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1 **δD and $\delta^{13}\text{C}$ analyses of atmospheric volatile**
2 **organic compounds by thermal desorption gas**
3 **chromatography isotope ratio mass**
4 **spectrometry**

5
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36 **Abstract**

37 This paper describes the establishment of a robust method to determine compound specific δD and
38 $\delta^{13}C$ values of volatile organic compounds (VOCs) in a standard mixture ranging between $C_6 - C_{10}$
39 [and was applied to various complex emission samples, e.g. from biomass combustion and car exhaust.](#)
40 ~~This was achieved by linking A~~ thermal desorption (TD) unit was linked to a ~~and~~-gas chromatography
41 isotope ratio mass ~~spectrometer-spectrometer~~ (TD-GC-irMS); [to enable compound specific isotope](#)
42 [analysis \(CSIA\) of gaseous samples. Samples were adsorbed on](#) TenaxTA [was used as an adsorbent](#)
43 [material in-using](#) stainless steel TD tubes. We determined instrument settings to achieve a minimal
44 water background level for reliable δD analysis and investigated the impact of storage time on δD and
45 $\delta^{13}C$ values of collected VOCs (176 days and 40 days of storage, respectively). Most of the standard
46 compounds investigated showed standard deviations (SD) $< 6 \text{ ‰}$ (δD) when stored for 148 days at
47 $4^\circ C$. However, benzene revealed occasionally ~~depleted δD~~ [depleted](#) values (21 % SD) for unknown
48 reasons. $\delta^{13}C$ analysis demonstrated that storage of 40 days had no effect on VOCs investigated. We
49 also showed that breakthrough (benzene and toluene, 37 % and 7 %_v, respectively) had only a
50 negligible effect (0.7 ‰ and 0.4 ‰, respectively) on $\delta^{13}C$ values of VOCs on the sample tube. We
51 established that the sample portion collected at the split flow effluent of the TD unit can be used as a
52 replicate sample for isotope analysis saving valuable sampling time and resources. We also applied
53 TD-GC-irMS to different emission samples (biomass combustion, petrol and diesel car engines
54 exhaust) and for the first time δD values of atmospheric VOCs in the above range are reported.
55 Significant differences in δD of up to 130 ‰ were observed between VOCs in emissions from petrol
56 car engine exhaust and biomass combustion (Karri tree). However, diesel car emissions showed a

57 high content of highly complex unresolved mixtures thus a baseline separation of VOCs was not
58 achieved for stable hydrogen isotope analysis. The ability to analyse δD by TD-GC-irMS
59 complements the characterisation of atmospheric VOCs and is maybe used for establishing further
60 source(s).

61 **Keywords**

62 volatile organic compounds

63 compound specific isotope analysis

64 BTEX

65 stable hydrogen isotopes

66 thermal desorption

67 active solid sorbent sampling

68 **1. Introduction**

69 Volatile organic compounds (VOCs) are ubiquitous in the environment (e.g. in soil, water and in the
70 atmosphere) emitted by anthropogenic or natural sources. The technique of compound specific isotope
71 analysis (CSIA) of organic compounds [achieved by gas chromatography isotope ratio mass](#)
72 [spectrometry \(GC-irMS\)](#) has been often used in the fields of organic geochemistry, in food and in
73 forensic investigations (including the provenance of food and drugs) [1-4]. Techniques are currently
74 available to measure $\delta^{13}C$ and δD of natural gas mixtures (e.g. methane to pentane), liquid
75 hydrocarbons (e.g. crude oil) and extracts from complex media (e.g. soil, sediments and modern
76 biological material) [5-8]. Thus, CSIA is useful to establish sources, processes, thermal history and
77 fractionations that occur by kinetic and exchange reactions. The analysis of atmospheric VOCs was
78 previously mainly restricted to $\delta^{13}C$ analysis [9-12]. A technique for measuring δD for a range of
79 VOCs in emissions to establish their sources is not currently available. Therefore this study
80 investigates a method to reliably measure [the stable hydrogen](#) isotope compositions of several VOCs
81 without significant isotopic fractionation. We combined a successful established technique for
82 collecting VOCs (thermal desorption) with traditional ~~gas chromatography isotope ratio mass~~

