**Compound Specific Oxygen Stable Isotope Analysis via High Temperature Conversion (HTC): Ideas and Assessment Strategies for GC-HTC-IRMS**

Kristina L. Hitzfeld, Hans H. Richnow, Matthias Gehre

Department for Isotope Biogeochemistry, Helmholtz-Centre for Environmental Research – UFZ

Permoserstr. 15, D-04318 Leipzig, Kristina.Hitzfeld@ufz.de

Despite the fact that commercial reactors for oxygen stable isotope analysis via gas chromatography high temperature conversion isotope ratio mass spectrometry (GC-HTC-IRMS) have long been available, analytical applications are rare. In contrast a diverse and common use of the elemental analyser (EA) technique1 for oxygen stable isotope ratio determination of pure compounds, bulk samples, and references in routine analysis and research applications can be found in literature. Based on this discrepancy and experiences with EA reactors, different reactor types and conversion approaches for online GC-HTC-IRMS oxygen analysis were evaluated. Commercial available and custom build tube-in-tube reactors were investigated for their performance in compound specific isotope analyis (CSIA) of oxygen in organic compounds like vanillin and metyl *tert*-butyl ether. It could be shown that physical and chemical properties of a given reactor design have significant impacts on its ability to convert oxygen bearing compounds into carbon monoxide for IRMS analysis. By means of a recently established GC-HTC-Ion Trap analysis method2, the emergence of interfering byproducts could be proven: (i) sample oxygen can be partially split and carbon dioxide is formed which should not be overseen if the fraction is >2% with respect to the desired carbon monoxide. (ii) C2Hx byproducts2, also not detectable by IRMS, are formed depending on reactor load during the conversion and interfere with the isotope ratio determination even at low concentrations of >1% compared to the produced amount of carbon monoxide. (iii) tube-in-tube reactors bear the risk of non-preferential flow resulting in a second carbon monoxide source of up to 30% and a bulk isotope information due to contact of the sample with the reactor ceramic. It goes without saying, that such drawbacks have to be examined and eliminated prior to accurate measurement of oxygen stable isotopes. Thus, in this study we raised the question about conversion conditions required to obtain reliable compound specific GC-HTC-IRMS results and developed an assessment strategy for reactors which highlights possible interfering oxygen sources and HTC byproduct formation processes and offers analytical approaches to their distinct identification.

**1** Kornexl, B. E.; Gehre, M.; Hofling, R.; Werner, R. A. *Rapid Commun. Mass Spectrom.* **1999,** *13*, 1685-1693.

**2** Renpenning, J.; Hitzfeld, K. L.; Gilevska, T.; Nijenhuis, I.; Gehre, M.; Richnow, H. H. *Anal. Chem.* **2015,** *87*, 2832-2839.