δD and δ13C analyses of atmospheric volatile organic compounds by thermal desorption gas chromatography isotope ratio mass spectrometry

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ABSTRACT

This paper describes the establishment of a robust method to determine compound specific δD and δ13C values of volatile organic compounds (VOCs) in a standard mixture ranging between C_6 and C_{10} and was applied to various complex emission samples, e.g. from biomass combustion and car exhaust. A thermal desorption (TD) unit was linked to a gas chromatography isotope ratio mass spectrometer (GC–irMS) to enable compound specific isotope analysis (CSIA) of gaseous samples. TenaxTA was used as an adsorbent material in stainless steel TD tubes. We determined instrument settings to achieve a minimal water background level for reliable δD analysis and investigated the impact of storage time on δD and δ13C values of collected VOCs (176 days and 40 days of storage, respectively). Most of the standard compounds investigated showed standard deviations (SD) < 6‰ (δD) when stored for 148 days at 4 °C. However, benzene revealed occasionally D depleted values (21‰ SD) for unknown reasons. δ13C analysis demonstrated that storage of 40 days had no effect on VOCs investigated. We also showed that breakthrough (benzene and toluene, 37% and 7%, respectively) had only a negligible effect (0.7‰ and 0.4‰, respectively) on δ13C values of VOCs on the sample tube. We established that the sample portion collected at the split flow effluent of the TD unit can be used as a replicate sample for isotope analysis saving valuable sampling time and resources. We also applied TD-GC–irMS to different emission samples (biomass combustion, petrol and diesel car engines exhaust) and for the first time δD values of atmospheric VOCs in the above range are reported. Significant differences in δD of up to 130‰ were observed between VOCs in emissions from petrol car engine exhaust and biomass combustion (Karri tree). However, diesel car emissions showed a high content of highly complex unresolved mixtures thus a baseline separation of VOCs was not achieved for stable hydrogen isotope analysis. The ability to analyse δD by TD-GC–irMS complements the characterisation of atmospheric VOCs and is maybe used for establishing further source(s).

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1. Introduction

Volatile organic compounds (VOCs) are ubiquitous in the environment (e.g. in soil, water and in the atmosphere) emitted by anthropogenic or natural sources. The technique of compound specific isotope analysis (CSIA) of organic compounds achieved by gas chromatography isotope ratio mass spectrometry (GC–irMS) has been often used in the fields of organic geochemistry, in food and in forensic investigations (including the provenance of food and drugs) [1–4]. Techniques are currently available to measure δ13C and δD of natural gas mixtures (e.g. methane to pentane), liquid hydrocarbons (e.g. crude oil) and extracts from complex media (e.g. soil, sediments and modern biological material) [5–8]. Thus, CSIA is useful to establish sources, processes, thermal history and fractionations that occur by kinetic and exchange reactions. The analysis of atmospheric VOCs was previously mainly restricted to δ13C analysis [9–12]. A technique for measuring δD for a range of VOCs in emissions to establish their sources is not currently available. Therefore this study investigates a method to reliably measure the stable hydrogen isotope compositions of several VOCs without significant isotopic fractionation. We combined a successful established technique for collecting VOCs (thermal desorption) with traditional GC–irMS. Active solid sampling and thermal desorption

(TD) in combination with TenaxTA as an adsorbent material are regularly used for sampling VOCs [13–15]. This sampling method has the advantages of: (i) being selective for compounds of interest (C_6–C_{10}), (ii) its economical maintenance and (iii) the convenient sample handling in contrast to e.g. whole air sampling procedures [16]. Previous studies could already demonstrate for stable carbon isotope analysis that TD-GC–irMS is a reliable technique to analyse $\delta^{13}C$ of some low-molecular-weight VOCs [17,19].

We investigated the suitability of TD-GC–irMS for analysing δD in addition to expanding the range of VOCs (C_6–C_{10}) for $\delta^{13}C$ using TenaxTA as an adsorbent. Essential aspects of the technique were evaluated, e.g. influence of background water, sample breakthrough (BT) and storage behaviour. We also established that recollecting the split flow does not cause isotopic fractionation and thus can be used as a replicated sample for δD and $\delta^{13}C$ analyses. The application to various emissions (e.g. biomass combustion and car exhaust emissions) confirmed the robustness of TD-GC–irMS for stable isotope analysis.

