

COMPOUND SPECIFIC SULFUR ISOTOPE ANALYSIS OF PETROLEUM AND PYROLITIC GASES

W. Said-Ahmad¹, K. Wong², M. Mcnall², L. Shawar¹, Y. O. Rosenberg¹, T. Jacksier², C. Turich³, A. Stankiewicz⁴, S. Feinshtein⁵, A. Amrani¹

1. The Hebrew University of Jerusalem, Israel.
2. Air Liquide, USA
3. Schlumberger, France
4. Schlumberger, USA
5. Ben-Gurion University of the Negev, Israel.

The development of compound specific sulfur isotope analysis (CSSIA) capabilities by GC coupled to MC-ICPMS for volatile sulfur compounds provided new mechanistic insights in several fields of geosciences (Amrani et al., 2009). This technique has been applied to several fields from petroleum geochemistry to oceanography (Greenwood et al., 2014). In the current study we have extended the capabilities of CSSIA to petroleum gases, including sour gases, with high percentage of H₂S. The analysis of trace sulfur compounds in natural gas is potentially informative for recognizing several reservoir processes which impact the quality and production of petroleum such as thermochemical and microbial sulfate reduction and thermal cracking of petroleum and source rocks. Other applications may include analysis of trace sulfur gases from the ocean, atmosphere, wetlands, sea ice and anoxic sediments. The analysis of ppm level sulfur compounds such as methanethiol or dimethyl sulfides in the presence of percent levels of H₂S is challenging because of the high reactivity of these compounds with surfaces and other compounds, the severe tailing of H₂S in the GC column and the sulfur saturation of the ICP-MS. We used a modified GC with passivated lines that is equipped with a gas inlet and a special valve that can transfer the H₂S away from the ICPMS and prevent its saturation. This valve transfers the gas to a thermal conductivity detector and thus enables a precise peak cut with no effect on the other sulfur peaks. This in turn enables analysis of sulfur compounds down to sub-ppm level in the presence of 30% H₂S. We prepared several gas mixtures that simulated sour gas with variable concentrations of methane (65-95%), H₂S (0.01 -30%) and organic sulfur compounds (0.1 – 20 ppm) to test the method. Precision and accuracy varied among the different sulfur compounds (2 ppm) and ranged from 0.1 to 0.6‰ after H₂S (20%) was cut out.

We applied this new method to several natural sour gas samples from basins around the world and to pyrolitic gases that were produced by laboratory heating experiments of source rock (Aderet Borehole, Ghareb Formation, Israel). In addition we conducted several heating experiments with model compounds and H₂S to study organic sulfur compounds formation pathways and their associated sulfur isotopic fractionations in the gas phase. Pyrolysis experiments (150 to 425 °C) were conducted in both semi-open and closed systems with and without the presence of water.

The S-isotope and molecular composition of OSCs in the collected products and natural oils were recorded and showed some interesting variability. The most abundant products of pyrolysis experiments, apart from H₂S, were methanethiol, ethanethiol, and thiophene. Other abundant products were methylthiophene and 1- and 2-propyl thiols. There is a temperature

dependent OSCs composition and $\delta^{34}\text{S}$ values. The $\delta^{34}\text{S}$ values of the thiols were relatively uniform and were about 1.5-2 ‰³⁴S-enriched compared with the coexisting H₂S. Thiophenes, however, had larger variability, differing by up to 6–7‰ from H₂S values. All $\delta^{34}\text{S}$ values of OSCs products were within 2–3‰ of the unheated source kerogen $\delta^{34}\text{S}$ value. The controlled laboratory experiments with model compounds can explain most of these sulfur isotope variability of OSCs. Thiols seem to closely represent the $\delta^{34}\text{S}$ value of the kerogen and could be used to trace oil shale retorting or natural maturation processes. We will discuss the potential of the specific S-isotope values of several OSC species in the gas phase to detect thermochemical processes in natural petroleum reservoirs.

References

- Amrani, A., Sessions, A.L., Adkins, J.F., 2009. Compound-Specific delta S-34 Analysis of Volatile Organics by Coupled GC/Multicollector-ICPMS. *Analytical Chemistry* 81, 9027-9034.
- Greenwood, P.F., Amrani, A., Sessions, A.L., Raven, M.R., Holman, A., Dror, G., Grice, K., Mcculloch, M., Adkins, J., 2014. Development and Initial Biogeochemical Applications of Compound-Specific Sulfur Isotope Analysis. *Principles and Practice of Analytical Techniques in Geosciences* 4, 285.