δD and δ^{13}C analyses of atmospheric volatile organic compounds by thermal desorption gas chromatography isotope ratio mass spectrometry

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Abstract

37   This paper describes the establishment of a robust method to determine compound specific δD and

38   δ^{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   δ^{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 ‰ (δD) when stored for 148 days at

47   4°C. However, benzene revealed occasionally ~~depleted δD~~ depleted values (21 ‰ SD) for unknown

48   reasons. δ^{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 %, respectively) had only a

50   negligible effect (0.7 ‰ and 0.4 ‰, respectively) on δ^{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).

Keywords

62 volatile organic compounds

63 compound specific isotope analysis

64 BTEX

65 stable hydrogen isotopes

66 thermal desorption

67 active solid sorbent sampling

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

3

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 [13-1~~5~~6]. ~~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 selective~~ity~~ 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 $\delta^{13}C$ 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.

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

4

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 to 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 x 0.25 mm i.d.

and a 0.25 µm film thickness.

Reference gases (H_2 and CO_2) for ~~CSIA~~ 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 hours) while a constant flow of pure helium (50 mL/min) was

passed through the tubes [20~~19~~].

Standard TD tubes were prepared in accordance to method TO-17 [20~~19~~]. An aliquot of 2 µL - 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~~mL/min. It is important to note that the TD-tube needs to be positioned vertically

during injection and sampling to avoid possible ~~breakthrough~~ BT by channelling. Thus a

~~breakthrough~~ BT experiment was also performed (see 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™) [21~~20~~]. 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.

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 (e*ucalyptus 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).

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.

6

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 andat an adjustable but constant helium flow (see Table 1). transported the The desorbed compounds were trapped onto 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 1min. and The sample was then transferred onto the GC-column through a heated deactivated fused-silica capillary (120°C) in thea helium carrier gas through a heated deactivated fused silica capillary (120°C) onto the GC-column (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 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). Sample tube and the subsequent cold trap were desorbed at 300°C for 5 min and for 1min, respectively. 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[TM] 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[TM] is provided by Bates et al. [1821].

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 splitless and constant pressure mode (108.3 kPa). Peak identification was performed in scan mode using *m/z* between 18 and 200.

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

~~Compound specific isotope analysis~~ (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) (Equation 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.

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

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~~22-25~~]. 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~~26~~]) were automatically included in software calculations.

210 $\delta^{13}C$ 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 CO_2 +H_2O (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 $\delta^{13}C$ 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 ‰ ($\delta^{13}C$).

3. Results and Discussion

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 beenwere previously discussed [22, 2927,28]. However, most published dataresearch 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 [2019]). Thorough leak

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 δD 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 $\delta^{13}C$ analysis of selected

254　VOCs ($C_2 – C_9$) [17,19]~~, [18]~~. In this study we investigated if any isotopic fractionation occurred for

255　VOCs of the standard mixture during compound specific δD 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 δD 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 3.1~~3.1~~) samples in order >500 ng per

10

260   compound needed to be collected on the adsorbent material. We could show repeatable results with

261   SDs between 1-5 ‰ (average of 2‰). δD values of most investigated compounds introduced by TD

262   are slightly heavier (on average 4 ‰) compared to δD 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 δD results of VOCs ranging between

266   C_6-C_{10}.

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

268   The impact of storage time on δD 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~~. δD

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 δD 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 δD values ~~with differences~~ of up to 44 ‰ compared to ~~between~~ δD values

278   obtained on day 0. ~~and day 176. As noted above benzene behaved differently~~ The acquired δD 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 δD values vary less than 3 ‰ to the reference δD value (day

281   0). ~~(SD of 21 ‰) but its~~ The variations in benzene's δD values show no clear trend with storage time

282   (Table 2), ~~The majority of benzene's δD values vary less than 3 ‰ to the reference δD value (at day~~

283   ~~0). H~~however, a random volatility effect cannot be excluded [30~~29~~] 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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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 ~~e.g.~~ specific sampling conditions or the nature of the real sample [31~~30~~]. Therefore it is important to monitor any possible BT by installing a BT tube just after the sample tube. ~~in the sampling train. In this study we~~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^{TM}. 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 regulations, UK [32~~31~~]. ~~From this experiment it was established~~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 $\delta^{13}C$ values of benzene and toluene obtained from the sample tube, from the BT tube and from a reference analysis by TD-GC-irMS ~~(sampled without BT occurrence)~~ during standard injection. The δ values from the BT tube were less depleted in ^{13}C by 1.6 ‰ (benzene) and 3.3 ‰ (toluene) compared to those from the sample tube. However, comparing ~~$\delta^{13}C$ of benzene and toluene~~ the results from sample tubes w~~h~~ere BT occurred to those without BT $\delta^{13}C$ values showed no significant differences ~~in $\delta^{13}C$~~ (0.7 ‰ and 0.4 ‰ for benzene and toluene, respectively) (Fig. 5). Therefore ~~it can be said that~~ the impact of BT of benzene and toluene on their $\delta^{13}C$ 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.

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

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~~O~~btaining ~~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 ‰ (δ^{13}C).

321 ### 3.7.   δD Analyses of VOCs in Different Emissions

322 δD analys~~i~~es 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.

13

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 reseourcses.

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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Captions

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

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

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

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).

Fig. 5: δ^{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 δ^{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)

Table 1: TD-unit flow settings for different tests

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 to day 176

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

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