

## $\delta^{13}\text{C}$ Analysis of Natural Gas Components via GC-IRMS

### 1. Introduction

The determination of the  $^{13}\text{C}/^{12}\text{C}$  ratio on components of natural gas (methane, ethane, propane, butanes, pentanes and carbon dioxide) has been historically used in combination with the D/H ratio of methane and compositional analysis to genetically type natural gases as being of thermogenic, mixed or bacterial origin (e.g., Schoell, 1980). In order to provide timely, accurate and precise carbon isotopic analyses, we utilize the latest continuous-flow technology to link a gas chromatograph to a modern isotope ratio mass spectrometer via an oxidative interface. All stable isotope methods employed by the Energy Geochemistry Laboratory follow the best practices and procedures as detailed in peer-reviewed literature.

### 2. Interfaces with Other Methods

None required.

### 3. Materials and Equipment

As described below in the Procedure.

### 4. Procedure

The  $^{13}\text{C}/^{12}\text{C}$  ratio of natural gas components is determined using methods modeled after Baylis et al (1994). A natural gas sample is introduced into a HP<sup>1</sup> 6890 gas chromatograph via an autosampler through a sample-loop injector. Natural Gas components are chromatographically separated on a Varian PoraBond-Q column (50 m x 0.32 mm x 5  $\mu\text{m}$ ). Typical GC conditions are as follows: He carrier gas @ 1.5 ml/min; 40 °C initial temp; hold for 6 min; ramp to 150 °C at 15 °C/min; ramp to 250 °C at 30 °C/min; hold for 5 min. The individual components are then combusted

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<sup>1</sup> Any use of trade names is for descriptive purposes only and does not imply endorsement by the U.S. Government.

in the He stream (with a trickle of O<sub>2</sub>) at 1050 °C in an in-line Alsint-99.7 ceramic reactor (0.5 mm I.D. x 6 mm O.D. x 500 mm length). The resulting combustion products (primarily CO<sub>2</sub> and H<sub>2</sub>O) are passed through an in-line Nafion drier, and the final analyte CO<sub>2</sub> is passively drawn via open split into the source of a GV-Elementar Isoprime isotope ratio mass spectrometer for subsequent carbon isotope analysis.

## 5. Calibration and Quality Control Samples

Carbon isotope values from the instrument (IonVantage Software) undergo off-line isotope corrections for drift (as many batch runs take more than 24 hours to complete), for isotopic linearity due to any systematic error in the autosampler, chromatographic and oxidation processes (<sup>13</sup>C vs amount), and finally are normalized on the PDB (PeeDee Belemnite) scale using two well-calibrated, working laboratory methane standards (after Paul et al, 2007). On average, for every 6 samples run in replicate (n = 3, 18 total determinations), ~6 or more analyses of standards are performed to ensure proper analytical calibration. The final carbon isotope values represent the average of multiple replicate analyses (generally, n=3) with a standard deviation of generally less than 0.2 per mil. The accuracy of stable isotope measurements historically is not specified, neither by commercial laboratories nor instrument manufacturers. That said, as we utilize two-point calibrations, our estimated accuracy is 2 times our precision, or ± 0.4 ‰. All final δ<sup>13</sup>C values are reported relative to the international standard, Pee Dee Belemnite Carbonate (PDB).

## 6. Limits, Precautions, and Interferences

Sample requirements are as such: pressurized gas cylinder/bottle (50-100 mL) containing 15-75 psi of total gas with a minimum methane concentration of 10 mole percent. Samples may have high pressures and significant concentrations of H<sub>2</sub>S and should be handled with caution.

## 7. Acceptance of Data

Data are deemed acceptable if methane peak response (area/height) and working isotopic standards are within acceptable parameters (e.g, accuracy and precision). Replicate analyses are usually better than 0.2 ‰ standard deviation.

## 8. Data Handling and Transfer

The following data are returned to the submitter: Sample ID,  $\delta^{13}\text{C}_{(\text{PDB})}$ , std, n; where Sample ID is the sample descriptor provided by the submitter,  $\delta^{13}\text{C}_{(\text{PDB})}$  is the average carbon isotope value for the sample component, std is the standard deviation of replicate analyses and n is the number of replicate analyses. An example of a final results data table is shown below.

Sample ID	component	$\delta^{13}\text{C}_{(\text{PDB})}$ ‰	stdev ‰	n
Pionce #24H	methane	-45.38	0.10	3
“	ethane	-30.24	0.08	3
“	propane	-28.65	0.12	3
“	isobutane	-27.57	0.15	3
“	n-butane	-27.73	0.10	3
“	isopentane	-28.12	0.14	3
“	n-pentane	-27.91	0.08	3
“	carbon dioxide	-5.40	0.05	3

Finally, data are submitted to the USGS Geochemical Database for general dissemination as per Energy Geochemistry Laboratory QA protocols.

## 9. References

Baylis S.A., Hall, K., and Jumeau, E.J., 1994, The analysis of the C<sub>1</sub>-C<sub>5</sub> components of natural gas samples using gas chromatography-combustion-isotope ratio mass spectrometry. *Organic Geochemistry*, v. 21, no. 6/7, p. 777-785.

Paul D., Skrzypek G. and Forizs, I., 2007 Normalization of measured stable isotopic compositions to isotope reference scales – a review. *Rapid Communications in Mass Spectrometry*, v. 21, p.3006-3014.

Schoell, M., 1980, The hydrogen and carbon isotopic composition of methane from natural gases of various origins. *Geochimica Cosmochimica Acta*, v. 44, p. 649-661.

## **10. Attachments**

None.

## **11. History of Changes**

R0: Initial Issue