2. Experimental

2.1. Chemicals, materials and gases

Standard mixtures contained VOCs ranging from C_6 to C_{10}. Compounds (benzene, toluene, ethylbenzene, styrene, *m*-xylene, *o*-xylene, *p*-xylene, *n*-propylbenzene, cumene, 1,2,4-trimethylbenzene, butylbenzene) were purchased from Sigma Aldrich and Fluka with purities ≥ 99.5%. Standard mixtures were prepared gravimetrically in *n*-pentane (A.R.). *n*-Pentane was found to be the most suitable solvent for the analyses of investigated VOCs by GC–MS and GC–irMS. Five different standard concentrations were prepared for TD-GC–MS calibration (230 ng/μL, 170 ng/μL, 115 ng/μL and 34 ng/μL) from a stock solution of 340 ng/μL. For analyses by GC–irMS (i.e. without a TD unit) standard solutions of 250 ng/μL were used. For analyses by TD-GC–irMS solutions consisting of ca. 520 ng of each compound per μL were prepared.

Commercially available adsorbent materials for TD are suitable for a wide range of compounds and different fields of application [14]. For the present study we chose TenaxTA due to its highly hydrophobic characteristics and its selectivity for VOCs of interest (C_6–C_{10}, boiling points between 80 °C and 220 °C). TenaxTA is a porous polymer resin on the basis of 2,6-diphenylene oxide and was purchased from Agilent Technologies in mesh 60/80.

In this paper we compared the chromatographic performance of the VOCs on two GC stationary phases: (i) a polyethylene glycol (DB-WAXetr) and (ii) a non-polar phenyl-arylene polymer (DB5-MS). Both columns were supplied from Agilent J&W with dimensions of 60 m length × 0.25 mm i.d. and a 0.25 μm film thickness. Reference gases (H_2 and CO_2) for stable isotope analyses were purchased from BOC Gases Australia Ltd. in ultra high purity (99.999%).

2.2. Preparation of the TD tubes

Tubes were manually packed with approximately 280 mg of TenaxTA with minimal compression. Backpressure tests for each TD tube confirmed that packing was consistent (approximately −1.2 kPa). TenaxTA was conditioned at 330 °C (4 h) while a constant flow of pure helium (50 mL/min) was passed through the tubes [20].

Standard TD tubes were prepared in accordance to method TO-17 [20]. An aliquot of 2–4 μL of the standard mix was injected directly onto the sorbent bed while pumping air through the tube for 1 min at 50 mL/min. It is important to note that the TD-tube needs to be positioned vertically during injection and sampling to avoid possible BT by channelling. Thus a BT experiment was also

performed (see Section 3.5). A standard solution of high concentration (i.e. 800 ng per compound/μL) was injected (3 μL) onto a sample tube using a Calibration Solution Loading Rig (CSLR[TM]) [21]. The CSLR[TM] consisted of an unheated injector port with a controlled carrier gas supply (i.e. helium). The standard mix was introduced through the injector septum using a standard GC syringe. A helium flow of 200 mL/min was swept through the injection port for 40 min. The solution vaporised in the flow of gas before it reached the sorbent bed in the TD tube.

2.3. Collection of emissions

Three different emissions were collected to investigate the applicability of TD-GC–irMS on real samples (biomass combustion, petrol and diesel car engine's exhaust). All samples were actively drawn through TenaxTA sample tubes using a compact Gilian LFS hand pump. Sampling volume was depending on the emission concentration to gain a sufficient amount of VOCs for stable isotope analysis. Sampling flow was adjusted accordingly but in the recommended range for active solid sampling [22,23].

(i) For the petrol engine exhaust emissions samples were taken from a 1993 Mitsubishi Magna Executive running on unleaded petrol (ULP). A sampling volume of 500 mL per sampling tube was collected (at 50 mL/min).
(ii) For the diesel engine exhaust emissions samples were taken from a 2008 Toyota Land Cruiser GXL. A sampling volume of 3 L per sampling tube was collected (at 200 mL/min).
(iii) For emission sampling from biomass combustion approximately 1 kg of Karri biomass (*Eucalyptus diversicolor*) was burnt in a 150 L drum with sufficient oxygen supply for a complete combustion. A sampling volume of 3 L per sampling tube was collected (at 200 mL/min).

