

GC-IRMS: Assessment of precision and accuracy of carbon isotope fingerprints measurements in natural gas

Authors: Gabriel Moraes Silva¹,
Tulio Alves Freire¹,
Alexandre de Andrade Ferreira¹,
Dieter Juchelka², Mario Tuthorn²;
¹Division of Geochemistry/PETROBRAS
Research and Development Center
(CENPES), Rio de Janeiro, Brazil,
²Thermo Fisher Scientific, Bremen,
Germany

Keywords: Carbon, isotope fingerprints,
compound specific isotope analysis,
GC-IRMS, natural gas, petroleum
exploration

Goal

Investigate precision and accuracy of isotope analysis of natural gas reference materials to contribute to standardization of laboratory gas analysis.

Introduction

Natural gas is a fossil energy source with diverse applications: transport of people and goods, heating and cooling at homes and industries, serving also as feedstock for manufacturing different chemicals and products, like plastics and detergents.



Natural gas is a relatively simple mixture consisting of C_1 - C_5 hydrocarbons with varying amounts of CO_2 , H_2S , and N_2 . The exact composition of different components varies with the maturity of the source from which the gas was generated. Isotope fingerprints have been used in geochemical applications and environmental forensics generally to determine the origin of organic and inorganic compounds as well as to identify chemical processes such as degradation. This technical brief reports about accuracy and precision at which isotope fingerprints can be analyzed in natural gas.

Isotope fingerprints in natural gas

The isotopic analysis of carbon and hydrogen isotopes of methane, ethane, propane, and butane in natural gas has wide application in oil–gas geochemistry. Isotope ratio mass spectrometry coupled online with gas chromatography (GC-IRMS) allows measurements of relative proportions of gaseous hydrocarbon (methane to pentane) and CO₂, and determination of the carbon isotope fingerprint of hydrocarbon molecules of these species. Access to these parameters provides valuable information about the source and the genesis of naturally occurring gas, as well as on post-formation physico-chemical processes which might have taken place in the geological environment. It is possible to distinguish hydrocarbon gas of bacterial origin from that of thermogenic origin based on both proportion and carbon isotope ratio of methane as measured by GC-IRMS¹.

Analytical setup

The Thermo Scientific™ GC IsoLink II™ IRMS System provides a fully automated solution for routine stable isotope analysis. For carbon isotope analysis, natural gas compounds are chromatographically separated by GC at the conditions described in Table 1. Subsequently, individual compounds are being quantitatively combusted to CO₂ in Thermo Scientific™ GC IsoLink II™ Conversion Interface and produced gases are transferred in a helium carrier gas flow to Thermo Scientific™ DELTA V™ Isotope Ratio Mass Spectrometer via Thermo Scientific™ ConFlo IV™ Universal Interface. For this study reference materials distributed by U.S. Geological Survey (USGS) were analyzed. The objective of this work was to establish a link to the international scale for natural gas samples using these reference materials and to validate the performance of the system.

Table 1. GC conditions.

GC inlet parameters	
GC column	CP-PoraPlot Q 27.5 m x 0.32 mm x 10 μm (incl. 2.5 m Particle Trap)
Injection volume (μL)	10
Liner	Single taper
Injector (°C)	250
Injector module and mode	SSL, split
Split mode	Ratios: 50:1, 10:1
Carrier gas (mL/min)	Helium, 2.0
Oven temperature program	
Initial temperature (°C)	40
Hold time (min)	1.7
Rate 1 (°C/min)	10
Temperature 1 (°C)	240
Hold time 1 (min)	1.5

Results

The reference materials analyzed in this study are natural gas mixtures intended to serve as the primary carbon and hydrogen stable isotope reference materials for methane, ethane, and propane, and have been used in applications and research development by industry, academia, and governmental agencies. They provide a useful tool to standardize laboratory gases with measurement traceability to the internationally accepted isotope ratio reference scale.

Figure 1 shows typical chromatograms of the analyzed reference materials, displaying the variety in composition values (%) for the analyzed compounds (Table 2).