83 spectrometry (GC-irMS). Active solid sampling and thermal desorption (TD) in combination with
84 TenaxTA as an adsorbent material are ~~often~~regularly used for sampling VOCs [13-156]. ~~The~~
85 ~~advantages of using TenaxTA and a TD unit with a split flow collection device (Markes Int. Ltd.)~~
86 ~~included~~ This sampling method has the advantages of (i) ~~being~~ selectivity for compounds of interest
87 ($C_6 - C_{10}$), (ii) ~~its~~ economical maintenance ~~and~~ (iii) ~~the~~ convenient sample handling ~~in contrast to e.g.~~
88 ~~whole air sampling procedures [16]. Previous studies could already demonstrate for stable carbon~~
89 ~~isotope analysis that TD-GC-irMS is a reliable technique to analyse $\delta^{13}C$ of some low-molecular-~~
90 ~~weight VOCs [17,19].~~
91 ~~and (iv) obtaining a replicate sample for further analyses. Previous studies could already demonstrate~~
92 ~~that TD-GC-irMS is a reliable technique to analyse $\delta^{13}C$ of low molecular weight VOCs [17,18].~~
93 We investigated ~~the suitability of~~ TD-GC-irMS for analysing ~~compound-specific- δD in addition to~~
94 ~~expanding the range of VOCs (C_6-C_{10}) for $\delta^{13}C$ and $\delta^{15}N$ of atmospheric VOCs ranging between C_6-~~
95 ~~C_{10} -using TenaxTA as an adsorbent. Essential aspects of the technique were evaluated, e.g. influence~~
96 of background water, sample breakthrough (BT) and storage behaviour. We also established that
97 recollecting the split flow ~~is does~~ not ~~causing-cause~~ isotopic fractionation and thus can be used as a
98 replicated sample for δD and $\delta^{13}C$ analyses. The application to various emissions ~~(e.g. biomass~~
99 ~~combustion and car exhaust emissions)~~ confirmed the robustness of TD-GC-irMS for ~~stable~~ isotope
100 analysis.

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101 2. Experimental section

102 2.1. Chemicals, Materials and Gases

103 Standard mixtures contained VOCs ranging from $C_6 - C_{10}$. Compounds (benzene, toluene,
104 ethylbenzene, styrene, *m*-xylene, *o*-xylene, *p*-xylene, *n*-propylbenzene, cumene, 1,2,4-
105 trimethylbenzene, butylbenzene) were purchased from Sigma Aldrich and Fluka with purities ≥ 99.5
106 %. Standard mixtures were prepared gravimetrically in *n*-pentane (A.R.). *n*-Pentane was found to be
107 the most suitable solvent for the analyses of investigated VOCs by GC-MS and GC-irMS. Five

108 different standard concentrations were prepared for TD-GC-MS calibration (230 ng/μL, 170 ng/μL,
109 115 ng/μL and 34 ng/μL) from a stock solution of 340 ng/μL. For analyses by GC-irMS (i.e. without
110 a TD unit) standard solutions of 250 ng/μL were used. For analyses by TD-GC-irMS solutions
111 consisting of ca. 520 ng of each compound per μL were prepared.

112 Commercially available adsorbent materials for TD are suitable for a wide range of compounds and
113 different fields of application [14]. For the present study we chose TenaxTA due to its highly
114 hydrophobic characteristics and its selectivity for VOCs of interest (C₆ to C₁₀, boiling points between
115 80 °C and 220 °C). TenaxTA is a porous polymer resin on the basis of 2,6-diphenylene oxide and was
116 purchased from Agilent Technologies in mesh 60/80.

