



Compound specific carbon and hydrogen isotope fractionation during solid phase extraction

T. Benbow (1,2), R. Frew (1,2) and A. Hayman (1)

(1) Department of Chemistry, University of Otago, Dunedin, New Zealand, (2) Iso-trace New Zealand Ltd, Dunedin, New Zealand (tbenbow@chemistry.otago.ac.nz)

Stable carbon and hydrogen isotope ratios of individual organic compounds can be measured using a gas chromatography-isotope ratio mass spectrometer (GC-IRMS). Semi-volatile organic compounds are usually introduced to the GC-IRMS system either absorbed to a solid phase micro-extraction fiber (SPME) or dissolved in an organic solvent. Unfortunately, SPME is a non-ideal isolation and introduction technique prior to IRMS because the absorption of organic compounds to the SPME fiber is an equilibrium partitioning process and can result in significant isotopic fractionation; for example, Gray et al, (2002) showed methyl *tert*-butyl ether prepared by SPME to fractionate by 0.9 per mil and 17 per mil for carbon and hydrogen respectively.

The simplest method used to introduce organic compounds to a GC-IRMS system is dissolved in an organic solvent. For environmental studies, this method requires the organic compounds to be isolated from their original matrix. Compound isolation is commonly achieved by solvent extraction. Unfortunately, solvent extractions are labor intensive, time consuming and require large volumes of solvent. By contrast, solid phase extraction (SPE) provides a solvent reduced method for the rapid and highly reproducible extraction of organic compounds from an aqueous matrix, and hence has become the extraction method of choice for quantifying organic contaminants in natural waters (Pichon et al, 1996; Mottaleb et al, 2004). However, while high extraction efficiency is important in IRMS applications, there is the additional problem of isotopic fractionation. A suitable SPE method requires both high compound extraction and negligible, or highly reproducible, isotope fractionation.

The objective of this study was to assess the suitability of reverse-phase SPE for the isolation of semi-volatile organic compounds from aqueous systems for $\delta^{13}\text{C}$ and $\delta^2\text{H}$

compound specific isotope analysis. SPE and sample concentration parameters were optimized to reduce or eliminate isotope fractionation.

Using an artificial contaminant solution and spiked natural water samples we found the extent of isotope fractionation to be dependant upon both the SPE type and the eluting solvent. Our results showed ENV+ SPE cartridges (Biotage, Uppsala, Sweden) eluted with dichloromethane to cause no significant $\delta^{13}\text{C}$ or $\delta^2\text{H}$ fractionation for any of the tested organic compounds.

References

Gray et al. (2002) Environmental Science and Technology 36, 1931-1938

Mottaleb et al. (2004) J. Environmental Sciences-China 06, 497-501

Pichon et al. (1996) J. Chromatography A 737, 25-33