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Solvent-based dissolution method to sample gas-phase volatile organic compounds for compound-specific isotope analysis

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ABSTRACT

An investigation was carried out to develop a simple and efficient method to collect vapour samples for compound specific isotope analysis (CSIA) by bubbling vapours through an organic solvent (methanol or ethanol). The compounds tested were benzene and trichloroethylene (TCE). The dissolution efficiency was tested for different air volume injections, using flow rates ranging from 25 ml/min to 150 ml/min and injection periods varying between 10 and 40 min. Based on the results, complete mass recovery for benzene and TCE in both solvents was observed for the flow rates of 25 and 50 ml/min. However, small mass loss was observed at increased flow rate. At 150 ml/min, recovery was on average 80 ± 17% for benzene and 84 ± 10% for TCE, respectively in methanol and ethanol. The $\delta^{13}C$ data measured for benzene and TCE dissolved in both solvents were reproducible and were stable independently of the volume of air injected (up to 6 L) or the flow rate used. The stability of $\delta^{13}C$ values hence underlines no isotopic fractionation due to compound–solvent interaction or mass loss. The development of a novel and simple field sampling technique undertaken in this study will facilitate the application of CSIA to diverse gas-phase volatile organic compound studies, such as atmospheric emissions, soil gas or vapour intrusion.

1. Introduction

Compound-specific isotope analysis (CSIA) is increasingly applied at contaminated sites to link the concentration decrease of volatile organic compounds (VOCs) in groundwater to microbial activity [1–3], to distinguish biodegradation mechanisms for a variety of common VOCs [4–6], or to differentiate several on-site sources of contaminant [7–9]. These investigations are usually performed on groundwater samples or directly on the non-aqueous phase liquid (NAPL) collected on site. Furthermore, some studies have also shown the possibility to perform CSIA on gas-phase VOCs collected in the unsaturated zone [10–12], during indoor air studies [13,14] or, at a larger scale, on atmospheric emissions [15,16]. Due to characteristically low VOC concentration in the gas phase compared to groundwater, the success of CSIA in VOC gas-phase studies relies on sampling techniques that allow collection of a sufficiently large mass of the targeted compound for isotopic analysis. This is especially true for indoor air and atmospheric emissions investigations as concentrations are commonly reported to be in the order of few $\mu g/m^3$ [17–20]. Hence, in contrast to bulk volume sampling of groundwater or gas-phase sampling with summa canisters, the application of CSIA in gas-phase VOC studies requires methods that can adequately accumulate the targeted compounds while processing large air volumes.

Based on reported studies, several methods can potentially be used at contaminated field sites to determine isotope ratios of gas-phase VOC. For instance, Hunkeler et al. [10] used dialysis cells (passive samplers) to sample gaseous chlorinated ethenes in a thick unsaturated zone. Each cell unit was filled with distilled water and closed from both sides using dialysis membranes through which gas-phase chlorinated ethene compounds could diffuse and accumulate in the water. The water samples were then analyzed in the laboratory using a purge and trap device as detailed in [21]. However, as the transfer of the compound from the soil gas to the cell is controlled by the air–water partitioning process, the accumulation of the compound in the water takes place until the equilibrium point is reached (and can be predicted using the Henry's Law coefficient). For this reason, the method is not suitable for low soil gas concentrations as an insufficient mass of compound will accumulate in the water to allow reliable isotope analysis. In a different soil gas study, a glass syringe was used to sample gaseous petroleum hydrocarbons in a shallow unsaturated zone via a narrow tubing system driven into the soil [12]. The soil gas samples were then stored in gas-tight glass vials. The samples were analyzed in the laboratory by first performing a solid-phase micro-extraction followed by direct injection into a GC–IRMS [22]. Although this sampling technique is more suitable for low soil gas concentration compared to the technique previously discussed above, a rapid turnaround

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of the samples is required as gas-phase samples commonly have short holding times. Finally, a sorbent-based sampling method was used to investigate the origin of the VOCs monitored inside buildings [13]. The latter study made use of sorption tubes to sample indoor air and sub-slab air, and the samples were analyzed in the laboratory using a thermal desorption-purge and trap sequential procedure. Sampling with sorption tubes was shown to be reliable for isotope measurements and has been used in several other studies [23–26]. However, this method still has several analytical constraints. In contrast to concentration analysis, the isotope analysis has a narrow working range in terms of mass of the element (C or H) delivered to the IRMS detector. Failing to be in the working range, results are found to be unreliable [27,28]. Therefore, the exact knowledge of the gas-phase VOC concentration prior to conducting the sampling event is required. In addition, only one analysis can be performed per tube, as the compound is entirely desorbed during the analysis process. This could become a severe restriction for chlorine (Cl) isotope analysis with GC–qMS, where five replicates of the same sample are commonly needed to calculate the $^{37}Cl/^{35}Cl$ ratio [29]. Finally, when several compounds of interest are present, but at different concentrations, dedicated sorption tubes for each targeted compound are required which increases the sampling effort necessary.

