GAS SAMPLING AND PRESERVATION IN DIFFERENT LIGHT GLASS CONTAINERS

A. Ferreira¹, G. Silva¹, T. Freire¹, E. T. de Morais¹, A. Prinzofer²

¹PETROBRAS, Brazil, ²Geo4U, Brazil

Due to tremendous progress in analytical techniques, knowledge in gas geochemistry has expanded considerably in the last decades: extreme sensitivity of chemical detectors, better chromatographic separation of gas compounds, increase of efficiency of mass spectrometers for stable isotope analyses, new methods as clumped isotopes, laser spectroscopy, etc.

However, gas sampling is still a process which did not evolve much. Apart from the sampling in stainless-steel cylinders, expensive and difficult to transport, several containers have been used for quick and non-expensive gas sampling. Unfortunately, the quality of gas preservation in these containers (generally glass-made, with rubber septa) is not routinely tested in general, mainly for chemical compositions.

We present in this work a test performed to evaluate the gas preservation in three kinds of containers (Vacutainers®, Vacutubes® and Exetainers®) during several weeks. We used a natural gas mixture, containing all saturate hydrocarbons from methane to pentane (including iso- and n-butane, neo-, iso- and n-pentane), CO₂, N₂, He and H₂. We monitored the chemical and the carbon isotopic composition evolution versus time.

The chemical composition of the mixture changed drastically, mainly for the hydrocarbons. The gas wetness (C₂-C₅)/(C₁-C₅) decreased in the monitored period, as well as any molecular ratio Cₙ/Cₙ₋₁. For butane and pentane, the normal isomer was more depleted with time than the iso one. Regarding neopentane, it was less depleted than the isopentane.

The container type that was most affected by compositional changes with time was the Vacutainer®, followed by the Vacutube® and the Exetainer®, as can be seen, for example, with the ratio n-C₄/n-C₁ shown in Figure 1. While the Exetainers® presented the smallest chemical fractionation, their small volumes imply in lower pressure injection in the GC, leading to a lower analytical sensitivity. Exetainers® are also the containers presenting the largest air-contamination through time, reducing also the remaining available natural gas amount gradually. A simple modelling of gas transfer out of the container including gas dissolution in the septum rubber, and molecular diffusion through the septum explains qualitatively and quantitatively the gas compounds concentrations evolution over the course of time.

Regarding the carbon isotopic composition, no significant change was observed during the period of this test for the three kinds of containers. Additional measurements are being provided in order to evaluate the moment in time from which the δ¹³C values start to be higher than the precision of the analytical method.

In conclusion, no perfect simple gas storage container has been found so far. Other possibilities may be tested in the future, in order to better use the new analytical performances of gas geochemistry.
Figure 1 Variation of the n-C₄/C₁ ratio over time, for the different containers evaluated in this study (the x-axis shows dates in the dd/mm format, all in 2018).