SHELF LIFE STUDY OF CALIBRATION STABLE ISOTOPE HYDROCARBON MIXTURES FOR PETROLEUM GEOCHEMISTRY LABORATORIES

S. Mehay[1], N. Luu[2], C.Turich[1], M. McNall[2], J. Cassidy[1], H. Calixto Neves[1], T. Jacksier[2], A. Stankiewicz[1]

1. Schlumberger, Germany, France, USA, UAE, Kuwait
2. Air Liquide, USA

Introduction

Gas hydrocarbon standard mixtures are used as standards for stable isotope analysis by gas chromatography coupled to isotope ratio mass spectrometry analysis (GC-IRMS) in petroleum geochemistry laboratories. In addition, international reference materials (NIST, IAEA) are important complementary secondary calibration standards used to monitor instrument performance and ensure cost effective high quality isotope analysis QA/QC. However, the shelf life of hydrocarbon standard mixtures with respect to the isotopic composition has yet to be systematically demonstrated. A dedicated analytical protocol was designed to perform a stability study of custom standard hydrocarbon mixtures. The results of the preliminary study, which evaluated several sub-sampling methods and gas packaging, has been previously presented (Turich et al., 2017). The combination of a septum flow-through regulator and a 34 gas volume cylinder was selected for this study due to the simplicity of use and repeatability of the results compared to a gas bag or a two-stage regulator. In addition, this valve did not require additional safety concerns which may be present in more complex regulators.

We studied both the operational stability (repeated sampling of the same cylinder) and storage stability (bottles filled at same time and sample once at specific intervals), measuring concentrations and isotope compositions of nitrogen ($\delta^{15}N$), C_1-C_3 hydrocarbon and CO_2 carbon ($\delta^{13}C$) and hydrogen (δD) isotope compositions of standard gas mixtures over at least eighteen months.

Results

Two types of mixtures containing (1) 3% C_3 in balance nitrogen and (2) 87% C_1, 7% C_2, 3% C_3, 1.5% N_2, 1.5% CO_2 were analysed for their composition by GC-FID/TCD as well as their compound specific $\delta^{13}C$, δD and $\delta^{15}N$ values by GC-IRMS. The operational stability was tested by subsampling the same cylinders multiple times throughout the study while the storage stability was tested by analysing a new stored cylinder during each analytical campaign.

After eighteen months, the isotopic and compositional values remained within the acceptable range for both the operational and storage stability studies. Indeed, the $\delta^{13}C$ values of hydrocarbons and CO_2 varied less than 0.3‰, the δD values of hydrocarbons less than 5‰ and the $\delta^{15}N$ values of N_2 varied within 1‰. The analysis of the single component mixture (3% C_3 in balance nitrogen) aimed to evaluate the potential impact of a multi-compound mixture on the isotope values.

Conclusions

The compositional and isotopic analysis of the standard gas mixtures using a dedicated analytical system were performed over eighteen months. Recorded variations in the $\delta^{13}C$ values

of hydrocarbons and CO_2, in the δD values of hydrocarbons and in the $\delta^{15}N$ values of N_2 were within the acceptable uncertainty range. The results for the operational stability and storage stability were consistent and showed that repetitive sampling did not affect the integrity of the mixtures. Long-term planning, including accurate calibration mixtures, subsampling method development as well as laboratory procedures optimization, enabled the achievement of these results.

References

Turich, C., Mehay, S., McNall, M., Neves, H., Luu, N., Jacksier, T., Stankiewicz, A., 2017. Stability Study of Stable Isotopic Composition of Hydrocarbon Gases. 28th International Meeting on Organic Geochemistry, Florence, poster P212.