117 In this paper we compared the chromatographic performance of the VOCs on two GC stationary
118 phases (i) a polyethylene glycol (DB-WAXetr) and (ii) a non-polar phenyl-arylene polymer (DB5-
119 MS). Both columns were supplied from Agilent J&W with dimensions of 60 m length x 0.25 mm i.d.
120 and a 0.25 μm film thickness.

121 Reference gases (H₂ and CO₂) for [CSIA-stable isotope analyses](#) were purchased from BOC Gases
122 Australia Ltd. in ultra high purity (99.999 %).

123 2.2. Preparation of the TD tubes

124 Tubes were manually packed with approximately 280 mg [of](#) TenaxTA with minimal compression.
125 Backpressure tests for each TD tube confirmed that packing was consistent (approximately -1.2 kPa).
126 TenaxTA was conditioned at 330 °C (4 hours) while a constant flow of pure helium (50 mL/min) was
127 passed through the tubes [\[2019\]](#).

128 Standard TD tubes were prepared in accordance to method TO-17 [\[2019\]](#). An aliquot of 2 μL - 4 μL
129 of the standard mix was injected directly onto the sorbent bed while pumping air through the tube for
130 1 min at 50 ~~mL~~ mL/min. It is important to note that the TD-tube needs to be positioned vertically
131 during injection and sampling to avoid possible ~~breakthrough-BT~~ breakthrough by channelling. Thus a
132 ~~breakthrough-BT~~ breakthrough experiment was also performed (see 3.5). A standard solution of high concentration
133 (i.e. 800 ng per compound/μL) was injected (3 μL) onto a sample tube using a Calibration Solution
134 Loading Rig (CSLR™) [\[2120\]](#). The CSLR™ consisted of an unheated injector port with a controlled

135 carrier gas supply (i.e. helium). The standard mix was introduced through the injector septum using a
136 standard GC syringe. A helium flow of 200 mL/min was swept through the injection port for 40 min.
137 The solution vaporised in the flow of gas before it reached the sorbent bed in the TD tube.

138 2.3. Collection of Emissions

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

145 (i) For the petrol engine exhaust ~~emissionsemissions~~ samples were taken from a 1993 Mitsubishi
146 Magna Executive running on unleaded petrol (ULP). A sampling volume of 500 mL per sampling
147 tube was collected (at 50 mL/min).

148 (ii) For the diesel engine exhaust emissions samples were taken from a 2008 Toyota Land Cruiser
149 GXL. A sampling volume of 3L per sampling tube was collected (at 200 mL/min).

150 (iii) For emission sampling from biomass combustion approximately 1kg of Karri biomass
151 (*eucalyptus diversicolor*) was burnt in a 150 L drum with sufficient oxygen supply for a complete
152 combustion. A sampling volume of 3 L per sampling tube was collected (at 200 mL/min).

153 2.4. Instrumentation

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

158 [In addition to isotope analysis conventional](#) TD-GC-MS analysis was used ~~for method development,~~
159 ~~especially~~ for compound identification ~~in the samples~~ and for evaluation of most suitable GC settings.

