



Multi-element compound specific stable isotope analysis of volatile organic compounds at trace levels in groundwater samples

Sara Herrero-Martín, Ivonne Nijenhuis, Marie Schmidt, Diana Wolfram, Hans. H. Richnow, and Matthias Gehre
Department of Isotope Biogeochemistry, Helmholtz Centre for Environmental Research (UFZ), Permoserstrasse 15, D-04318
– Leipzig, Germany (sara.herrero-martin@ufz.de)

Groundwater pollution remains one of the major environmental and health concerns. A thorough understanding of sources, sinks and transformation processes of groundwater contaminants is needed to improve risk management evaluation, and to design efficient remediation and water treatment strategies. Isotopic tools provide unique information for an in-depth understanding of the fate of organic chemicals in the environment. During the last decades compound specific isotope analysis (CSIA) of complex mixtures, using gas chromatography-isotope ratio mass spectrometry (GC-IRMS), has gained popularity for the characterization and risk assessment of hazardous waste sites and for isotope forensics of organic contaminants. Multi-element isotope fingerprinting of organic substances provides a more robust framework for interpretation than the isotope analysis of only one element.

One major challenge for application of CSIA is the analysis of trace levels of organic compounds in environmental matrices. It is necessary to inject 1 nmol carbon or 8 nmol hydrogen on column, to obtain an accurate and precise measurement of the isotope ratios, which is between two and three orders of magnitude larger than the amount of compound needed for conventional analysis of compound concentrations. Therefore, efficient extraction and pre-concentration techniques have to be integrated with GC-IRMS. Further research is urgently needed in this field, to evaluate the potential of novel and environmental-friendly sample pre-treatment techniques for CSIA to lower the detection limits and extending environmental applications.

In this study, the novel coupling of a headspace autosampler (HS) with a programmed temperature vaporizer (PTV), allowing large volume injection of headspace samples, is proposed to improve the sensitivity of CSIA. This automatic, fast and solvent free strategy provides a significant increase on the sensitivity of GC-based methods maintaining the simple headspace instrumentation.

The method was developed for the multi-element isotope analysis (carbon and hydrogen) of priority volatile organic groundwater pollutants (methyl tert-butyl ether (MTBE), benzene, toluene, ethylbenzene and o-xylene (BTEX)), and for carbon isotope analysis of chlorinated benzenes and ethenes. The extraction and injection conditions were optimized in terms of maximum sensitivity and minimum isotope effects. During the injection of the headspace sample, the liner is maintained at a low temperature, such that the compounds are retained in a hydrophobic insert packing while the water vapor is eliminated through the split line. With the optimized conditions, it was possible to inject up to 5mL headspace sample with no significant carbon or hydrogen isotopic effects except for the most hydrophobic substance (MTBE), which was subject to a small and reproducible isotope fractionation for hydrogen. The increment on method sensitivity was at least 20 fold in comparison with conventional static headspace analysis.

The environmental applicability of the HS-PTV-GC-IRMS method was evaluated by the analysis of groundwater samples from different contaminated field sites, containing BTEX and chlorinated volatile organic contaminants in the low $\mu\text{g/L}$ range. The results obtained demonstrate that this pre-concentration technique is highly promising to enhance the limits of detection of current CSIA methods and broaden its possibilities.