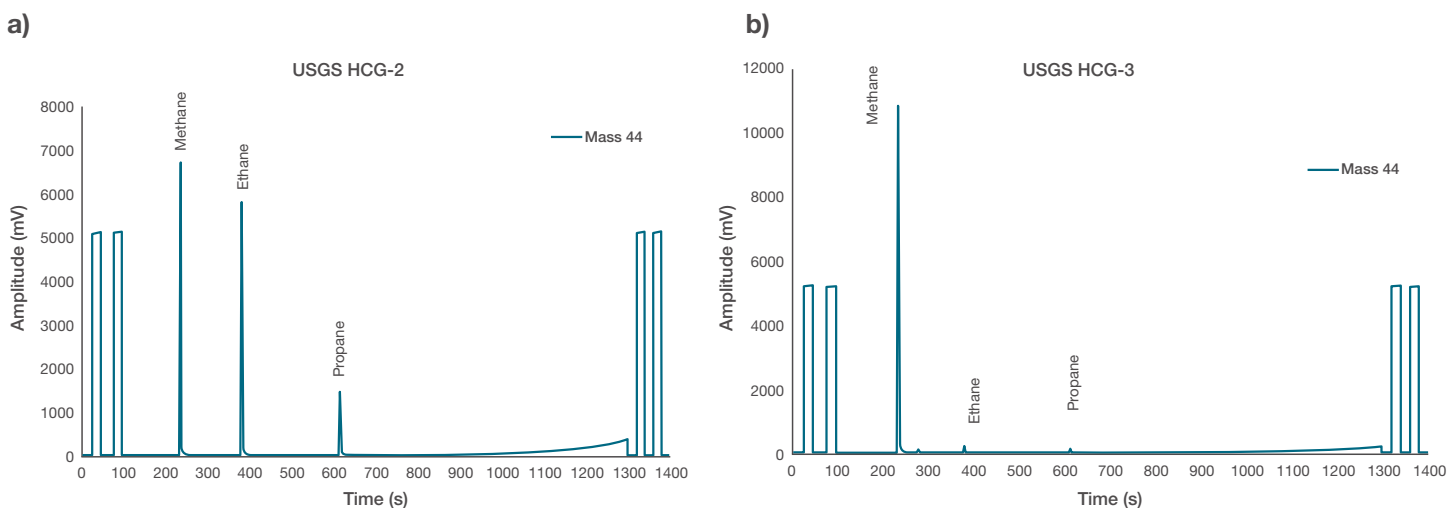


Figure 1. Typical chromatograms of the analyzed reference materials: USGS HCG-2 (a) and USGS HCG-3 (b).

Table 2. Composition values (%) for the analyzed USGS standards.

Compound	HCG-1	HCG-2	HCG-3
C ₁	46	59	94
C ₂	43	33	1
C ₃	11	8	0

The measured $\delta^{13}\text{C}$ values were used to study if there would be any scaling behavior for different carbon isotopic ratios and substances (methane, ethane and propane) during the GC-IRMS analysis of gas samples. The expected versus measured values can be seen in Table 3.

Table 3. Expected and measured values (‰) for carbon isotopes of the USGS reference materials.

Standard	Compound	Expected $\delta^{13}\text{C}$ (‰)	Measured $\delta^{13}\text{C}$ (‰) mean value*	STDEV of the measured value
USGS HCG-1	C ₁	-1.51	-1.42	0.09
	C ₂	-10.22	-10.14	0.09
	C ₃	-15.43	-15.34	0.11
USGS HCG-2	C ₁	-43.09	-43.11	0.11
	C ₂	-29.8	-29.74	0.10
	C ₃	-19.35	-19.38	0.18
USGS HCG-3	C ₁	-61.39	-61.49	0.18

*N=5 for USGS HCG-1 and HCG-3, N=9 for HCG-2

A high correlation between the measured and the expected data was observed (Figure 2), confirming the high accuracy of the obtained carbon isotope values. The measurements of different reference material, with diverse molecular composition values, demonstrate stability and precision of the GC IsoLink II IRMS System for isotope analysis of natural gas.

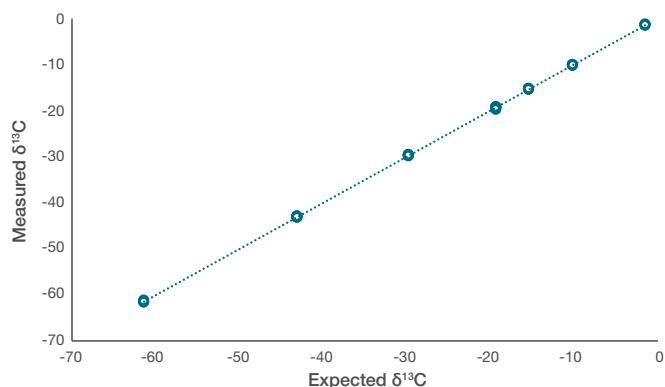


Figure 2. Plotted measured vs. expected carbon isotope values (‰) of the investigated reference materials.

Conclusions

Application of isotope fingerprints in oil exploration allows, for example, the differentiation of biogenic and thermogenic gases. Several factors can influence the carbon isotopic composition of individual compounds in those natural gases, like source, level of maturity and biodegradation^{2,3,4,5,6}. In order to overcome big uncertainties of isotope data that might make those geochemical interpretation and interlaboratory comparisons more challenging, it is important to be able to gain precise and accurate isotope values in natural gases and reference materials.

References

- Philp, R.P. and Lo Monaco, G. (2011) Applications of Stable Isotopes in Hydrocarbon Exploration and Environmental Forensics. In: Baskaran, M. (ed) Handbook of Environmental Isotope Geochemistry, vol.1, Springer-Verlag Berlin Heidelberg 2011, p. 639-677
- Schoell, M. (1984) Recent advances in petroleum isotope geochemistry. *Org Geochem* 6, p. 645-663
- Schoell, M. (1984) Stable isotopes in petroleum research. In: Brooks, J., Welte, D. (eds) Advances in petroleum geochemistry, vol 1. Academic, London, pp 215-245
- Hunt JM (1996) Petroleum geochemistry and geology. W.H. Freeman, New York
- Schoell, M. and Jenden, P.D. (1993) Isotope analysis of gases in gas field and gas storage. SPE Paper 26171, 337-344. SPE Gas Technology Symposium, Calgary, Alberta, Canada, June 1993
- Milkov, A. V., Etiope, G. Revised genetic diagrams for natural gases based on a global dataset of >20,000 samples. *Organic Geochemistry*, 125, 109-120, 2018.

Find out more at thermofisher.com/IsotopeFingerprints

For Research Use Only. Not for use in diagnostic procedures. © 2020 Thermo Fisher Scientific Inc. All rights reserved. All trademarks are the property of Thermo Fisher Scientific. This information is presented as an example of the capabilities of Thermo Fisher Scientific products. It is not intended to encourage use of these products in any manner that might infringe the intellectual property rights of others. Specifications, terms and pricing are subject to change. Not all products are available in all countries. Please consult your local sales representative for details. **AN30771-EN 1120C**

ThermoFisher
SCIENTIFIC