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Heart-cutting two-dimensional gas chromatography–isotope ratio mass spectrometry analysis of monoaromatic hydrocarbons in complex groundwater and gas-phase samples

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ABSTRACT

Compound-specific isotope analysis (CSIA) is increasingly used to evaluate the origin and fate of petroleum hydrocarbons in the environment. However, as samples often contain a complex mixture of compounds and the method requires a full chromatographic separation, it can be challenging to obtain accurate and precise isotope values. In this study, in order to develop a method to analyze carbon isotopes in benzene, toluene, ethylbenzene, and xylenes (BTEX) in complex environmental samples, a two-dimensional heart-cutting gas chromatograph (GC) was hyphenated to an isotope ratio mass spectrometer (IRMS). The focus was placed on benzene and toluene, which are the main compounds of concern in contaminated sites. A full separation for BTEX was successfully achieved using a 60 m polar column in the first dimension and a 30 m non-polar column in the second dimension. Accuracy and precision of carbon isotope measurements of standards were not impacted by the new setup compared to classic one-dimensional (1D) GC-C–IRMS. For benzene and toluene, precision remained very good (≤0.2‰) for concentrations comprised between 5 and 20 μg/L. A high matrix load did not influence the precision and accuracy of isotope measurements. The method was tested on several samples from two different field sites. For all samples tested, full chromatographic baseline resolution was achieved for benzene and toluene. Spatial variability of isotopes values linked to biodegradation was evidenced for one field site. This new 2D-GC-C–IRMS method will broaden the spectrum of samples suitable for isotope analysis and will be therefore able to give new insights into attenuation processes of BTEX in contaminated sites or source fingerprinting.

1. Introduction

Compound-specific isotope analysis (CSIA) is a powerful tool to evaluate the origin and fate of volatile organic compounds such as benzene, toluene, ethylbenzene, and xylenes (BTEX) or chlorinated solvents, which are widespread contaminants in the environment. Therefore, CSIA is increasingly applied, for example to track the extent of biodegradation of contaminants [1,2], to distinguish between biodegradation mechanisms [3,4], or to differentiate several sources of contamination [5,6]. Isotope fractionation factors have been determined for numerous degradation pathways and provide a basis to evaluate field data [7–10]. A guidance document from US EPA outlining good practice for CSIA application is also available [11].

CSIA is commonly performed using a gas chromatograph coupled to an isotope-ratio mass spectrometer (GC–IRMS). In this instrument, the compounds eluting from the GC column are transformed into a single analyte (for example CO_2 for carbon). Thus, unlike for a GC hyphenated to a quadrupole mass spectrometer (GC–qMS) for example, where co-eluting compounds can still be identified and quantified in the selected ion monitoring (SIM) mode, excellent chromatographic resolution is crucial for GC–IRMS.

While chlorinated solvents can typically be easily resolved in samples from contaminated sites, (BTEX) present a much greater challenge because they occur as part of a complex mixture of hydrocarbons at most field sites. In gas samples from sites with nonaqueous phase liquid (NAPL), BTEX are masked by very high amounts of other compounds (paraffins, isoparaffins, olefins...) with a high vapor pressure [12]. In water samples, BTEX dissolve

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preferentially compared to other compounds. However, as spills age, the ratio between target to matrix compounds can decrease due to the higher solubility of BTEX (and consequently a fast depletion in NAPL compared to non-aromatic compounds), making their analysis more challenging.

During biodegradation of organic contaminants, molecules with light isotopes are usually degraded more rapidly than those with heavy isotopes, leading to an enrichment of heavy isotopes in the remaining fraction[2]. While for chlorinated hydrocarbons isotope enrichment factors for carbon (ε_C) can be as high as −30‰ [2], for benzene and toluene, ε_C for anaerobic degradation range from −0.8 to −3.6‰ [2] and from −0.5 [2] to −6.7‰ [13], respectively. As a result, the change in the carbon isotope ratio for a given amount of degradation is usually smaller for BTEX than for chlorinated hydrocarbons. Thus, reaching high precision of isotope values through full peak separation is particularly critical for BTEX measurements to evidence isotope enrichment or depletion.

To date, two strategies have been developed to separate compounds of interest from non-target compounds for isotope ratio measurements by GC–IRMS. The first strategy relies on the use of long GC columns. For instance, Kawashima and Murakami [14] successfully used a 150 m long column bonded with polydimethylsiloxane to analyze selected individual components in a mixture of VOCs following thermal desorption. However, a dedicated high-pressure regulator was required to maintain the pressure in such a long column and each run lasted more than two hours. Furthermore, resolution improves with an increase in column length but this improvement is proportional to the square root of column length. The second strategy implements two-dimensional heart-cutting GC hyphenated to an IRMS detector. This approach has been used to analyze flavor components [15], steroids in urine [16], wax compounds in tobacco leaf and smoke samples [17], selected congeners in polychlorobiphenyls (PCB) and polychloronaphthalene (PCN) [18], C_2 to C_5 hydrocarbons produced from biomass burning experiments [19], and raspberry aroma compounds from food products [20]. Because of the complexity of petroleum, 2D-GC has been widely applied to characterize various classes of compounds such as paraffins, olefins or aromatics [21]. However, 2D-GC was often hyphenated to a mass spectrometer to overcome difficulties in identifying compounds that were still overlapping despite a multidimensional separation. For example, Henderickx and Ramaekers [22] applied 2D-GC–MS to identify about 70 individual compounds in a C_9-C_{10} aromatic hydrocarbon pyrolysis distillate. 2D-GC has been also used to determine the concentration of aromatic and oxygenated compounds in gasoline with a quadrupole MS [23]. Although BTEX are common environmental contaminants and there is growing interest in the use of CSIA, no studies have yet been conducted on 2D-GC hyphenated to an IRMS detector for BTEX in complex environmental samples.

