

1 | **Challenges of fast sampling of volatiles for thermal desorption gas**
2 | **chromatography - mass spectrometry**

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28 Abstract

29 | Fast active sampling of volatile organic compounds (VOCs) under field conditions still
30 | is a great challenge especially when the exposure time to the source of emissions is
31 | a restricting factor. Hence, to identify ideal conditions for such applications, we
32 | systematically compared *fast active sampling* of VOCs collected on two common
33 | adsorbents under two regimes: first, very low gas volumes (from 300 mL) sampled at
34 | nominal flow rate and, second, sampling at the maximal applicable flow rate
35 | (0.5 L/min) before loss of sorbent material was experienced. For XAD-2 and
36 | Tenax TA, efficient sorbents for on-site VOC-sampling followed by thermal desorption
37 | GC-MS, *significant differences* in the signal response of volatile compounds were
38 | related not only to the varied experimental factors alone, but also to their interactions
39 | and to compound volatility. In the first regime, volatiles (~ 0.004 - 3.13 mM) from
40 | Tenax TA gave the highest signal response only above 800 mL sampled gas volume
41 | while at low concentrations (~ 0.004 - 0.12 mM), satisfactory recovery from XAD-2
42 | required longer analyte-sorbent interaction. For the second regime, the *relative*
43 | *recovery* was severely impaired down to 73 ± 23 %, n=56 for Tenax TA and 72 ± 17
44 | %, n=56 for XAD-2 at **equimolar**-intermediate concentration, and 79 ± 11 %, n=84 for
45 | Tenax TA at high concentration compared to the relative recovery at standard flow
46 | rate. Neither Tenax TA nor XAD-2 provided a 100% total recovery (calculated using
47 | breakthrough values) for any of the evaluated compounds. Finally, two-way and
48 | three-way interactions identified in a multi-variable model, explained not only the
49 | dependence of the signal response on different experimental variables, but also their
50 | complex interplay affecting the recovery of the VOCs. In conclusion, we show for the
51 | first time that XAD-2, a material only recently introduced for the adsorption of volatiles
52 | from the gas phase, competes well with the standard material Tenax TA under
53 | conditions of fast sampling. Due to the similar absolute recovery with Tenax TA even
54 | at low concentration and with regard to the better detection limits, we consider XAD-2
55 | the better choice for fast sampling of VOCs, particularly with low sample volumes at
56 | regular flow. For fast sampling with high flow rate, however, both sorbents might be
57 | selected only if the corresponding recovery loss can be accepted for the study.

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59 Keywords

60 | Fast sampling; short time exposure; thermal desorption GC-MS; field sampling

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61 | 1. Introduction

62 The adsorption of gaseous compounds to sorbent materials by chromatographic
63 equilibration is widely applied, e.g. for the determination of toxic volatile organic
64 compounds (VOCs) [1], trace impurities [2,3] and studies on pollutants in the
65 atmosphere [4–9] or other gaseous samples. For sampling, the sampled gas (i.e. the
66 gas in which the volatiles are dissolved) passes through the sorbent material until
67 both, the concentration of the analyte in the gas phase and in the sorbent reach the
68 equilibrium state [6]. Individual components are trapped according to their partition
69 coefficients, inversely related to their volatility [4]. Indeed, in a sorption system the
70 maximum possible sample volume enabling optimal analyte recovery is inversely
71 related to the volatility of a component; therefore, the most volatile component in a
72 mixture usually delimits the maximal sample volume [2]. When the equilibrium zone is
73 expanded through all the sorbent bed length and the capacity of the sorbent tube is
74 exceeded, the volatiles leave the material and breakthrough occurs [9].

75 | The properties of several sorbents [10,11] and the effects of experimental parameters
76 such as the sample flow rate and the concentration of analytes have been
77 systematically evaluated for application in sampling tubes for volatile compounds with
78 particular attention to breakthrough volumes [8,12–16]. Indeed, the flow rate during
79 sampling is considered a very critical parameter because insufficient interaction time
80 leads to inefficient or poor adsorption of the analytes to the packing material. This is
81 especially relevant when sorbents of low surface area are used, such as Chromosorb
82 101 [8], Tenax TA and Carbotrap C [17].