2.4.1 Thermal Desorption (TD) Unit

160 The TD unit (UNITY2TM, Markes International Limited) used was a single tube, two-stage desorber
161 (primary sample tube desorber and cold trap desorber). The desorption oven was suitable for stainless
162 steel sample tubes (0.635 cm O.D. and 8.89 cm length). The installed cold trap contained also the
163 adsorbent material and was cooled by a 2-stage peltier cell to temperatures ranging between -10 °C
164 and 30 °C. The first step of the analyses was the thermal desorption of the sample tube at 300 °C for 5
165 min and at an adjustable but constant helium flow (see Table 1). ~~transported the~~ The desorbed
166 compounds were trapped onto the cold trap (at 10 °C). In a second step the refocused sample was
167 rapidly desorbed from the cold trap at 100 °C/s to 300 °C and held for 1 min. ~~and The sample was then~~
168 transferred onto the GC-column through a heated deactivated fused-silica capillary (120 °C) in ~~the~~
169 helium carrier gas ~~through a heated deactivated fused silica capillary (120 °C) onto the GC column~~
170 (Fig. 1). The instant desorption process focused the sample on the GC-column to improve the
171 chromatographic resolution. The helium flow during trap desorption represents the sum of GC helium
172 flow and split flow (when required) but needs a minimum flow of 2 mL/min for sufficient desorption.
173 Prior to each sample desorption the TD unit performed an automated leak test and sample tube and
174 cold trap were purged for 2 min and 1 min, respectively using helium to remove any residual oxygen.
175 The purge flow used was equivalent to the desorption flow (Table 1). ~~Sample tube and the subsequent~~
176 ~~cold trap were desorbed at 300 °C for 5 min and for 1 min, respectively.~~ During both desorption steps it
177 was possible to divert a split flow from the sample flow as required depending on the sample
178 concentration. The actual split ratio is achieved by adjusting the volume of the split flow. A special
179 feature offered by UNITY2TM is a device for quantitative re-collection of the split flow on a separate
180 sample tube (SecureTD-Q) (Fig. 1). Thus the split sample provides a replicate of the injected sample.
181 Detailed information about general instrument operation of the UNITY2TM is provided by Bates et al.
182 [\[182\]](#).

184 2.4.2 *Gas Chromatography - Mass Spectrometry (GC-MS)*

185 The method development for TD-GC-MS analysis was carried out on an HP6890 GC linked to an
186 HP5973 MS detector. The GC oven temperature was held isothermally at 50 °C for 5 min and heated
187 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
188 for 2 min. The GC had to be set to splitless and constant pressure mode (108.3 kPa). Peak
189 identification was performed in scan mode using *m/z* between 18 and 200.

190 2.4.3 *Gas Chromatography - isotope ratio Mass Spectrometry (GC-irMS)*

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

201
$$\delta_{\text{sample}} = \left[\frac{R_{\text{sample}} - R_{\text{standard}}}{R_{\text{standard}}} \right] * 1000 \quad (1)$$

202 R is the ratio of heavy to light isotope (D/H, ¹³C/¹²C)

203

204 The basic principles of δ D analysis are shown in Fig. 2 and relevant calculations are previously
205 described elsewhere [24-27,22-25]. In brief, GC chromatographically separated compounds are
206 pyrolysed at 1050 °C to H₂ + C + CO in a quartz furnace containing a sieved chromium catalyst. δ D
207 values were calculated by integrating the peaks of resulting ion currents of masses 2 and 3 (H₂ and
208 HD). The results of the H³⁺ corrections (performed after Sessions et al. [28,26]) were automatically
209 included in software calculations.

210 $\delta^{13}\text{C}$ values were calculated by integration of the masses 44, 45 and 46 ion currents of the peaks
211 produced by combustion (CuO reactor at 850°C) of the chromatographically separated compounds to
212 $\text{CO}_2 + \text{H}_2\text{O}$ (see Fig. 3). The generated water was trapped at -100 °C to avoid the interference of
213 HCO_2^+ (m/z 45).
214 For samples, average values of at least three analyses are reported and standard deviations (SD) are
215 given (Table 4). For direct injections an internal standard mix of five compounds (*n*-undecane, *n*-
216 tridecane, *n*-tetradecane, *n*-heptadecane, *n*-octadecane, *n*-nonadecane, pentacosane) with known δD
217 and $\delta^{13}\text{C}$ values was analysed after every 10th sample to monitor accuracy and precision of δ
218 measurements. During the measurements, SDs of the internal standard for analyses were typically less
219 than 4 ‰ (δD) and less than 0.3 ‰ ($\delta^{13}\text{C}$).