2.4. Instrumentation

Compound specific δD and $\delta^{13}C$ analyses of atmospheric VOCs were achieved by linking two established techniques: (i) thermal desorption (to collect and pre-concentrate the sample) and (ii) GC–irMS (to separate the compounds in the sample mixture and allowing accurate δD and $\delta^{13}C$ measurements).

In addition to isotope analysis conventional TD-GC–MS analysis was used for compound identification and for the evaluation of most suitable GC settings.

2.4.1. Thermal desorption (TD) unit

The TD unit (UNITY2[TM], Markes International Limited) used was a single tube, two-stage desorber (primary sample tube desorber and cold trap desorber). The desorption oven was suitable for stainless steel sample tubes (0.635 cm O.D. and 8.89 cm length). The installed cold trap contained also the adsorbent material and was cooled by a 2-stage peltier cell to temperatures ranging between −10 °C and 30 °C. The first step of the analyses was the thermal desorption of the sample tube at 300 °C for 5 min at an adjustable but constant helium flow (see Table 1). The desorbed compounds were trapped on the cold trap at 10 °C. In a second step the refocused sample was rapidly desorbed from the cold trap at 100 °C/s to 300 °C and held for 1 min. The sample was then transferred onto the GC-column through a heated deactivated fused-silica capillary (120 °C) in the helium carrier gas (Fig. 1). The instant desorption process focused the sample on the GC-column to improve the chromatographic resolution. The helium flow during trap desorption represents the sum of GC helium flow and split flow (when required) but needs a minimum flow of 2 mL/min for sufficient desorption. Prior to each sample desorption the TD unit performed an automated leak test and sample tube and cold trap were purged for

Table 1
TD-unit flow settings for different tests.

Parameter	Linearity test settings	Storage test settings	Split tube test δD settings	Split tube test δ¹³C settings	Breakthrough test settings	Concentration test settings
Column flow	1 mL/min	0.9 mL/min	0.9 mL/min	1.1 mL/min	1.1 mL/min	1.1 mL/min
Desorb flow	50 mL/min	45 mL/min	45 mL/min	15 mL/min	15 mL/min	10; 20 mL/min
Split flow during tube desorb	10 mL/min	No split	45 mL/min	No split	No split	No split
Split flow during trap desorb	10 mL/min	No split	No split	25 mL/min	2; 12 and 25 mL/min	80; 19 mL/min

2 min and 1 min, respectively using helium to remove any residual oxygen. The purge flow used was equivalent to the desorption flow (Table 1). During both desorption steps it was possible to divert a split flow from the sample flow as required depending on the sample concentration. The actual split ratio is achieved by adjusting the volume of the split flow. A special feature offered by UNITY2™ is a device for quantitative re-collection of the split flow on a separate sample tube (SecureTD-Q) (Fig. 1). Thus the split sample provides a replicate of the injected sample. Detailed information about general instrument operation of the UNITY2™ is provided by Bates et al. [18].

2.4.2. Gas chromatography–mass spectrometry (GC–MS)

The method development for TD-GC–MS analysis was carried out on an HP6890 GC linked to an HP5973 MS detector. The GC oven temperature was held isothermally at 50 °C for 5 min and heated at 5 °C/min to 80 °C, held for 5 min and heated again at 12 °C/min to a final temperature of 220 °C for 2 min. The GC had to be set to split-less and constant pressure mode (108.3 kPa). Peak identification was performed in scan mode using m/z between 18 and 200.
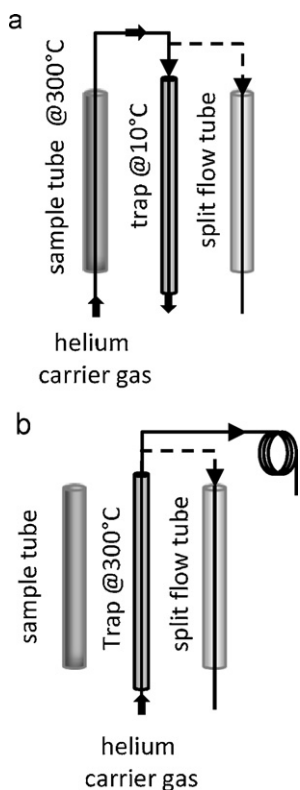

Fig. 1. Sequences of TD operation (a) sample tube desorption and (b) cold trap desorption. An optional split flow is illustrated in a discontinuous line.

