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How to Apply Compound-Specific Isotope Analysis to Complex Environmental Samples

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Compound-Specific isotope analysis (CSIA) is an increasingly applied tool to evaluate the origin and fate of volatile organic compounds such as benzene, toluene, ethylbenzene, and xylenes (BTEX), which are widespread contaminants in the environment. CSIA is commonly performed using a gas chromatograph coupled to an isotope-ratio mass spectrometer (GC-IRMS). The compounds eluting from the GC column are transformed into a single analyte before entering the source of the mass spectrometer (CO₂ for carbon, H₂ for hydrogen). Thus, an excellent chromatographic resolution is crucial for GC-IRMS to obtain accurate isotope measurements. BTEX present a great challenge for GC-IRMS because they occur as part of a complex mixture of hydrocarbons at most contaminated field sites. The objective of this study was to implement a two-dimensional heart-cutting GC

hyphenated to an IRMS detector to analyze carbon isotope in BTEX in complex environmental samples (groundwater and gas-phase samples), *i.e.* with a high load of non-targeted compounds.

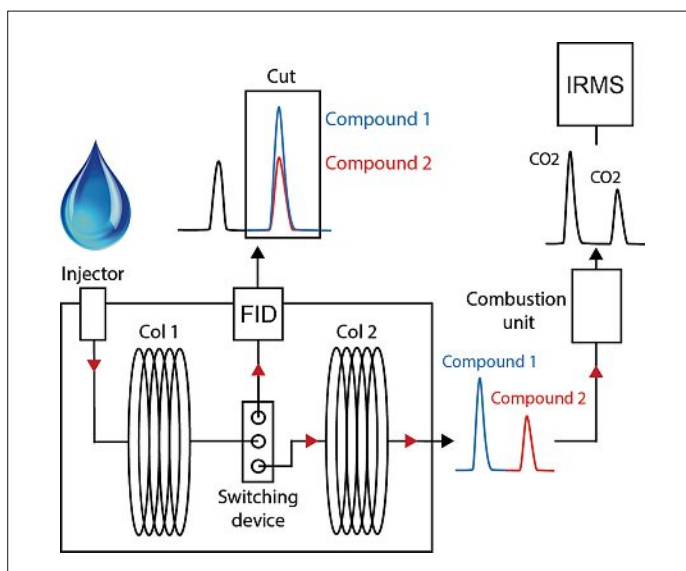
Accuracy of carbon isotope values measured with the newly implemented 2D-GC-IRMS system remained comparable to classic 1D-GC-IRMS whilst precision was still very high. Samples from two field sites were successfully analyzed, and substantial enrichment of ¹³C in toluene was shown in some samples, which is a proof of *in situ* biodegradation by indigenous microorganisms. The final 2D-GC oven program was shorter than programs previously implemented for 1D-GC for similar compounds for a much better resolving capacity. Furthermore, there was no need for an additional oven for the second column as both columns lie within the same GC oven.

2D-GC-IRMS was successfully applied to groundwater and gas-phase samples that could not be analyzed by classic 1D-GC-IRMS for the determination of carbon isotope ratios in BTEX. This technique expands the spectrum of environmental samples suitable for isotope ratio measurements, and will provide new insights into attenuation processes of BTEX in contaminated sites.

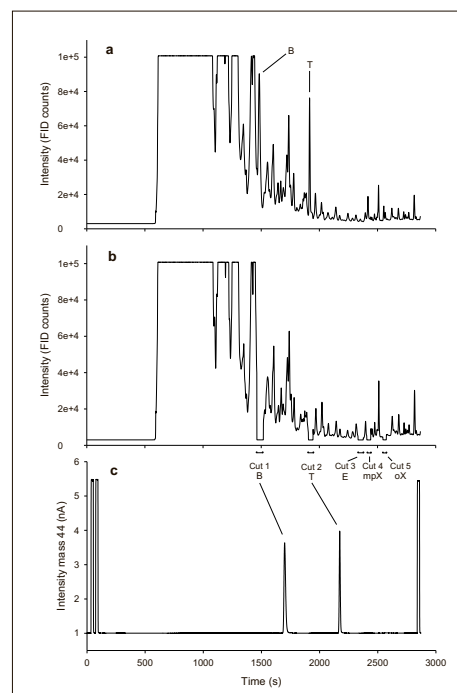
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2D-GC-IRMS configuration for carbon isotope analysis. The switching device after the first column directs by default the flow to the FID detector. Compounds of interest are sent to the second column by heart-cuts defined according to their retention time on the first column, and then to the IRMS detector.



2D-GC-IRMS analysis of a gas-phase sample. a) FID chromatogram without heart-cuts, b) FID chromatogram with heart-cuts for BTEX and c), the corresponding IRMS chromatogram. Only benzene (B) and toluene (T) were sent to the IRMS. Reprinted with permission from Elsevier, Ponsin *et al.*, *J. Chromatogr. A* **2017**, *1492*, 117.

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