83 | Previously, breakthrough volumes of several organic vapors were found to be
84 significantly different in response to the sampling flow rate [12]. The highest sampling
85 efficiency was found at 50 mL/min using Tenax GC desorption tubes of standard
86 dimensions [12]. This value was recognized as the theoretical optimum flow rate for
87 such standard tubes with negligible effects on the retention behavior at flow rates
88 between 5 and 200 mL/min; values outside this range, on the other hand, were not
89 recommended [18]. However, other studies suggested that the application of higher
90 flow rates may indeed be feasible after experimental testing [8].

91 | For transient volatile signals in the environment, fast but still efficient sampling, at
92 high flow rates or collecting lower sample volumes is often a crucial requirement. The
93 application of adsorbents at flow rates beyond the optimal value to minimize sampling
94 time is a desired option in situations such as sampling the body odor of free-roaming
95 animals or transient, environmentally relevant volatiles such as air pollutants from a
96 particular source. For instance, fast sampling at ~1 L/min during 0.5 min was used for
97 collecting volatiles in the body odor of common marmosets (*Callithrix jacchus*) [19]
98 without apparent loss in the number of detected compounds compared to lower flow
99 rates. Similarly, fast sampling achieved by reduction of the sampling volume of body
100 odor samples of meerkats (*Suricata suricatta*) from 1 L to 0.5 L, resulted in no
101 differences in signal intensity, complexity of profiles, and sample composition.
102 Interestingly however, the application of higher flow rates (0.88 ± 0.26 L/min) resulted

103 in higher overall signal intensities and changes in sample composition biased
104 towards an increased relative response of semi-volatiles [20]. ~~However, these studies~~
105 ~~generally exhibited a high variance in repeated measurements suggesting insufficient~~
106 ~~knowledge of the influence from experimental conditions. Moreover, the mostly~~
107 ~~unknown structure of the target compounds made it even more difficult to interpret~~
108 ~~the cause of the observed variance. However, we found that the interpretation of~~
109 ~~these results often struggled with the noise potentially produced by non-identified~~
110 ~~disturbing influences and insufficient knowledge on the quantitative impact of known~~
111 ~~experimental parameters on the results as well as the evaluation of structurally often~~
112 ~~unknown target compounds.~~

113 Therefore, this work anticipated to provide a better understanding of the interaction of
114 volatile compounds with two common adsorbents during fast sampling approaches
115 avoiding other potential influences active under field conditions. In the present
116 project, suitable conditions for fast sampling of volatiles were systematically tested.
117 For this, sampling was set up following two principal regimes: first, the use of an
118 unusually high flow rate for common sample volumes and, second, sampling small
119 volumes at the nominal flow rate of 100 mL/min. Under these conditions, we
120 assessed the feasibility of two popular sorbents for field sampling: XAD-2, a common
121 sorbent for sampling of organic substances in liquid samples [21–24] recently
122 recommended for VOCs sampling and thermal desorption from gaseous samples
123 [25], and the well-established and widely used standard sorbent Tenax TA. The
124 recovery of volatiles from XAD-2 and Tenax TA was assessed after one adsorption-
125 desorption cycle employing a multicomponent mixture covering a broad range of
126 volatility and chemical classes.

127 **2. Experimental**

128 **2.1 Materials and chemicals**

129 Thermal desorption tubes (TD) filled with Tenax TA and XAD-2 were assembled
130 in-house and equilibrated as described previously [25]. Briefly, empty and pre-
131 cleaned TD glass tubes were purchased from Supelco (Sigma-Aldrich, Taufkirchen,
132 Germany) and filled with Tenax TA Porous Polymer (matrix Tenax TA, 60-80 mesh)
133 or, alternatively, Amberlite XAD-2 (Supelco/Sigma-Aldrich, Taufkirchen, Germany),
134 following the guidelines of the U.S. Environmental Protection Agency (EPA) in the
135 *Compendium Method TO-17 Determination of Volatile Organic Compounds in*
136 *Ambient Air Using Active Sampling onto Sorbent Tubes* [18]. A TD Clean Cube unit
137 (SIM Scientific Instruments Manufacturer GmbH, Oberhausen, Germany) flushed
138 with nitrogen at a constant flow of 50 mL/min from a nitrogen generator (Nitrox
139 UHPLCMS 18 Domnick Hunter, Gateshead, UK), was employed for conditioning of
140 thermal desorption tubes using temperature programs from 40 to 200 and 250 °C for
141 XAD-2 and Tenax TA, respectively, during a period of 152 min.