2.4.3. Gas chromatography–isotope ratio mass spectrometry (GC–irMS)

CSIA was performed on a Micromass IsoPrime irMS interfaced with an HP6890 GC, programmed with the same temperature settings as described above for GC–MS analysis. An auto-sampler (HP6890) was used for direct injections of the sample mix (split/splitless injector) in pulsed-splitless mode. Isotopic compositions of sample components are given in the delta (δ) notation in per mil (‰) relative to the Vienna Standard Mean Ocean Water (VSMOW) (hydrogen) or to the VPDB carbonate standard (carbon) (Eq. (1)). A reference gas pulse of a known D/H or $^{13}C/^{12}C$ content was introduced into the isotope mass spectrometer at a time different to the analyses. Stable isotopic ratios are reported relative to that of the reference gas which was determined daily using organic standards (with known δ values) to monitor the instrument's performance and reliability of the results.

$$\delta_{sample} = \left[\frac{R_{sample} - R_{standard}}{R_{standard}} \right] \times 1000 \qquad (1)$$

where R is the ratio of heavy to light isotope (D/H, $^{13}C/^{12}C$).

The basic principles of δD analysis are shown in Fig. 2 and relevant calculations are previously described elsewhere [24–27]. In brief, GC chromatographically separated compounds are pyrolysed at 1050 °C to $H_2 + C + CO$ in a quartz furnace containing a sieved chromium catalyst. δD values were calculated by integrating the peaks of resulting ion currents of masses 2 and 3 (H_2 and HD). The results of the H^{3+} corrections (performed after Sessions et al. [28]) were automatically included in software calculations.

δ¹³C values were calculated by integration of the masses 44–46 ion currents of the peaks produced by combustion (CuO reactor at 850 °C) of the chromatographically separated compounds to $CO_2 + H_2O$ (see Fig. 3). The generated water was trapped at −100 °C to avoid the interference of HCO_2^+ (m/z 45).

For samples, average values of at least three analyses are reported and standard deviations (SD) are given (Table 4). For direct injections an internal standard mix of five compounds (n-undecane, n-tridecane, n-tetradecane, n-heptadecane, n-octadecane, n-nonadecane, n-pentacosane) with known δD and δ¹³C values was analysed after every 10th sample to monitor accuracy and precision of δ measurements. During the measurements, SDs of the internal standard for analyses were typically less than 4‰ (δD) and less than 0.3‰ (δ¹³C).

3. Results and discussion

3.1. Background water

The impact of water on results obtained by TD and active solid sampling in its many forms were previously discussed [22, 29]. However, most published data refer to a scan range above m/z 30 excluding the detection of water during measurements. The presence of water anywhere in the system will have an impact on δD analyses since pyrolysis will transfer water to hydrogen gas (H_2, DH). Therefore we monitored m/z ion 18 during TD-GC–MS preliminary tests on two different GC-columns (DB-5MS
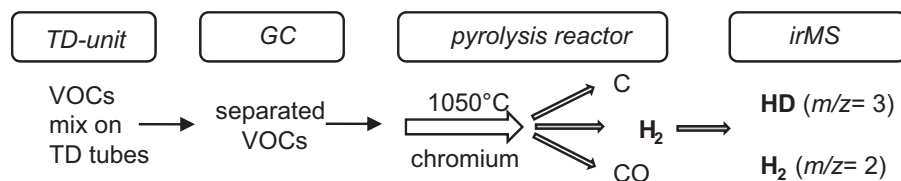
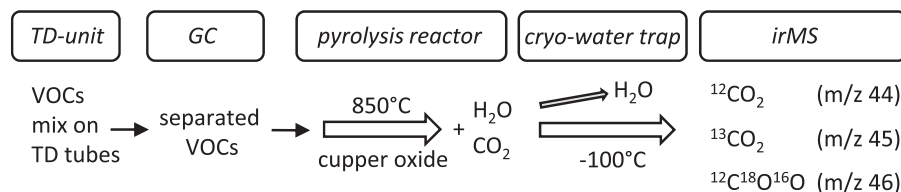**Fig. 2.** Principle of δD analysis by TD-GC–irMS.