220 3. Results and Discussion

221 3.1. Background Water

222 The impact of water on results obtained by TD and ~~the use of~~ active solid sampling in its many forms
223 ~~have been~~ were previously discussed [22, 29,27,28]. However, most published data research refers to a
224 scan range above m/z 30 excluding the detection of water during measurements. The presence of
225 water anywhere in the system will have ~~especially~~ an impact on δD analyses since pyrolysis will
226 transfer water to hydrogen gas (H_2 , DH) ~~would be produced by pyrolysis~~. Therefore we monitored m/z
227 ion 18 during TD-GC-MS preliminary tests on two different GC-columns (DB-5MS and DB-Waxetr)
228 and noted an increased background and an additional peak in contrast to GC-MS analysis (~~i.e.~~ without
229 TD unit). The mass spectrum indicated that the component was water. The occurrence of the peak and
230 background elevation during D/H analysis using TD-GC-irMS verified the hydrogen content. Tests
231 with packed (adsorbent without a sample) and empty (unpacked) TD tubes showed no difference of
232 the background level. Efforts were made to minimise the water content by using a highly hydrophobic
233 adsorbent material (TenaxTA) and following the TD unit's water restriction measures as well as
234 applying standardised sampling methods (e.g. guidelines from U.S. EPA [20+9]). Thorough leak

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235 checks on the TD-unit and all connections to the GC were carried out and various instrument
236 parameters were investigated. Despite these efforts, the elevated background level and peak due to
237 water was still observed but ~~the action taken reduced the water intake sufficiently for reliable results,~~
238 ~~e.g. we found that the GC oven temperatures described above enabled the separation of toluene from~~
239 ~~the water peak (Fig. 4b). We we found also~~ that by using cold trap temperatures of 10 °C and by
240 maintaining a split flow of > 1 mL/min during trap desorption the background water was
241 significantly reduced (Fig. 4) allowing accurate δ D measurements (see 3.3). Additionally the
242 determined GC oven temperatures (see 2.4.2) enabled the separation of toluene from the remaining
243 water peak (Fig. 4b).

244 3.2. Comparison of GC-columns

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

252 3.3. Isotopic Fractionation

253 Previous work established that TD does not cause isotopic fractionation for $\delta^{13}\text{C}$ analysis of selected
254 VOCs ($\text{C}_2 - \text{C}_9$) [17,19,118]. In this study we investigated if any isotopic fractionation occurred for
255 VOCs of the standard mixture during compound specific δ D analysis using TD. Therefore results
256 achieved by TD-GC-irMS were compared to those obtained by GC-irMS (direct injection) analyses.
257 The specifications of the irMS required sample sizes of >250 ng per compound on the GC column to
258 measure δ D in the limits of instrument linearity. Due to the essential split flow setting of >1 mL/min
259 during trap desorption (see water restriction measures in ~~3.13.1~~) samples in order >500 ng per

260 compound needed to be collected on the adsorbent material. We could show repeatable results with
261 SDs between 1-5 ‰ (average of 2‰). δ D values of most investigated compounds introduced by TD
262 are slightly heavier (on average 4 ‰) compared to δ D values obtained by direct injection. However,
263 the differences are still in range of instrument error (with the exception of 1,2,4-trimethylbenzene
264 having a 11‰ difference between the two techniques) and therefore are deemed negligible. Thus we
265 have shown that TD-GC-irMS is a reliable method for obtaining δ D results of VOCs ranging between
266 C₆-C₁₀.

