Novel strategy for pre-concentration of volatile organic compounds from water samples for Carbon and Hydrogen stable isotope analysis at trace levels

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One major challenge for application of compound specific isotope analysis (CSIA) is the analysis of trace levels of organic compounds in environmental matrices. Hence, efficient extraction and pre-concentration techniques have to be integrated with gas chromatography (GC)- isotope ratio-mass spectrometry (IRMS).

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 combined with CSIA. This automatic, fast and solvent free strategy provides a significant increase on the sensitivity maintaining the simple headspace instrumentation.

The method was optimized for the multi-element isotope analysis ($\delta^{13}C$ and δD) of 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. It was possible to inject up to 5mL headspace sample with no significant isotopic effects. The increment on sensitivity was at least 20 times from static-HS analysis. The Detection Limits (DLs) for $\delta^{13}C$ were from 2 to 60 µg/L, which is within the same order of magnitude, or slightly higher than the best reported by Purge and Trap (P&T) [1]. To the best of our knowledge, this is the first study reporting DLs for δD of BTEX (60-100 µg/L). The DL for δD of MTBE was 50 µg/L, which is in the same order than previously reported by P&T [2]. With the objective to further increase the method sensitivity, we are testing the multiple injection of up to 6 aliquots of headspace sample with very promising results.

The environmental applicability of the HS-PTV-GC-IRMS method was evaluated by the analysis of groundwater samples from different contaminated field sites.

[1] Jochmann, M.A., *et al Rapid Communications in Mass Spectrometry*, 2006. **20**(24): p. 3639-3648; [2] Kuder, T., *et al Environmental Science & Technology*, 2005. **39**(1): p. 213-220.