Fig. 3. Principle of δ^{13}C analysis by TD-GC–irMS.

and DB-Waxetr) and noted an increased background and an additional peak in contrast to GC–MS analysis without the TD unit. The mass spectrum indicated that the component was water. The occurrence of the peak and background elevation during D/H analysis using TD-GC–irMS verified the hydrogen content. Tests with packed (adsorbent without a sample) and empty (unpacked) TD tubes showed no difference of the background level. Efforts were made to minimise the water content by using a highly hydrophobic adsorbent material (TenaxTA) and following the TD unit's water restriction measures as well as applying standardised sampling methods (e.g. guidelines from U.S. EPA [20]). Thorough leak checks on the TD-unit and all connections to the GC were carried out and various instrument parameters were investigated. Despite these efforts, the elevated background level and peak due to water were still observed but we found that by using cold trap temperatures of 10 °C and by maintaining a split flow of >1 mL/min during trap desorption the background water was significantly reduced (Fig. 4) allowing accurate δD measurements (see Section 3.3). Additionally the determined GC oven temperatures (see Section 2.4.2) enabled the separation of toluene from the remaining water peak (Fig. 4(b)).

3.2. Comparison of GC-columns

The performance of a DB-Waxetr and a DB-5MS GC column was investigated for VOCs of the standard mixture analysed by TD-GC–MS. The DB-5MS is known to be less prone to damage by oxygen and generally has less column-bleed compared to the DB-Waxetr column. The advantage of the DB-Waxetr column over the DB-5MS is its higher polarity and thus its ability to separate p- and m-xylene isomers. For this study the column bleed had negligible impact on the compounds investigated. Therefore the DB-Waxetr was chosen
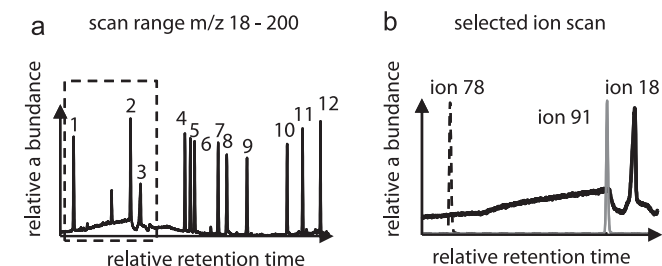
for further analysis due to the efficient separation of all compounds of interest.

3.3. Isotopic fractionation

Previous work established that TD does not cause isotopic fractionation for δ^{13}C analysis of selected VOCs (C_2–C_9) [17,19]. In this study we investigated if any isotopic fractionation occurred for VOCs of the standard mixture during compound specific δD analysis using TD. Therefore results achieved by TD-GC–irMS were compared to those obtained by GC–irMS (direct injection) analyses. The specifications of the irMS required sample sizes of >250 ng per compound on the GC column to measure δD in the limits of instrument linearity. Due to the essential split flow setting of >1 mL/min during trap desorption (see water restriction measures in Section 3.1) samples in order > 500 ng per compound needed to be collected on the adsorbent material. We could show repeatable results with SDs between 1 and 5‰ (average of 2‰). δD values of most investigated compounds introduced by TD are slightly heavier (on average 4‰) compared to δD values obtained by direct injection. However, the differences are still in range of instrument error (with the exception of 1,2,4-trimethylbenzene having a 11‰ difference between the two techniques) and therefore are deemed negligible. Thus we have shown that TD-GC–irMS is a reliable method for obtaining δD results of VOCs ranging between C_6 and C_{10}.

