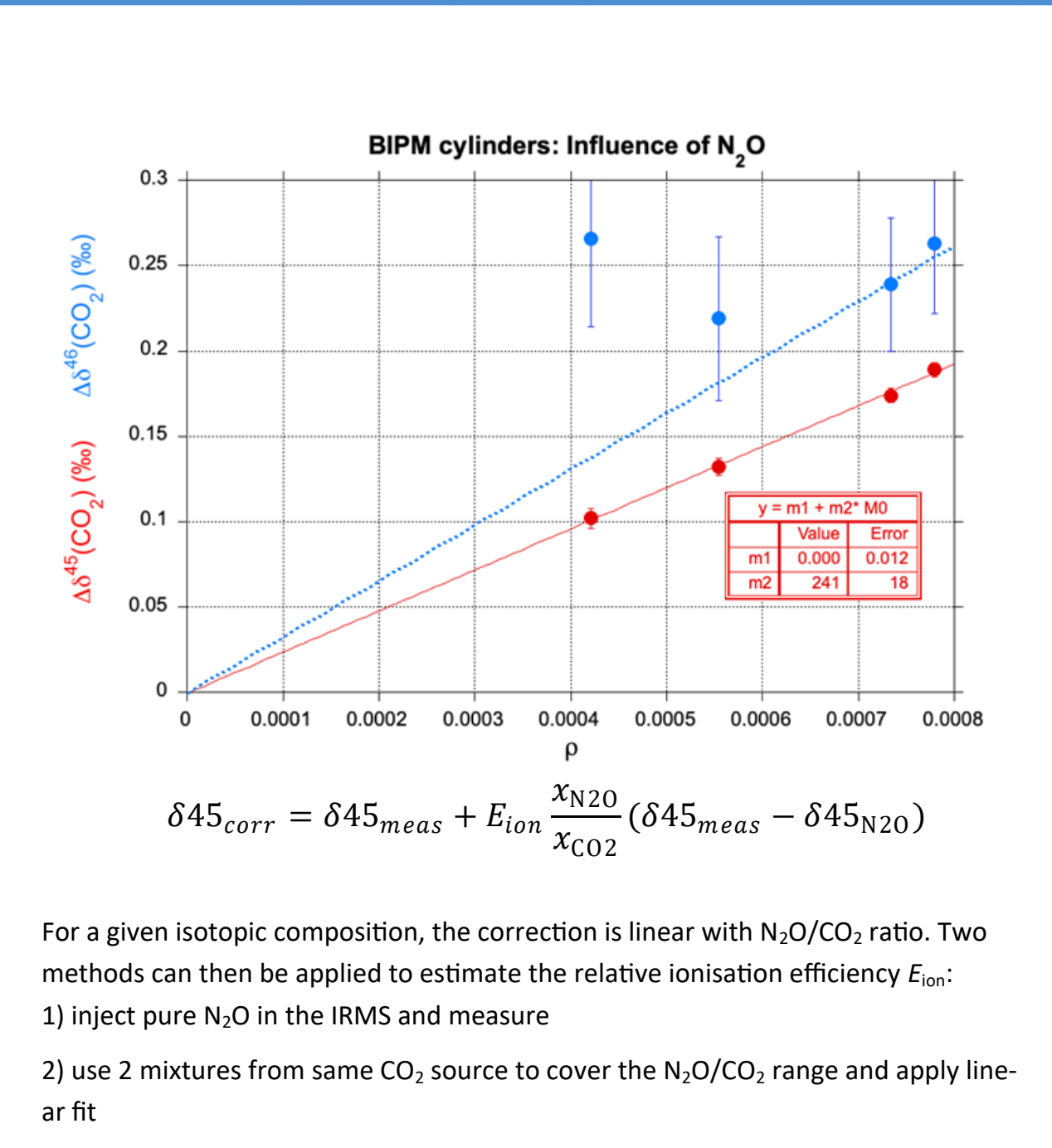
Photos of the valves used for controlling the cooling of all cold traps. Left is the old model and on the right the new one.



IRMS System Configuration Diagram



Photos of new sample cylinder inlet system (left) and close-up on new manual valve and pressure gauge



For a given isotopic composition, the correction is linear with N₂O/CO₂ ratio. Two methods can then be applied to estimate the relative ionisation efficiency $E_{\text{N}_2\text{O}}$:
1) inject pure N₂O in the IRMS and measure
2) use 2 mixtures from same CO₂ source to cover the N₂O/CO₂ range and apply linear fit.

Most significant instrument updates in 2022-2024:

- New valves for a better control of the cooling of the traps
- A new trap 3 design with an increased thermal mass, thermal conductivity (copper block) and increased residence time of liquid nitrogen (flow restriction, and longer path) to improve the cooling
- Optimisation of BAT system routine measurements (one single configuration for all types of samples)
- Technical instructions for measuring and verifying the N₂O correction parameters, and updated equations to correct IRMS data.

Metrological traceability:

Hierarchy of low-pressure CO₂ standards with $\delta^{13}\text{C}$ values nominally at -1 ‰, -35 ‰ and -43 ‰, calibrated on the VPDB scale via IAEA 603 carbonate standard material.

10 NMIs & Dis / ~ 25 Cylinders			4 Expert Laboratories / 12 Cylinders		
IAEA	IRMS	2 Cylinders 600 L	BGC-IsoLab	IRMS	3 Cylinders 7500 L
KRIS	IRIS (FTIR)	3 Cylinders 600 L	InstAAR	IRMS	4 Cylinders 4130 L
KRIS	IRMS	2 Cylinders 1000 L	UniGröningen	IRIS	2 Cylinders 1500 L
Joint Research Institute	IRMS	2 Cylinders 600 L	Environment Canada	IRMS	3 Cylinders 4130 L
NIST	IRIS	4 Cylinders 1000 L			
NPL	IRMS & IRIS	4 Cylinders 1000 L			
PIB	IRMS	2 Cylinders 750 L			
PIB	IRIS	# Cylinders? vol?			
IRI	IRMS	2 Cylinders 350 L			
IRI	IRMS	2 Cylinders 750 L			

On-demand comparison for:

- NMIs and expert labs that have been developing CO₂ (isotope ratio) in air cylinder standards including for calibrating optical spectroscopic techniques.
- Atmospheric community labs measuring isotopes of CO₂ in air (using JRAS[®] or other systems).
- The NMI and expert lab community developing CO₂ in air amount fraction standards that need CO₂ isotope ratios values for accurate amount fraction measurements.

Acknowledgements to visiting scientists

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