Carbon isotope analysis ($\delta^{13}C$) of hydrocarbon gases by Gas Chromatogram – Combustion (GCC) – Isotope Ratio Mass Spectrometry

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Overview:

Compound specific $^{13}C/^{12}C$ ratios of the C_1 to C_5 alkanes in natural gas are determined using continuous flow technology. Aliquots of sample gas are injected manually using gas-tight syringes into the helium carrier stream of a Thermo *Trace GC Ultra – IsoLink*® system interfaced to a Thermo *253*® mass spectrometer via a Thermo *Conflo IV*®. Air, CO_2 and the hydrocarbon compounds of the gas are separated on a GC column before passing through a high temperature combustion reactor (maintained at 1000ºC). All hydrocarbon gas species are quantitatively converted to CO_2 in passing through the combustion furnace. The separate CO_2 gas pulses are then swept sequentially by the carrier gas through a water trap (Nafion®) then into the open split interface, which 'leaks' the gas into the ion source of the mass spectrometer. The $\delta^{13}C$ values of the unknown species are calculated by the instrument software (ISODAT 3.0 SP 0.83). Prior to sample analysis all instrument conditions (reactor temperatures, GC oven temperature, carrier gas flow, ion beam background(s), ion source stability and signal linearity) are checked and recorded ("Daily check" routine).

Extraction:

All gas samples received by the ISL for isotopic analysis must have first been analyzed for composition (compositional analysis can be arranged with the Agg-Chem lab upon request. Contact Michael Nightingale: mnightin@ucalgary.ca). Samples may be delivered in any suitable gas sampling container. If samples are under pressure, the gas pressure must be clearly marked on the vessel and must be less than 10 atm. Gases from natural gas production wells supplied in stainless steel "lecture bottles" are sub-sampled and run by GC-C-IRMS as described here. It is also essential to provide accurate H_2S concentrations of gas samples where applicable.

Gas Injection:

- Depending on the gas species of interest and their respective concentrations, between 50 and 1200 μL of gas is withdrawn via a septa port on the sample container using a gas tight syringe
- The gas aliquot is then injected into the inlet of the Trace GC Ultra
- A column flow rate of between ~2.0 - 2.4 ml/min is maintained using the constant flow option of the Trace GC Ultra. In order to get reasonable run times, the oven

temperature of the GC is typically ramped from 30 to 180°C (e.g. C_1 to C_5 runtime typically takes 20 minutes). The GC column used for natural gas work is an HP Plot U, 30m x 320μm column (J&W Scientific: 19091P-U04) or a GS Carbonplot, 30m x 320um column (J&W Scientific: 113-3133)

- The high temperature combustion oven is maintained at a temperature of 1030°C ensuring quantitative conversion to CO_2. The combustion oven is re-oxidized weekly (or more frequently if deemed necessary) using UHP 5.0 O_2
- The carrier gas then passes though a water trap to remove water vapor before passing through the open split/interface to the ion source of the mass spectrometer

Mass Spectrometric Measurements:

- Ion currents of masses 44, 45 and 46 are measured simultaneously and the $^{13/12}$Carbon ratio of the sample gas is compared to that of a "working" CO_2 reference gas (Research purity, 99.99%, Praxair Air, Canada).
- Stable isotope ratios are expressed as delta (δ) and are measures of a 'per mill' (‰), or parts per thousand difference between the isotope ratio of a sample and that of a known (International) standard material
- Result are expressed in the usual per mil notation relative to the international V-PDB scale defined by the following International Reference materials:

Identifier	$\delta^{13}C$
NBS 18	-5.01 ±0.06 ‰
NBS 19	1.95 ‰ (by definition)
USGS 44	-42.2 ‰

- Final sample values are calculated using a 2-point calibration (linear regression) against specially prepared *AirLiquide Alphagaz*® calibration standards analyzed typically at the beginning and end of each workday:

Identifier	$\delta^{13}C$
ISL-Alphagaz 1 (5% CO_2 bal. helium)	+26.4 ±0.3 ‰ *
ISL-Alphagaz 2 (5% CO_2 bal. helium)	-40.1 ±0.3 ‰ *
ISL-Alphagaz 3 (5% CH_4 bal. helium)	-23.9 ±0.3 ‰ *
ISL-Alphagaz 4 (5% CH_4 bal. helium)	-69.0 ±0.3 ‰ *

* note: Alphagaz $\delta^{13}C_{CO2}$ values have been carefully checked against NBS-19 via Dual Inlet measurement. Alphagaz methane gases were tested against our "ISL-Roto-CH_4" and were all found to be within analytical uncertainty. A final, more thorough calibration of the CH_4 gases is pending receipt of USGS NG1, NG2 and NG3 references. https://www.usgs.gov/news/usgs-releases-new-standards-natural-gas

- Other commercially available gas mixtures occasionally used to gauge instrumental efficiency are:

Identifier	$\delta^{13}C$
IsoMetric (CH_4-239)	-23.9 ± 0.2 ‰
IsoMetric (CH_4-383)	-38.3 ± 0.2 ‰
IsoMetric (CH_4-545)	-54.5 ± 0.2 ‰
OzTech CALG-1997C	-3.58 ± 0.01 ‰
OzTech CALG-1954C	-10.41 ± 0.01 ‰
OzTech CALG-1976C	-47.52 ± 0.01 ‰

Accuracy and Precision:

Accuracy and precision of $\delta^{13}C$ is ±0.5 per mill based on the long term record of our in-house standards.

References:

Dai, J. et al., *Inter-laboratory calibration of natural gas round robins for δ^2H and $\delta^{13}C$ using off-line and on-line techniques*, Chemical Geology, 310-311 (2012) 49-55

Matthews, D.E., Hayes, J.M., *Isotope-ratio-monitoring gas chromatography-mass spectrometry*. Anal. Chem. 1978, 50, 1465– 1473

Merritt D.A. et al., *Performance and Optimization of a Combustion Interface for Isotope Ratio Monitoring Gas Chromatography/Mass Spectrometry*, Anal. Chem., 1995, 67 (14), 2461-2473

Investigating $^{13}C/^{12}C$ Isotope Ratios of Methane-Pentane in Natural Gas by GC-IRMS
Andreas Hilkert, Thermo Fisher Scientific, Bremen, Germany. Application Note 30088

http://www.thermoscientific.com/en/product/gc-isolink-interface-irm-gc-ms.html