3.4. Impact of storage time on δD and δ^{13}C of VOCs

The impact of storage time on δD and δ^{13}C values of VOCs was investigated for the VOCs in the standard mix adsorbed on TenaxTA. All desorption tubes were stored at 4 °C in an air tight jar containing activated charcoal. δ^{13}C results were determined after 8, 14, 16 and 40 days of storage and showed negligible differences (SD between 0.1 and 0.3‰) for all VOCs (Table 3). δD values were obtained during 176 days of storage (i.e. after 2, 4, 8, 24, 32, 50, 72, 240 h and after 148 and 176 days) (Table 2). SDs of δD analyses were negligible for most compounds of the standard mixture ranging between 3 and 6‰ during the first 148 days of storage. However, results obtained after 176 days of storage showed generally more depleted δD values of up to 44‰ compared to δD values obtained on day 0.The acquired δD values of benzene showed dissimilarities to other VOCs during the first 146 days of storage with a SD of 21‰ although the majority of benzene's δD values vary less than 3‰ to the reference δD value (day 0). The variations in benzene's δD values show no clear trend with storage time (Table 2) however, a random volatility effect cannot be excluded [30] possibly due to the lowest boiling point among

Fig. 4. TD-GC–MS analysis of a standard mix (a) from all compounds 1-benzene, 2-toluene, 3-water, 4-ethylbenzene, 5-p-xylene, 6-m-xylene, 7-cumene, 8-o-xylene, 9- n-propylbenzene, 10-styrene, 11-1,2,4-trimethylbenzene, 12-butylbenzene, respectively and (b) its extracted ion chromatogram for ion 78 (benzene), 91 (toluene) and 18 (water).

Table 2
Results for δD [‰] analyses of VOCs (standard mixture) for up to 176 days of storage; mean δD ± SD [‰] over 146 days; shift in δD between day 0 and day 176.

| Time of storage [h] | 0 | 2 | 4 | 8 | 24 | 32 | 50 | 72 | 240 | 3552 | Mean ± SD |
Time of storage [d]	0	0.1	0.2	0.3	1.0	1.3	2.1	3.0	10	148	
Benzene	−86	−85	−107	−84	−85	−89	−129	−128	−133	−87	−101 ± 21
Toluene	−58	−67	−53	−64	−64	−66	−57	−53	−61	−62	−61 ± 5
Ethylbenzene	−41	−33	−30	−30	−31	−32	−31	−30	−31	−47	−34 ± 6
p-Xylene	−60	−55	−52	−53	−52	−54	−53	−53	−52	−61	−55 ± 3
m-Xylene	−85	−86	−83	−84	−81	−85	−84	−85	−84	−91	−85 ± 3
Cumene	−47	−44	−41	−44	−43	−44	−44	−42	−45	−54	−45 ± 4
o-Xylene	−146	−144	−143	−149	−143	−149	−149	−143	−150	−156	−147 ± 4
n-Propylbenzene	−88	−87	−85	−88	−85	−88	−88	−79	−89	−92	−87 ± 3
Styrene	−52	−47	−45	−46	−49	−48	−49	−50	−47	−55	−49 ± 3
1,2,4-Trimethylbenzene	−100	−103	−100	−104	−102	−102	−104	−98	−102	−111	−103 ± 3
Butylbenzene	−20	−20	−22	−26	−22	−23	−26	−24	−19	−20	−22 ± 3

Table 3
Results for δ13C [‰] analyses of VOCs in the standard mixture for up to 40 days of storage.

Time of storage [d]	0	8	14	16	40	SD
Benzene	−26.7	−26.6	−26.6	−26.6	−26.7	0.1
Toluene	−25.9	−25.8	−25.7	−25.6	−25.9	0.1
Ethylbenzene	−28.4	−27.5	−28.2	−27.8	−28.1	0.3
p-Xylene	−27.6	−27.4	−27.3	−27.4	−27.7	0.2
m-Xylene	−27.0	−26.8	−26.7	−26.7	−27.1	0.2
Cumene	−26.5	−27.0	−26.4	−26.4	−26.3	0.3
o-Xylene	−29.7	−29.8	−29.7	−29.7	−30.1	0.2
n-Propylbenzene	−28.5	−28.3	−28.9	−28.6	−29.0	0.3
Styrene	−28.4	−28.5	−28.2	−28.0	−28.1	0.2
1,2,4-Trimethylbenzene	−26.5	−26.5	−26.6	−26.5	−26.8	0.1
Butylbenzene	−25.1	−24.9	−25.3	−25.1	−25.5	0.2

the VOCs of the standard mixture. Benzene could have been also subjected to hydrogen exchange with a depleted hydrogen source. Although the exact cause is unclear; therefore it is suggested to use multiple sampling tubes for real samples to identify occasional shifts in δD values for benzene during storage.

