



## **Compound-specific isotope analysis at trace concentrations: evaluation of a large volume injection (LVI) based method**

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Compound-specific isotope analysis (CSIA) with on-line gas chromatography-isotope ratio mass spectrometry (GC-C-IRMS) is an important tool for the characterization of origin and fate of organic contaminants in environmental analytical chemistry. However, in particular for field applications, a major drawback of CSIA is its rather poor sensitivity in terms of amount of compound required on column. This currently limits or even prevents the use of CSIA in some application areas such as fate studies of semivolatile compounds, and differentiation between sources of contaminants based on their isotope signature. Field studies of transformation are often restricted to source-near zones of contaminated sites with high aqueous concentrations of contaminants.

To overcome this problem, we have optimized various enrichment/injection techniques, some of which are already well established in quantitative water analysis at trace levels. For the trace isotope analysis of polycyclic aromatic hydrocarbons (PAHs) in soils we have developed a procedure that combines accelerated solvent extraction (ASE), silica gel clean-up and large volume injection (LVI). Especially in case of interfering matrix components enrichment and clean-up methods are necessary to achieve precise results. Conventional preconcentration is time consuming and losses of volatile compounds or isotopic fractionation may occur. Large volume injection in capillary gas chromatography can eliminate the necessity for preconcentration steps for sam-

ples containing organic compounds at trace concentrations. LVI allows a reduction of the total time of analysis and lowers the detection limit of the instrument about a 100 times compared to a standard 1  $\mu\text{L}$  injection. In combination with a programmable temperature vaporizer (PTV-Injector) we injected up to 150  $\mu\text{L}$  solvent in a cooled packed liner. Within the PTV-Injector the solvent evaporated and was subsequently vented through the injector split, while the analytes were sorbed to the liner packing. After a thermal desorption the analytes were transferred into the GC column.

All methods were thoroughly validated for an intrinsic carbon isotope fractionation to avoid artifacts stemming from the analytical method itself. For soil samples, ASE and the following clean-up do not significantly fractionate between isotopes. During LVI, the solvent evaporation occurring in the injector was expected to influence isotope composition but this effect was shown to be small. However, more volatile compounds that do not differ sufficiently in vapor pressure from the solvent are lost during this step. This is the case, e.g., for naphthalene when using cyclohexane as solvent. Carbon isotope composition changes due to different injection volumes, concentrations, split settings, PTV initial temperatures and the use of different solvents have been evaluated, followed by an optimisation of several parameters. Selected field applications for the determination of carbon isotope compositions of PAHs in environmental samples will be discussed. Possible technical pitfalls for the determination of precise and accurate isotope data of environmental samples will be highlighted in exemplary field applications.