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^{13}C of Carbon Dioxide (CO_2) by GasBench-IRMS

Methodology

Analysis of atmospheric CO_2 is performed in 12 mL Labco Exetainer vials on a Thermo Scientific GasBench II coupled to a Thermo Finnigan Delta Plus XL isotope-ratio mass spectrometer^[1]. An autosampler with a 2-hole sampling needle uses a helium carrier stream (2.0 mL/min) to push CO_2 out of the vial and into a 100 μL sample loop. Once the loop is adequately flushed, pulses of sample gas are injected into the IRMS for isotopic measurement. Prior to entering the IRMS, water is removed from the gas stream using a Nafion dryer, and sample CO_2 is chromatographically separated from other gases (e.g., N_2O) using an Agilent PoraPLOT Q GC column (25 m x 0.32 mm ID x 10 μm film thickness, 50 $^\circ\text{C}$, 2 mL/min). Samples with CO_2 concentrations above 5 % (i.e., 50,000 ppm) can be analyzed after dilution with helium in a second Exetainer vial.

Sample replicates are the responsibility of the client and must be paid for as individual samples. Replicates of the quality control and assurance reference materials are measured every ten samples.

Calibration and Reporting of Stable Isotope Ratios

Calibration procedures for CO_2 are applied identically across reference and sample materials and are directly traceable to the primary isotopic reference material (i.e., VPDB).

First, a pure CO_2 reference gas is used to calculate provisional isotopic values of the sample peaks. Next, isotopic values are adjusted for changes in linearity and instrumental drift using secondary reference materials (i.e., UCDC1, and a dilution series from UCDC2). Finally, measurements are scale-normalized to the primary reference material using three pure CO_2 secondary reference materials (i.e., OZ-3, OZ-10, and OZ-40) that have been calibrated against certified standard reference materials (i.e., NBS 18, NBS 19, and LSVEC) available from NIST and the IAEA.

Final quality assessment is based on the accuracy and precision of unbiased quality control materials, $\delta^{13}\text{C}$ -calibrated CO_2 gases (i.e., UCDC3 and UCDC4).

Quality assurance reference materials: OZ-3, OZ-10, OZ-40, UCDC1, UCDC2

Quality control reference materials: UCDC3, UCDC4

Measurement Uncertainty

Sample materials are inherently variable in composition, and measurement error may vary between different sample types due to differences in composition. Mean measurement error (σ) and accuracy, as determined by replicate measurements of the quality control and assurance materials, must fall below expected measurement error (± 0.10 ‰ for $\delta^{13}\text{C}$). Accuracy and precision of the co-measured calibrated quality control and assurance materials are provided with data reports. Limit of quantification (LOQ), based on total peak area, is 3 V-s for $\delta^{13}\text{C}$.

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Approved By

Richard Doucett



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Glossary

°C	degree Celsius
%	percent
‰	per mil; 1 ‰ is equivalent to 0.001 or 1 mUr
¹³ C	stable isotope of carbon; mass number of 13
δ	delta notation for isotopic composition; in per mil (‰) or mUr; 1 ‰ equals 1 mUr
μL	microliter
μm	micron or micrometer
σ	standard deviation
CO ₂	carbon dioxide
GC	gas chromatograph
IAEA	International Atomic Energy Agency
ID	inner diameter
IRMS	isotope-ratio mass spectrometry
L	liter
LOQ	limit of quantification; minimum signal for analyte to meet required signal-to-noise ratio
LSVEC	lithium carbonate prepared in 1973 by H. Svec, Iowa State University
m	meter
mg	milligram
min	minute
mL	milliliter
mm	millimeter
mUr	milliurey; 1 mUr is equivalent to 0.001 or 1 ‰
N ₂ O	nitrous oxide
NBS	National Bureau of Standards; renamed NIST in 1998
NBS 18	calcite prepared by I. Friedman, J. R. O'Neil, and G. Cebula, USGS
NBS 19	carbonatite prepared by I. Friedman, J. R. O'Neil and G. Cebula, USGS
NIST	National Institute of Standards and Technology
Oztech	Oztech Trading Corporation, Safford, Arizona
OZ-3	pure CO ₂ gas reference available from Oztech
OZ-10	pure CO ₂ gas reference available from Oztech
OZ-40	pure CO ₂ gas reference available from Oztech
ppm	parts per million; equivalent to mg/L
QA	quality assurance; overall laboratory measures to ensure measurement quality
QC	quality control; activities and procedures used to evaluate quality requirements
UCDC1	gas reference comprising 3 000 ppm CO ₂ with balance helium
UCDC2	gas reference comprising 50 000 ppm CO ₂ with balance helium
UCDC3	gas reference comprising 10 000 ppm CO ₂ with balance helium
UCDC4	gas reference comprising 400 ppm CO ₂ with balance helium
VPDB	Vienna PeeDee Belemnite; primary reference for measurements of carbon isotopes
V-s	volt-second

General Resources

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