142 For loading liquid standards onto sorbent tubes, a nominal flow rate of 100 mL/min
143 nitrogen was adjusted by a *CFC-14PM* multi-channel gas flow regulator for *GC-14A*
144 *GC-MS* (Shimadzu, Kyoto, Japan). A high flow rate of 500 mL/min was adjusted with

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145 a flow restrictor valve connected to a nitrogen gas cylinder ($\geq 99.999\%$, Air Liquide
146 Deutschland GmbH, Düsseldorf, Germany) using an Ellutia 7000 GC flowmeter
147 (Ellutia Ltd, UK).

148 | Methanol (solvent, HiPerSolv Chromanorm) was purchased from VWR International
149 S.A.S., USA. Diethyl ether p.a. $\geq 99.5\%$ was purchased from Carl Roth GmbH & Co.
150 KG (Karlsruhe, Germany). Pyridine p.a. $\geq 99.8\%$, 2-fluoroaniline p.a. $\geq 99.8\%$, 2-
151 chlorobenzaldehyde p.a. 99% , isobutanal p.a. $\geq 99\%$ and *trans*-2-hexenal p.a. 98%
152 were purchased from Sigma-Aldrich (Taufkirchen, Germany). Pentafluorobenzene
153 p.a. 98% and pentafluoropyridine p.a. 99% were purchased from Alfa Aesar GmbH
154 & Co KG (Karlsruhe, Germany). Aniline p.a. 99.8% was purchased from Acros
155 Organics – Fisher Scientific GmbH (Schwerte, Germany). 3,4-Dichlorophenol and 4-
156 chlorophenol were purchased from Riedel-de Häen (Seelze, Germany). 3-Methyl-2-
157 butenyl acetate p.a. $\geq 97\%$, cyclohexyl acetate p.a. $\geq 98\%$ and 4-
158 methoxybenzylacetate p.a. $\geq 98\%$ were kindly provided by Dr. Andreas Petri from
159 Miltitz Aromatics GmbH (Bitterfeld-Wolfen, Germany). 2,4,5-Trichlorophenol p.a.
160 $\geq 99\%$ was purchased from Fluka (Neu-Ulm, Germany). Ethylpentafluorobenzoate
161 p.a. $> 98\%$ was purchased from TCI (Eschborn, Germany). 2-Hydroxybutyric acid
162 p.a. $> 99\%$ was purchased from Fluka AG (Buchs, Switzerland).

163 | 2.2 Preparation of mixtures of volatile compounds

164 | A liquid standard mixture composed of 14 volatile compounds dissolved in methanol
165 was used to assess the performance of XAD-2 and Tenax TA in two experimental
166 regimes for fast sampling. These compounds were selected considering their stability
167 during short-term storage (less than 24 hours), a broad range of volatility to cover a
168 long elution range, appropriate chromatographic separation and absence from
169 ambient air to ensure an analysis free of contamination. Isobutanal, *trans*-2-hexenal
170 and 2-hydroxybutyric acid were also included in the standard mixture, but not
171 evaluated due to their poor detection limits [25].

172 | Stock solutions of the authentic standards at concentrations between 10 and 100 mM
173 were prepared by weighing the pure standard material ~~calculated according to~~
174 ~~density, and~~ directly added into the required volume of solvent. Then, secondary
175 dilutions were prepared by mixing defined volumes of each stock solution in
176 methanol, adapted from the recommended procedure in the U.S. Environmental
177 Protection Agency (EPA) *Method 8260C Volatile Organic Compounds by Gas*
178 *Chromatography/Mass Spectrometry (GC/MS)* [26]. One μL of the corresponding
179 dilution was quickly injected above each sorbent bed [25] into a constant flow of
180 nitrogen (100 or 500 mL/min) carrying the sample through the sorbent bed at varying
181 collection times. The spiking was performed in a climate-controlled environment at
182 22°C .