267 3.4. Impact of Storage Time on δ D and δ^{13} C of VOCs

268 The impact of storage time on δ D and δ^{13} C values of VOCs was investigated for the VOCs in the
269 standard mix adsorbed on TenaxTA. ~~For this experiment all~~ All desorption tubes were stored at 4 °C
270 in an air tight jar containing ~~a vial of~~ activated charcoal. δ^{13} C results were determined after 8, 14, 16
271 and 40 days of storage ~~and showed showing~~ negligible differences (SD between 0.1 and 0.3 ‰) for all
272 VOCs (Table 3) ~~Therefore sampling tubes for δ^{13} C measurements can be safely stored for 40 days.~~ δ D
273 values were obtained during 176 days of storage (i.e. after 2, 4, 8, 24, 32, 50, 72, 240 hours and after
274 148 and 176 days) (Table 2). SDs of δ D analyses were negligible for most compounds of the standard
275 mixture ~~were negligible~~ ranging between 3 – 6 ‰ during the first 148 days of storage, ~~(with the~~
276 ~~exception of 21 ‰ for benzene).~~ However, results obtained after 176 days of storage showed
277 generally more depleted δ D values ~~with differences~~ of up to 44 ‰ ~~compared to between~~ δ D values
278 obtained on day 0, ~~and day 176. As noted above benzene behaved differently~~ The acquired δ D values
279 of benzene showed dissimilarities to other VOCs during the first 146 days of storage with a SD of 21
280 ‰. ~~although the majority of benzene's δ D values vary less than 3 ‰ to the reference δ D value (day~~
281 0), (SD of 21 ‰) but its The variations in benzene's δ D values show no clear trend with storage time
282 (Table 2), ~~The majority of benzene's δ D values vary less than 3 ‰ to the reference δ D value (at day~~
283 0). ~~How~~ However, a random volatility effect cannot be excluded [3029] possibly due to the lowest boiling
284 point among the VOCs of the standard mixture. Benzene could have been also subjected to hydrogen
285 exchange with a depleted hydrogen source. Although the exact cause is unclear; therefore it is

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286 suggested to use multiple sampling tubes for real samples to identify occasional shifts in δD values for
287 benzene during storage.

288

289 3.5. Effects of Breakthrough

290 BT can occur during active solid sampling due to ~~e.g.~~ specific sampling conditions or the nature of the
291 real sample [3130]. Therefore it is important to monitor any possible BT by installing a BT tube just
292 after the sample tube. ~~in the sampling train. In this study we~~We evaluated whether any carbon
293 isotopic fractionation occurred during BT by analysing the standard mixture. An aliquot of the
294 standard (3 μL) was introduced onto the sampling tube using a CSLRTM. The sampling tube and BT
295 tube were linked with a brass connector and purged with a helium flow of 200 mL/min (40 min) to
296 allow for BT of benzene and toluene based on parameters from the Health and Safety Executive
297 regulations, UK [3234]. ~~From this experiment it was established~~We found that 37 % of benzene and 7
298 % of toluene broke through. Other compounds in the standard mix did not show any significant BT.
299 Fig. 5 illustrates the $\delta^{13}C$ values of benzene and toluene obtained from the sample tube, from the BT
300 tube and from a reference analysis by TD-GC-irMS (~~sampled without BT occurrence~~) during standard
301 injection. The δ values from the BT tube were less depleted in ^{13}C by 1.6 ‰ (benzene) and 3.3 ‰
302 (toluene) compared to those from the sample tube. However, comparing ~~$\delta^{13}C$ of benzene and toluene~~
303 ~~the results~~ from sample tubes where BT occurred to those without BT ~~$\delta^{13}C$ values~~ showed no
304 significant differences ~~in $\delta^{13}C$~~ (0.7 ‰ and 0.4 ‰ for benzene and toluene, respectively) (Fig. 5).
305 Therefore ~~it can be said that~~ the impact of BT of benzene and toluene on their $\delta^{13}C$ is negligible. The
306 effect of BT on δD values for benzene and toluene was not investigated. It is assumed that BT of
307 benzene and toluene would have also only a minimal effect on their δD values since stable isotopes of
308 C and H have similar physical properties in this regard.

