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STABLE ISOTOPE FACILITY
DEPARTMENT OF PLANT SCIENCES
ONE SHIELDS AVE
DAVIS, CALIFORNIA 95616
530-752-8100

UNIVERSITY OF CALIFORNIA
COLLEGE OF AGRICULTURAL AND
ENVIRONMENTAL SCIENCES

^{13}C and/or ^{2}H of Methane (CH_4) by GasBench-PreCon-IRMS

Methodology

Analysis of atmospheric methane (CH_4) is performed using 12 mL Labco Exetainer vials on a Thermo Scientific GasBench II + PreCon trace gas concentration system coupled to a Thermo Scientific Delta V Plus isotope-ratio mass spectrometer [1]. Gas samples are purged from vials through a double-needle sampler into a helium carrier stream (12 mL/min). The gas sample passes through a CO_2 scrubber (Ascarite), and then CH_4 is trapped and concentrated on segments of GS-Q capillary column (Agilent, 0.32 mm) inside two LN_2 cryo-traps operated in series, such that CH_4 is held in the first trap until the non-condensing portion of the sample gas has been replaced by helium before passing to the second trap. When the second trap is warmed to ambient temperature, CH_4 is carried by helium to an Agilent GS-CarbonPLOT capillary column (30 m x 0.32 mm ID x 3 µm film thickness, 30 °C, 1.0 mL/min) that separates CH_4 from residual CO_2 and other gases trapped in LN_2. Finally, CH_4 is either combusted to CO_2 (for ^{13}C analysis) using an alumina reactor containing NiO and Pt wires at 1000 ºC or is thermally decomposed to H_2 (for ^{2}H analysis) using a hollow alumina reactor heated to 1400 ºC. Water is subsequently removed through a Nafion dryer before CO_2 or H_2 is transferred to the IRMS. Samples with CH_4 concentrations above 500 ppm can be analyzed via a sample loop or following dilution with helium into 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 CH_4 are applied identically across reference and sample materials and are directly traceable to the primary isotopic reference material for each element (i.e., VPDB for $\delta^{13}C$ and VSMOW for $\delta^{2}H$).

First, a pure CO_2 or H_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 in-house reference materials UCDM1 and UCDM2. Finally, measurements are scale-normalized using four secondary reference materials available from Airgas: H-iso, L-iso, B-iso, and T-iso. There are no certified standard reference materials for ^{13}C or ^{2}H measurements of CH_4, so our secondary reference materials were calibrated against gas mixtures (i.e., HCG-1, HCG-2, and HCG-3) anchored to the VPDB and VSMOW scales.

Final quality assessment is based on the accuracy and precision of unbiased quality control materials, including $\delta^{13}C$- and $\delta^{2}H$-calibrated in-house reference materials Beecher, AH024079, 043332T, and Scotty.

Quality assurance reference materials: UCDM1, UCDM2, H-iso, L-iso, B-iso, T-iso
Quality control reference materials: Beecher, AH024079, 043332T, Scotty, HCG-1, HCG-2, HCG-3

Measurement Uncertainty

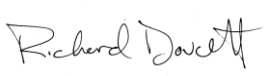
Sample materials are inherently variable in composition, and measurement error may vary between different sample types due to differences in composition. Mean measurement error (σ) and accuracy, as determined by replicate measurements of the quality control and assurance material, must fall below expected measurement error (± 0.20 ‰ for $\delta^{13}C$ and ± 2.0 ‰ for $\delta^{2}H$). 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 $\delta^{13}C$ and 6 V-s for $\delta^{2}H$.

Revision Date

September 6, 2019

Approved By

Richard Doucett



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Glossary

ºC	degree Celsius
%	percent
‰	per mil; 1 ‰ is equivalent to 0.001 or 1 mUr
043332T	natural gas reference obtained from CERSC
^{2}H	stable isotope of hydrogen; mass number of 2
^{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
µm	micron or micrometer
σ	standard deviation
AH024079	natural gas reference obtained from CERSC
Ascarite	sodium hydroxide-coated silica; carbon dioxide adsorbent
Beecher	natural gas reference obtained from CERSC
B-iso	gas reference comprising 0.25 % methane with balance air; from Airgas, Air Liquide
CERSC	USGS Central Energy Resources Science Center, Lakewood, Colorado
CH_4	methane
CO_2	carbon dioxide
H_2	dihydrogen
HCG-1	natural gas reference obtained from CERSC
HCG-2	natural gas reference obtained from CERSC
HCG-3	natural gas reference obtained from CERSC
H-iso	gas reference comprising 0.25 % methane with balance air; from Airgas, Air Liquide
ID	inner diameter
IRMS	isotope-ratio mass spectrometry
L	liter
L-iso	gas reference comprising 0.25 % methane with balance air; from Airgas, Air Liquide

LN_2	liquid nitrogen
LOQ	limit of quantification; minimum signal for analyte to meet required signal-to-noise ratio
m	meter
mg	milligram
min	minute
mL	milliliter
mm	millimeter
mUr	milliurey; 1 mUr is equivalent to 0.001 or 1 ‰
NiO	nickel oxide
ppm	parts per million; equivalent to mg/L
Pt	platinum
QA	quality assurance; overall laboratory measures to ensure measurement quality
QC	quality control; activities and procedures used to evaluate quality requirements
Scotty	gas reference comprising 100 % methane; from Scott Gas, Air Liquide
T-iso	gas reference comprising 0.25 % methane with balance air; from Airgas, Air Liquide
UCDM1	gas reference comprising 10 ppm methane with balance helium
UCDM2	gas reference comprising 500 ppm methane with balance helium
USGS	United States Geological Survey
VPDB	Vienna PeeDee Belemnite; primary reference for measurements of carbon isotopes
V-s	volt-second
VSMOW	Vienna Standard Mean Ocean Water; primary reference for measurements of oxygen and hydrogen isotopes

General Resources

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