3.5. Effects of breakthrough

BT can occur during active solid sampling due to specific sampling conditions or the nature of the real sample [31]. Therefore it is important to monitor any possible BT by installing a BT tube just after the sample tube. We evaluated whether any carbon isotopic fractionation occurred during BT by analysing the standard mixture. An aliquot of the standard (3 μL) was introduced onto the sampling tube using a CSLR™. The sampling tube and BT tube were linked with a brass connector and purged with a helium flow of 200 mL/min (40 min) to allow for BT of benzene and toluene based on parameters from the Health and Safety Executive regu-

lations, UK [32]. We found that 37% of benzene and 7% of toluene broke through. Other compounds in the standard mix did not show any significant BT. Fig. 5 illustrates the δ13C values of benzene and toluene obtained from the sample tube, from the BT tube and from a reference analysis by TD-GC–irMS during standard injection. The δ values from the BT tube were less depleted in 13C by 1.6‰ (benzene) and 3.3‰ (toluene) compared to those from the sample tube. However, comparing the results from sample tubes where BT occurred to those without BT δ13C values showed no significant differences (0.7‰ and 0.4‰ for benzene and toluene, respectively) (Fig. 5). Therefore the impact of BT of benzene and toluene on their δ13C is negligible. The effect of BT on δD values for benzene and toluene was not investigated. It is assumed that BT of benzene and toluene would have also only a minimal effect on their δD values since stable isotopes of C and H have similar physical properties in this regard.

Table 4
δD values [‰] of VOCs in car exhaust emissions (petrol and diesel engine) and in biomass combustion emissions (Karri – *Eucalyptus diversicolor*) with related standard deviations (SD) [‰]; *n* = number of analyses; δ_K = δD values Karri; δ_p = δD values petrol engine.

| Compound | Diesl car emission | | Petrol car emission | | Karri combustion emission | | $\Delta \delta_K - \delta_p$ |
	δD ± SD		δD ± SD		δD ± SD		
Benzene	10 ± 9	n = 4	−94 ± 5	n = 5	−121 ± 5	n = 3	27
Toluene	−3 ± 8	n = 6	−65 ± 3	n = 6	−102 ± 6	n = 3	37
Ethylbenzene			−47 ± 4	n = 3			
p-Xylene			−44 ± 3	n = 3			
m-Xylene	−70 ± 14	n = 5	−61 ± 3	n = 5	−191 ± 5	n = 3	130
o-Xylene	−49 ± 12	n = 3	−48 ± 4	n = 3			
Limonene					−242 ± 2	n = 3	
Eucalyptol					−279 ± 5	n = 3	
Styrene					−113 ± 2	n = 3	
Trimethylbenzene	−117 ± 14	n = 5	−43 ± 5	n = 3			
Naphthalene	−65 ± 4	n = 6			−102 ± 1	n = 3	