309 3.6. Usage of the Split Flow Sample

310 Having the opportunity to obtain a replicate sample from the split flow presents several advantages
311 over traditional TD-units. These include (i) obtaining a duplicate sample allowing [TD-GC-irMS](#)

312 measurements at different concentrations ~~of the same sample.~~ ~~This which~~ is achieved by varying the
313 split ratio of the TD unit. ~~(The merit of the split flow collection is demonstrated in its application to~~
314 ~~emission samples (see 3.7).)~~ (ii) ~~o~~Obtaining ~~a~~ required replicate ~~δ values~~~~sample for stable isotope~~
315 ~~analysis~~, (iii) obtaining a duplicate sample for identifying compounds by TD-GC-MS which leads to
316 (iv) saving important sampling time and resources. It reduces significantly the number of samples to
317 be taken in the field without compromising the ~~need for number of~~ replicate analyses.

318 The δD results obtained for VOCs from the split flow tube were similar/ identical to those obtained on
319 the sample tube (Fig. 6). This is supported by results from multiple sample collection of the split flow
320 effluent (circle of 6 split flow collections) with SD < 0.2 ‰ (δ¹³C).

321 3.7. δD Analyses of VOCs in Different Emissions

322 δD analyses by TD-GC-IRMS was applied to three emission sources (biomass combustion, petrol and
323 diesel car engines).

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

330 ~~It was necessary to analyse the samples in~~ ~~To obtain reliable δD values for an array of compounds~~
331 ~~samples needed to be analysed at~~ different concentrations (different split ratios) in order to ~~be assess~~
332 ~~the data~~ within the linear range of the instrument ~~by using the replicate samples of the split flow~~
333 ~~collection. to obtain reliable δD values for an array of compounds.~~ ~~This was possible due to the~~
334 ~~ability of repeatedly using a sample by collecting the split flow effluent.~~ The comparison of δD values
335 of benzene, toluene and *m*-xylene (Table 4) demonstrate significant differences (27 ‰, 37 ‰ and 130
336 ‰, respectively) between emissions from a petrol car engine and from biomass combustion (Karri).
337 Thus clear source differentiation carries the potential to be used in source tracking of VOCs.

338 **4. Conclusions**

339 In this study we investigated compound specific δD and $\delta^{13}\text{C}$ analysis using thermal desorption to
340 collect and concentrate atmospheric VOCs ($\text{C}_6 - \text{C}_{10}$) using TenaxTA as adsorbent material. We
341 established a reliable method enabling reproducible results for δD and $\delta^{13}\text{C}$ analyses with negligible
342 isotopic fractionation compared to direct standard analyses. We evaluated the impact of storage time
343 on δD and $\delta^{13}\text{C}$ values and revealed that breakthrough has only minor impact on δ values. We also
344 showed that the sample portion collected of the split flow effluent can be used as a replicate sample
345 for isotope analysis saving valuable sampling time and [resources](#).

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

349

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443 **Captions**

444
445 **Fig. 1:** Sequences of TD operation a) sample tube desorption and b) cold trap desorption. An optional
446 split flow is illustrated in a discontinuous line

447 **Fig. 2:** Principle of δD analysis by TD-GC-irMS

448 **Fig. 3:** Principle of $\delta^{13}C$ analysis by TD-GC-irMS

449 **Fig. 4:** TD-GC-MS analysis of a standard mix a) from all compounds 1-benzene, 2-toluene, 3-water,
450 4-ethylbenzene, 5-*p*-xylene, 6-*m*-xylene, 7-cumene, 8-*o*-xylene, 9- *n*-propylbenzene, 10-
451 styrene, 11-1,2,4-trimethylbenzene, 12-butylbenzene, respectively and b) its extracted ion
452 chromatogram for ion 78 (benzene), 91 (toluene) and 18 (water).

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

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

458

459 **Table 1:** TD-unit flow settings for different tests

460 **Table 2:** Results for δD [‰] analyses of VOCs (standard mixture) for up to 176 days of storage; mean
461 $\delta D \pm SD$ [‰] over 146 days; shift in δD between day 0 to day 176

462 **Table 3:** Results for $\delta^{13}C$ [‰] analyses of VOCs in the standard mixture for up to 40 days of storage.

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