

# International comparison of isotope ratio measurement capabilities for CO<sub>2</sub>: From pure CO<sub>2</sub> to CO<sub>2</sub> in air samples

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## CCQM-P204

During 2021, the BIPM and the IAEA conducted the international comparison CCQM-P204 on samples of pure CO<sub>2</sub> produced at the BIPM and measured by 19 participants.

Comparison samples produced at BIPM – 4 per participant

Nominal values of δ<sup>13</sup>C vs. VPDB :

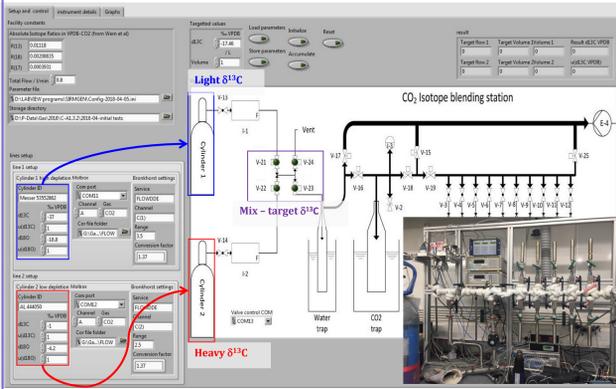


Participants used either IRMS or IRIS to measure δ<sup>13</sup>C<sub>VPDB</sub> and δ<sup>18</sup>O<sub>VPDB-CO2</sub> in the gas phase. Participants included 11 National Metrology Institutes, 5 expert laboratories, and the 2 coordinators BIPM and IAEA.

KRIS	IRMS	KRIS	
NIM	IRMS		
NIST	IRMS	NIST	
NMIJ	IRMS	NMIJ	
NPL	IRIS	NPL	
NRC-CNRC	IRMS	Canada	
PTB	IRMS, IRIS	PIB	CSIRO IRMS
UME	IRMS	UWE	BGC-IsoLab IRMS
VNIIM	IRMS		InstAAR IRMS
INMETRO	IRMS		LSCE CRDS
IJS	IRMS		Env. Canada IRMS

## SIRMGGEN

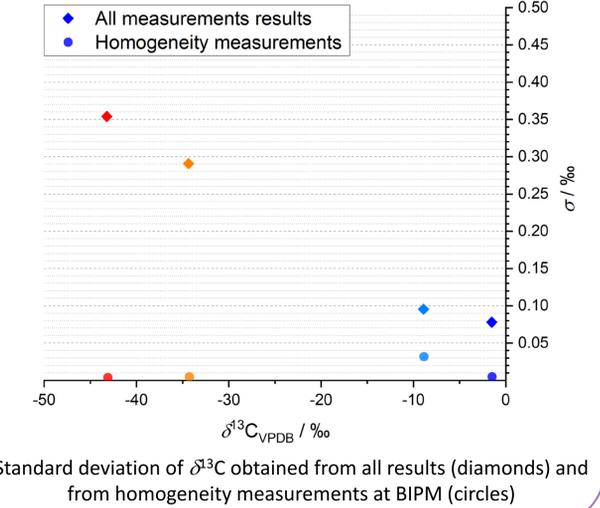
120 samples were prepared by batches of 10, including 2 for homogeneity and stability assessment.



The Stable Isotope reference mixtures generator allows mixing two gaseous CO<sub>2</sub> by volume ratio to obtain on-demand samples with defined δ<sup>13</sup>C.

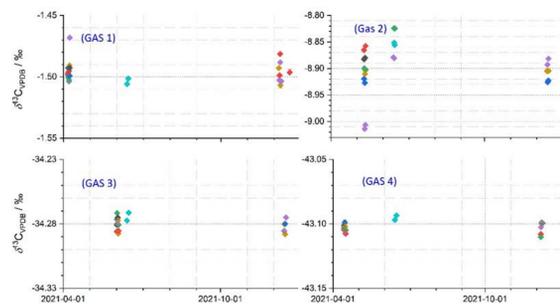
## HOMOGENEITY

6 samples of the same carbon isotope delta value (3 batches) were measured together to assess their homogeneity.



## STABILITY

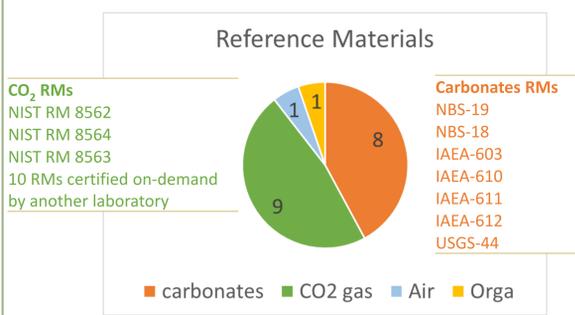
3 samples per nominal carbon isotope delta value were used to assess their stability over the course of the comparison.