183 | Compound concentrations of the diluted standard mixture were adjusted to obtain a
184 similar response from each standard with respect to the corresponding molar
185 response from Tenax TA. In a previous work, the standard mix was prepared and

186 evaluated for adsorption to XAD-2 and Tenax TA in terms of sensitivity (lower limit of
187 quantitation, LLOQ), linearity, reproducibility and relative recoveries in a range
188 between 0.10 - ~250 ng/tube depending on the compound [25].

189 | For this evaluation, a higher concentration level was added to the experimental set
190 up for Tenax TA; the evaluation of linearity (4 - 6 calibration levels, slope, intercept,
191 coefficient of determination $R^2 > 0.9$ and $RSD < 25\%$, $n = 4$), reproducibility, relative
192 recoveries and breakthrough values for concentrations between 0.30 - ~ 740 ng/tube
193 is provided in the supplementary section (Supp. A.1 and A.2).

194 | Concentration-dependent effects during sampling were assessed at three levels: low
195 level (0.004 - 0.12 mM according to the compound-specific lower calibration range),
196 intermediate level (0.09 – 0.96 mM) and high level (0.31 - 3.13 mM). The behavior of
197 | ~~near to equimolar~~ similar concentrations was also evaluated at intermediate level
198 (0.32 - 0.35 mM) and high level (0.96 - 1.22 mM according to the compound-specific
199 upper part of the linear range). Table 1 describes the composition of the standard
200 mixture at each concentration level with the analytes organized by increasing
201 retention time.

202 | The analytes were classified in three groups based on their boiling points as very
203 volatile organic compounds (VOCs, bp. < 0 to 50 - 100 °C) for *Group 1* and volatile
204 organic compounds (VOCs, bp. 50 - 100 to 240 - 260 °C) for *Group 2*, according to
205 the WHO, 1989 [27]. (Note: this definition has overlapping ranges [28]). An additional
206 *Group 3* comprised the chlorinated VOCs due to their already found lower sensitivity
207 in both sorbent materials [25] and compounds with high boiling points (SVOCs, bp.
208 240 - 260 to 380 - 400 °C).

209 | Boiling points were retrieved in February 2018 from the public database SciFinder -
210 CAS [29].

211 | **2.3 Fast sampling by two experimental regimes**

212 | In a previous work comparing Tenax TA and XAD-2 [25], the signal response of
213 volatiles varied depending on the collection time and sorbent material, indicating an
214 impact on sampling efficiency at standard flow rate. Therefore, a new experimental
215 set up was created to evaluate fast sampling at two regimes: low sample volume at
216 regular flow rate (first approach, *ISV*) and constant sample volume at uncommonly
217 higher flow rate (second approach, *hFR*). For evaluation, a two-variable matrix with
218 regular and fast sampling flow rates (100 and 500 mL/min) and different sample gas
219 volumes (300, 500, 800, 1,000, 1,300, 1,500 and 1,800 mL) resulting in the
220 corresponding collection times (3, 5, 8, 10, 13, 15, 18 min for *ISV* and 0.6, 1.0, 1.4,
221 2.0, 2.6, 3.0, 3.6 min for *hFR*) was used. In addition, we considered three levels of
222 concentrations for each analyte between 0.004 and 3.13 mM as described above.
223 Triplicate or quadruplicate ($n = 3 - 4$) tubes were loaded per collection time, flow rate,
224 sorbent material and concentration level.

225 | An orthogonal experimental design was used to assess all parameters using
226 | ~~equimolar-similar~~ as well as ~~near-to~~-response-adjusted concentrations (see 2.2) of
227 | standard solutions. Table 2 summarizes the different sampling conditions applied to
228 | the mixture of volatiles with Tenax TA and XAD-2.

229 | The orthogonal experimental design enabled a systematic comparison of the two
230 | approaches for fast sampling.

