STABILITY STUDY OF STABLE ISOTOPIC COMPOSITION OF HYDROCARBON GASES

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

[1]Schlumberger (USA, France, UAE)
[2]Air Liquide, USA

Introduction

Valid shelf life of petroleum gases for isotopic analysis is relatively unknown from formal, designed experiments which require long-term planning of methodology and availability of appropriate resources (instrumentation, analysts, analytes, and storage). We designed and created custom gas mixtures, a fit-for-purpose subsampling strategy, and dedicated analytical program to study the operational stability, storage stability, and individual component stability of the C1–C3 carbon and C1 hydrogen isotopes of standard gases over at least two years. We present the experimental design, and results showing variation of $\delta^{13}C$ and $\delta^{2}H$ in both the operational and storage stability studies.

Results

To prepare for the stability study, we tested several methods for optimal sample transfer from different Scott cylinders. Direct injection from the Scotty 14 would be ideal due to the low sample volume. However, better overall results were achieved with two other methods: the Scotty 110 cylinder with the two-stage regulator, and the Scotty 34 cylinder with the flow-through regulator. The two-stage regulator with Scotty 110 cylinder uses the least amount of sample but is at high pressure and requires additional safety-handling procedures. The septum flow-through regulator consumed the greatest amount of gas but yielded the lowest standard deviation for carbon isotope composition of C1 (0.2‰), C2 (0.1‰), and C3 (0.1‰) as well as hydrogen isotope composition of C1 (3‰). Therefore, we chose this subsampling method because of the simplicity and repeatability.

Air Liquide performed the blending, filling, and shipment of Scotty 34 cylinders to Schlumberger Reservoir Laboratories. Most cylinders contain 87% C1, 7% C2, 3% C3 and minor (1.5% each) CO_2 and N_2. From these mixtures, three cylinders are repeatedly subsampled for operational stability tests (e.g. to measure the impact of repeated subsampling on isotope ratio). The remaining cylinders are subsampled sequentially over time and only once for the storage stability study. We also filled several cylinders with only one component, 3% C3 gas, in balance nitrogen, in order to test the possible impact of individual components v. mixtures. C3 cylinders were also subjected to both the operational and storage stability analytical schedule.

The analytical procedure involves analysis of three cylinders per analytical event, with each subsampling analysis performed in duplicate. Laboratory data sheets for each subsampling, compositional analysis, and isotope analysis is used to record all possible variations in analytical conditions.

As of December 2016, we have performed seven subsampling and analysis events for the operational, storage, and component stability studies. In the operational stability study (e.g., resampling of the same cylinder), the $\delta^{13}C$ values for methane decreased over the initial eight-month period. The storage stability study (e.g., cylinders sampled only one time) shows the same trend. In contrast, C2 and C3 $\delta^{13}C$ values increased. The hydrogen isotopic composition of methane increased over the initial eight-month period in both operational stability and storage stability studies. There is also variation between cylinders in both values and trends. These measurements will continue over the next 1.5 years, and by September 2017 we will have additional data points. Additional results, including potential mechanisms for change and significance of variation, will be discussed as the study continues for next 1.5 years.

Conclusions

Long-term study of the impact on isotopic composition on both repeated sampling from a single cylinder (operational stability) and of cylinders stored for longer periods requires dedicated samples, facilities and methods to ensure consistency and interpretation potential of results. We have carefully designed and implemented a study using synthetic gas mixtures, fit-for-purpose rigorous subsampling method, and laboratory standard procedures to measure and ultimately interpret changes in stable isotope compositions in hydrocarbon gases that have been in long-term storage or in operating use. After eight months, we have observed changes in $\delta^{13}C$ values of methane, C2 and C3 and in δD in methane. We also observe variation on a cylinder-by-cylinder basis. Analysis and interpretation will continue over the next 1.5 years to ultimately determine the significance of observed changes.