δ<sup>13</sup>C<sub>VPDB</sub> measured on in-house samples by IRMS in April (7 samples) and December 2021 (subset of 3 samples). Each sample is represented with a different color. Error bars represent the standard deviation of each measurement (k = 1).

## TRACEABILITY

Among 19 laboratories, 8 performed the phosphoric acid reaction with carbonates RMs to obtain their CO<sub>2</sub> reference gases, 9 used pure CO<sub>2</sub> RMs, 1 extracted CO<sub>2</sub> from two RMs made of whole air, and 1 combusted organic RMs, resulting in different traceability schemes.

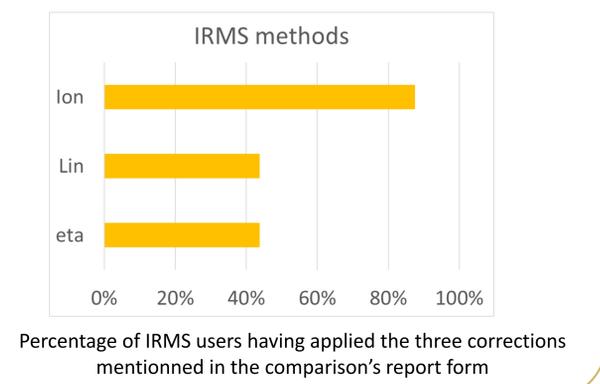


Type and list of reference materials used by participants

## IRMS METHODS

16 laboratories used Isotope Ratio Mass Spectrometry for their measurement. They were asked if they applied the following data treatments:

- (1) Ion correction – incl. IUPAC 2010, SSH 1985, Craig 1957
- (2) Linearization – using 2 or more standards
- (3) Eta correction – cross-contaminations between gases



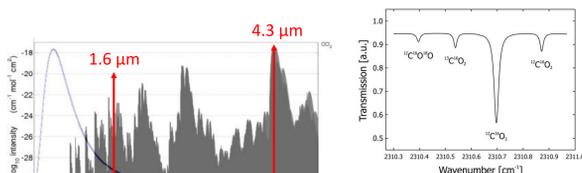
## IRIS METHODS

3 laboratories used Isotope Ratio Infrared Spectroscopy to analyse the samples, and all used different instruments and different RMs:

**VCOF-CRDS:** V-shaped Cavity Optical Feedback Cavity Ring-Down Spectroscopy (1.6 μm) calibrated with CO<sub>2</sub> from carbonates RMs

**OA-ICOS:** Off-Axis Integrated Cavity Output Spectroscopy (1.6 μm) calibrated with CO<sub>2</sub> in air RMs prepared on site

**TILDAS:** Tunable Infrared Laser Direct Absorption Spectroscopy (4.3 μm) calibrated with CO<sub>2</sub> RMs diluted dynamically during measurements



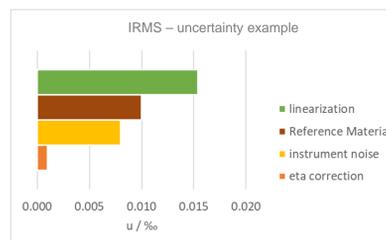
CO<sub>2</sub> absorption spectrum showing the two bands used by IRIS analyzers

CO<sub>2</sub> transmission spectrum (4.3 μm) showing the three isotopologues

## SCHEDULE

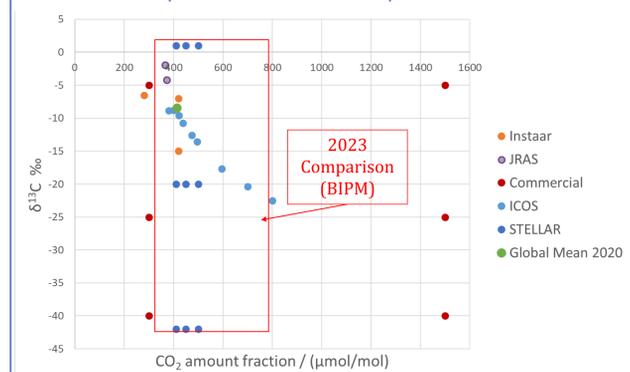
Participants were informed about the results, which still need to be discussed in series of meetings late 2022. Publication is expected in 2023, including recommendations on:

- Best practices for IRMS analysis
- How to ensure traceability to the same scale
- Impact of using different types of Reference Materials & needs of harmonization
- Uncertainty estimation for carbon isotope delta values



## NEXT – AIR SAMPLES

In 2023, the BIPM will conduct a comparison on CO<sub>2</sub> in air samples. Participants will be invited to send two samples of their choice, within the carbon delta values -42 ‰ and 1 ‰, and CO<sub>2</sub> amount fraction range between 350 μmol mol<sup>-1</sup> and 800 μmol mol<sup>-1</sup>



CO<sub>2</sub> amount fraction vs. <sup>13</sup>C isotope delta value in air in different projects/reference materials