231 | **2.4 Instrumental parameters of thermal desorption GC-MS**

232 | Samples were analyzed as described earlier [25] on a thermal desorption system *TD-20*
233 | *20* coupled to a *GC-2010 Plus* and a *TQ-8040* triple quadrupole mass spectrometer
234 | (Shimadzu, Kyoto, Japan). The desorption unit *TD-20* was set to 60 mL/min purge
235 | flow rate and the following temperatures: valve 250 °C, trap cool -19 °C, trap heat
236 | 250 °C, interface 260 °C, transfer line 260 °C, and block 190 and 250 °C for XAD-2
237 | and Tenax TA, respectively.

238 | Compounds were separated on two GC columns connected with each other: Rxi-
239 | 1 ms, 30 m x 0.25 mm ID, 0.25 µm df, and SGE Analytical Science BPX50,
240 | 2 m x 0.15 mm ID, 0.15 µm df (Restek GmbH, Bad Homburg vor der Höhe,
241 | Germany) were used for chromatographic separation. Helium 5.0 (Alphagaz Air
242 | Liquide, Düsseldorf, Germany) was used as carrier gas with a flow of 1.55 mL/min
243 | (linear velocity of 35 cm/s) and a split ratio of 10. The GC oven was set to the
244 | following program: initial temperature 50 °C for 0.5 min, an increment of 10 °C/min
245 | until 250 °C during 19.5 min, and finally, the maximum temperature 250 °C for 5 min;
246 | the interface was set to 250 °C. In the MS, the ion source operated at 200 °C and
247 | 70 eV. The acquisition mode was Q3 scan in an *m/z* range between 30 and 300 and
248 | at a scan speed of 1428 amu/s.

249 | **2.5 Data evaluation**

250 | GCMS solution software version 4.20 (Shimadzu, Kyoto, Japan) was used for peak
251 | identification and integration of the compounds based on three selective mass traces,
252 | i.e. one ion used for quantitation (denoted as “quan ion”) and two confirming selective
253 | ions as described in [25]. For clarity, all quan ions are listed in Table A.1
254 | (supplementary material). For most calculations including normalization of data and
255 | Student’s t-test, Microsoft Excel (Microsoft Office 365, Redmont, USA) was used.

256 | **Normalization of data:** Earlier experiments [25] showed that the signal intensity from
257 | our standard mixture sampled at standard conditions in general compares very well
258 | between XAD-2 and Tenax TA. Even so, two normalization strategies were used to
259 | eliminate the effect of the different relative intensity of the compounds' quan ions and
260 | emphasize the effect of sampling conditions enabling a comparison of the latter and
261 | bringing the data to one scale for illustration in bar diagrams. First, for a **signal**
262 | **comparison among different sample gas volumes** per sorbent, the areas of each
263 | compound under different sampling conditions were normalized to the mean area of
264 | this particular compound within the sample batch of that specific sorbent (labelled as

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265 “normalized response 1”). (Note: batch is defined as all samples in an experiment
266 from the same sorbent material, Tenax TA, XAD-2.) Second, for **signal comparison**
267 **between different flow rates** per sorbent, the areas were normalized to the mean
268 area of each particular compound across the data sets of sample batches for *both*
269 sampling flow rates (labelled as “normalized response 2”). Depending on the flow
270 rate and/or sorbent, compounds with a very different behavior compared to the others
271 were not included in the mean values to clearly illustrate general tendencies (stated
272 when applied).

273 | Our normalization strategy facilitated a quick, general overview of the behavior of a
274 volatile multicomponent mixture at different sampling conditions for both sorbent
275 materials to identify the most appropriate parameter set. For clarity, an example for
276 normalization of data is available in the supplementary section (Supp. A.3).

277 | **Student’s t-test:** *p-values* (paired, two-tailed distribution) were calculated between
278 the corresponding mean of the “normalized response 1” per compound at each
279 applied sample gas volume and the mean of the same analyte at the maximal tested
280 volume.