The present work was carried out to develop a simple and robust sampling technique for CSIA in vapour samples. The sampling technique uses solvent-based dissolution tubes and consists of injecting vapour through a limited amount of an organic solvent which acts as a trap for the VOCs. More specifically, the study aims (i) to evaluate VOC dissolution in organic solvents during constant air flow circulation, and (ii) to evaluate the carbon (C) isotope fractionation associated with gas–solvent phase mass transfer for selected VOCs and organic solvents. Benzene and trichloroethene (TCE) were selected to conduct the experiment because of their historically documented occurrence in indoor air and regulated content due to their carcinogenic characteristics. Methanol and ethanol were the organic solvents tested in the study.

2. Materials and methods

2.1. Experimental set up

A permeation tube (VICI) emitting either benzene or TCE vapours was introduced in a 15 cm long stainless-steel cylinder which acted as a source chamber (Fig. 1). The source chamber was then placed inside a GC oven to keep the permeation tube at constant temperature (45 °C) during the experiment. The inlet of the source chamber was connected to a bottle of synthetic air (80% N_2, 20% O_2) which acted as a carrier gas. The outlet of the source chamber was extended to reach a 10 ml vial filled with 8 ml of an organic solvent. The outlet tubing reached the bottom of the vial resulting in a 4.5 cm long solvent column through which the VOC contaminated air flowed. Both inlet and outlet connections were made of 1.6 mm i.d. stainless steel tubing. A flow regulator and a flow metre (Vögtlin Instruments) were connected along the flow line respectively before and after the source chamber in order to ensure stable flow throughout the injection period.

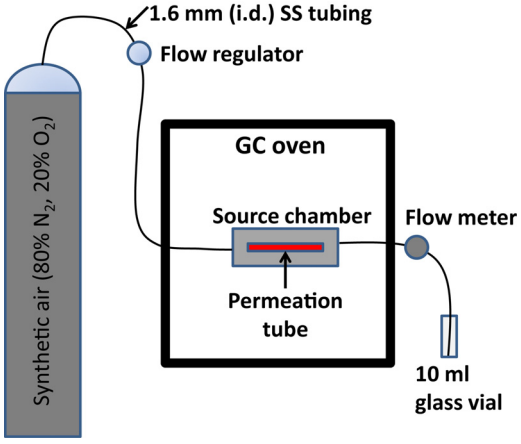

Fig. 1. Schematic representation of the experiment setup.

Table 1
Gas-phase benzene and TCE concentration exiting the source chamber according to flow rate.

Flow rate (ml/min)	Benzene (μg/L)	TCE (μg/L)
25	98.0 ± 15%	480.6 ± 15%
50	49.0 ± 15%	240.3 ± 15%
100	24.5 ± 15%	120.2 ± 15%
150	16.3 ± 15%	80.0 ± 15%

The dissolution efficiency of benzene and TCE was tested in methanol and ethanol (Fluka, MS analysis grade). Methanol and ethanol were selected due to the expected high level of VOC dissolution. For instance, methanol is commonly part of laboratory protocols for extracting soil VOCs [30,31]. In addition, methanol offers the possibility of direct liquid injection for GC–MS analysis. However, fewer losses by evaporation and larger trapping capacity are expected with ethanol. Finally, both selected solvents are highly soluble in water and are expected to have excellent chromatography separation from the VOCs.

The dissolution efficiency was tested for four different flow rates: 25, 50, 100 and 150 ml/min. The selected flow rates are in the range of those used during field-site sampling using sorption tubes [32]. The emission rates for benzene and TCE were 2.451 ± 15% μg/min and 12.016 ± 15% μg/min, respectively. Hence, VOC concentration at the outlet of the injection system varied according to the flow rate (Table 1). The injection periods were 10, 20 and 40 min. The dissolution efficiency for different flow rates and injection periods was tested in duplicate for each VOC.

2.2. Source isotope signature

The $\delta^{13}C$ value of benzene and TCE emitted by the permeation tube was determined in gas-phase samples collected using a 250 ml glass bottle closed with a Mininert valve (VICI). The bottle was filled via a needle temporarily placed at the extremity of the outlet line (Fig. 1). The collected gas sample was then injected into a GC–IRMS using a gas-phase loop injector (see Section 2.3.2). The source sampling events for $\delta^{13}C$ analysis were carried out before, between and after the series.

2.3. Sample preparation and analysis

2.3.1. Concentration analysis

Respectively 50 μl and 300 μl of solvent containing TCE or benzene was added to 10 ml of Mili-Q water (Direct-Q uv, Milipore) in a 20 ml glass vial. Concentration analysis was conducted using a Thermo-Finnigan™ Trace GC Ultra gas chromatograph coupled to a Thermo-Finnigan™ DSQ II quadrupole mass spectrometer (GC/qMS). Five hundred (500) microlitre of the headspace was sampled and injected into the GC using a CombiPal Autosampler (CTC Analytics, Zwingen, Switzerland). The chromatographic separation was performed using a DB-VMS column (30 m, 0.25 mm, 0.25 μm). The temperature oven was initially at 40 °C for 1 min and then was increased to 150 °C at a rate of 10 °C/min. Helium was used as the carrier gas (1.2 ml/min). Concentration calibration was performed using a reference standard from which four different dilutions were prepared to establish the calibration curve. Each