Hydrogen isotope analysis (δ^2H) of hydrocarbon gases by High Temperature Conversion - Gas Chromatogram (HTC) – Isotope Ratio Mass Spectrometry

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Overview:

Compound specific $^2H/^1H$ 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 reactor (maintained at 1420ºC). All hydrocarbon gas species are quantitatively converted to H_2 in passing through the HTC furnace. The separate H_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 δ^2H values of the unknown species are calculated by the instrument software (ISODAT 3.o 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-HTC-IRMS as described here. It is also essential to provide accurate H_2S concentrations along with 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- Depending on the gas species of interest and their respective concentrations, between 50 and 1200 μL of gas is withdrawn, via a septa port on the sample container, using a gas tight syringe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 ~2.0 to 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 run time 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 reactor is maintained at a temperature of 1420°C ensuring quantitative conversion to H_2. The reactor is re-carbonated periodically with high purity CH_4
- 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 3 and 2 are measured simultaneously and the $^{3/2}$Hydrogen ratio of the sample gas is compared to that of a "working" H_2 reference gas (Research purity, 99.998%, 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
- Results are expressed in the usual per mil notation relative to the international V-SMOW – SLAP2 scale using the following Reference materials:

Identifier	δ^2H .
VSMOW	0 exactly
SLAP2	-427.5 ‰

- Final sample values are currently corrected using a 1-point calibration based on our "ISL-Roto-CH_4" but will in the future be corrected 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	δ^2H .
ISL-Alphagaz 3 (5% CH_4 bal. helium)	TBD *
ISL-Alphagaz 4 (5% CH_4 bal. helium)	TBD *

* note: calibration of Alphagaz δ^2H values 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:

OzTech CALG-1726H	+2.80 ± 0.13 ‰
OzTech CALG-1545H	-364.01 ± 0.10 ‰
OzTech CALG-1464H	-761.86 ± 0.20 ‰

Accuracy and Precision:

Accuracy and precision of δ^2H is ±2 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

T. B. Coplen, *Guidelines and recommended terms for expression of stable-isotope-ratio and gas-ratio measurement results*. Rapid Commun. Mass Spectrom. 2011, 25, 2538

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