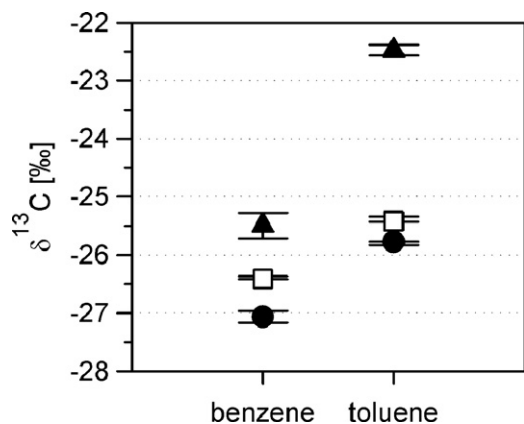**Fig. 5.** $\delta^{13}C$ values of benzene and toluene in the standard mix collected on a (●) sample tube and on the subsequent (▲) breakthrough tube compared to a $\delta^{13}C$ value of a (□) reference analysis (adsorption without breakthrough).
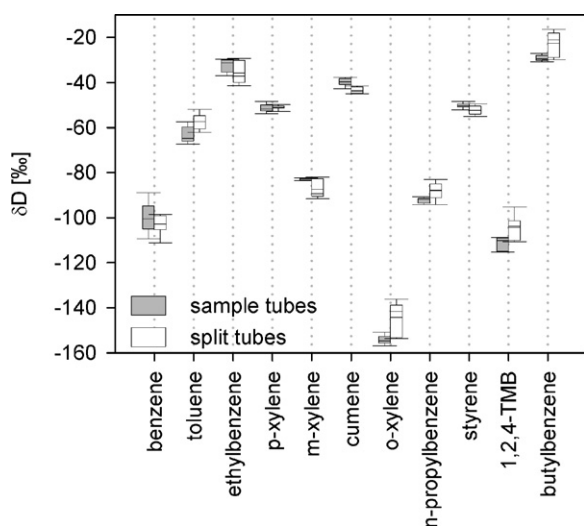

Fig. 6. Differences between δD values of VOCs in the standard mix on the sample tube and on the associated split flow tube (TMB = trimethylbenzene).

3.6. Usage of the split flow sample

Having the opportunity to obtain a replicate sample from the split flow presents several advantages over traditional TD-units. These include: (i) obtaining a duplicate sample allowing TD-GC–irMS measurements at different concentrations of the same sample, which is achieved by varying the split ratio of the TD unit (the merit of the split flow collection is demonstrated in its application to emission samples (see Section 3.7)), (ii) obtaining required replicate δ values, (iii) obtaining a duplicate sample for identifying compounds by TD-GC–MS which leads to (iv) saving important sampling time and resources. It reduces significantly the number of samples to be taken in the field without compromising the need for replicate analyses.

The δD results obtained for VOCs from the split flow tube were similar/identical to those obtained on the sample tube (Fig. 6). This is supported by results from multiple sample collection of the split flow effluent (circle of 6 split flow collections) with SD < 0.2‰ ($\delta^{13}C$).

3.7. δD analyses of VOCs in different emissions

δD analysis by TD-GC–irMS was applied to three emission sources (biomass combustion, petrol and diesel car engines).

Table 4 shows the δD values of collected VOCs. Most SDs for δD analyses of VOC in the emissions from a petrol engine and biomass combustion range between 1 and 5‰ and are well within the instrument precision. However, SDs are up to 14‰ for analyses of VOCs from the diesel engine emissions which is related to a highly complex unresolved mixture of compounds. For CSIA it is essential to obtain baseline separation for compounds of interest. This was not the case for the diesel sample.

To obtain reliable δD values for an array of compounds samples needed to be analysed at different concentrations (different split ratios) in order to assess the data within the linear range of the instrument by using the replicate samples of the split flow collection. The comparison of δD values of benzene, toluene and m-xylene (Table 4) demonstrate significant differences (27‰, 37‰ and 130‰, respectively) between emissions from a petrol car engine and from biomass combustion (Karri). Thus clear source differentiation carries the potential to be used in source tracking of VOCs.

4. Conclusions

In this study we investigated compound specific δD and $\delta^{13}C$ analysis using thermal desorption to collect and concentrate atmospheric VOCs (C_6–C_{10}) using TenaxTA as adsorbent material. We established a reliable method enabling reproducible results for δD and $\delta^{13}C$ analyses with negligible isotopic fractionation compared to direct standard analyses. We evaluated the impact of storage time on δD and $\delta^{13}C$ values and revealed that breakthrough has only minor impact on δ values. We also showed that the sample portion collected of the split flow effluent can be used as a replicate sample for isotope analysis saving valuable sampling time and resources.

This paper presents for the first time δD values of VOCs in emission samples showing a clear distinctions of δD between emissions from biomass combustion and car exhaust emissions (petroleum engine). TD-GC–irMS is a reliable technique and maybe used for establishing further source(s).

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