The objective of this study was to develop a 2D-GC-C–IRMS method to analyze carbon isotope in BTEX in complex environmental samples (groundwater and gas-phase samples). The method was tested with samples from field sites for which 1D-GC-C–IRMS, even under optimized conditions for baseline resolution of benzene and toluene, failed to yield sufficient chromatographic resolution. As a first step of the 2D-GC method development, two samples containing a high load of matrix were analyzed with different combinations of columns in the first and second dimensions to determine the combination of columns and oven program giving the best separation for the compounds of interest (i.e. BTEX with a focus on benzene and toluene). Then, the analytical performance of the new setup was assessed through the determination of metrics such as precision, accuracy, limit of detection (LOD), peak width, and linearity range. The influence of matrix load on these metrics and on isotope values was assessed by varying the ratio between target compound to matrix based on material from a field site. Finally, the application of this method was illustrated with samples from two field sites.

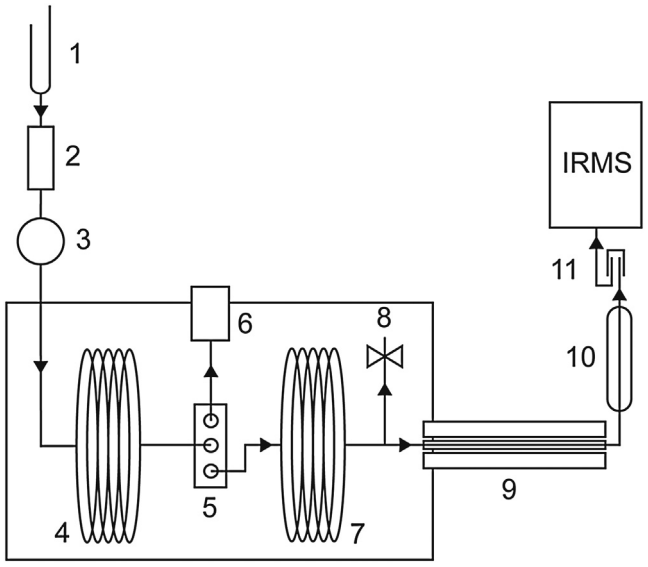

Fig. 1. 2D-GC-C–IRMS configuration. (1) sparge vessel; (2) Trap concentrator; (3) cryotrap; (4) first GC column; (5) Deans Switch; (6) FID; (7) second GC column; (8) Heart Split valve; (9) combustion furnace; (10) Nafion tube; (11) open split.

2. Material and methods

2.1. Chemicals

Reference compounds were obtained in high purity from different suppliers as follows: Ethylbenzene and *m*-xylene from Fluka (both min. 99% purity, Steinheim, Germany) toluene from Riedel-de-Haën (min 99.5% purity, Seelze, Germany), benzene from Sigma Aldrich (min 99.7% purity, Steinheim, Germany) and *o*-xylene from Alfa Aesar (99% purity, Karlsruhe, Germany).

2.2. Carbon isotope analysis

Carbon isotope ratios were determined using an Agilent 7890A gas chromatograph coupled to an Isoprime 100 IRMS via an Isoprime GC5 combustion interface (Elementar) operated at 970 °C. A scheme of the instrumentation for 2D-GC-C–IRMS is shown in Fig. 1. Water samples were preconcentrated using a purge-and-trap module (Stratum, Teledyne Tekmar); 25 mL of sample was purged with N_2 gas in a sparge vessel (40 mL/min, Fig. 1, number 1) for 10 min and the degassed compounds were absorbed on a Vocarb 3000 trap (VICI, Fig. 1, number 2). Compounds were then transferred to a cryogenic trap at −100 °C (Tekmar Dohrmann, Fig. 1, number 3) which was rapidly heated to 180 °C (ramp of 15 °C/s) to transfer the entire mass of compound to the GC. The carrier gas was helium.

2.2.1. 1D-GC-C–IRMS

In order to highlight the need for 2D-GC, 1D-GC-C–IRMS was also performed. Compounds were injected in a DB-VRX column (60 m × 0.32 mm, 1.8 μm, Agilent J&W) operated in constant flow mode (1.2 mL/min). Initially, the oven program was 60 °C (0 min), 1.5 °C/min–125 °C (0 min), 30 °C/min–230 °C (2 min). This program was then optimized to try to improve peak separation for samples with a heavy load of matrix and became: 40 °C (0 min), 1.5 °C/min–55 °C (25 min), 5 °C/min–65 °C (20 min), 30 °C/min–240 °C (5 min). Benzene was eluting during the first plateau at 55 °C and toluene during the second at 65 °C.