281 | **Linear mixed model:** A multi-dependent variable model was used to search for
282 possible **interactions of the investigated experimental factors**. The linear mixed
283 model was performed in R version 3.4.3 [30] using the package lme4 version 1.1-15
284 [31]. It was built with *normalized response 1* as the Gaussian response variable. As
285 fixed effects test predictors, we fitted sorbent, collection time, flow and retention time
286 (as a proxy for volatility, see A.4, supplementary material) and all their interactions as
287 well as concentration and its interaction with sorbent. The type of response (**adjusted**
288 **similar response** or **equimolar similar concentration**) was fitted as fixed effects control
289 predictor. The sample batch, sample and analyte were fitted as random effects
290 control predictors with full random slopes structure [32]. Significance of the full model
291 including all terms compared to a null model excluding the test predictors, as well as
292 significance of interactions and main terms, was assessed using Likelihood Ratio
293 tests (LRT, R functions *anova* and *drop1*). Non-significant interactions were removed
294 for easier interpretation of lower-level interactions and terms; the final model included
295 all main predictors and significant interactions. We detected no deviations from model
296 assumptions (see A.4, supplementary material for model details).

297 | **3. Results and discussion**

298 | **3.1 First regime of fast sampling: low sample volume at standard flow rate**

299 | **3.1.1 Signal response at different collection times**

300 | Considering that the recovery-critical breakthrough values depend on compound
301 concentration and sampling flow rate [12], we first investigated sampling of a volatile
302 mixture (14 analytes) at the standard flow rate (100 mL/min) for sampled volumes
303 between 300 - 1,800 mL for Tenax TA and XAD-2, respectively. The results are
304 illustrated in Fig. 1.

305 | As shown previously, using XAD-2 the signal response of volatiles was improved
306 | increasing the collection time (and, hence, the sampled gas volume) at low
307 | concentration, while for Tenax TA the signal response was not affected by longer
308 | interaction times (Fig. 1 A.0 and B.0 reprinted with permission of J. Chromatogr. A)
309 | [25]. This tendency reversed with increasing concentration: for Tenax TA at
310 | intermediate (adjusted response, Fig. 1 A.1) and high concentration range
311 | (~~equimolar~~ similar concentration, Fig. 1 A.2), the recovery of volatiles was significantly
312 | impaired with sampled gas volumes below 800 mL; p -values < 0.05 (paired t-test,
313 | two-tailed distribution) were obtained for the relative response at 300 and 500 mL
314 | compared to the maximum tested volume (Table 3). At very high concentrations in
315 | Tenax TA (adjusted response, Fig. 1 A.3), the maximal signal response was
316 | achieved already with 500 mL, but smaller volumes seem to be insufficient to carry
317 | the analytes through the entire sorbent bed length. The p -values for the comparison
318 | of response from Tenax TA (Table 3) showed that a significantly lower signal
319 | response occurred with low sample gas volumes in all tested concentrations except
320 | the lowest level and, therefore, recovery loss may be mostly related to the insufficient
321 | interaction between the analyte and the surface. It seems that starting from ~700 -
322 | 800 mL sampled gas, the maximum recovery can be achieved. Indeed, the
323 | application of higher sample volumes did not improve the relative response of
324 | volatiles in the adsorption process (Fig. 1 A). This finding corresponds very well with
325 | the recommendation of the EPA TO-17 method [18], where optimal sample volumes
326 | starting from 1 L are recommended.

327 | In contrast to Tenax TA, the signal intensity with XAD-2 seemed to increase with
328 | larger sample gas volumes, particularly at low concentrations (Fig. 1 B.0). Here, a
329 | better adsorption of several analytes due to longer interaction may be expected and
330 | less breakthrough might occur compared to Tenax TA where an inverse behavior
331 | was observed at short interaction times. However, already from the intermediate level
332 | (Figs. 1 B.1 and 2), the maximum recovery can be achieved even with gas volumes
333 | below 500 mL. XAD-2 seemed less affected by breakthrough (stronger interaction
334 | with the surface) when larger sample gas volumes were applied. Consequently, the
335 | material seems to be the preferable material for fast adsorption when low sample gas
336 | volumes at nominal flow rate (first regime) are considered.

337 | **3.1.2 Signal response in dependence on compound volatility**

338 | The impact of volatility on breakthrough and recovery was assessed after grouping
339 | the evaluated analytes in three categories labelled as *Group 1*, *Group 2* and *Group 3*
340 | (refer to section 2.2 for further explanation). In Fig. 2, each colored block (black, gray
341 | or white) represents the mean over all compounds featuring a corresponding boiling
342 | point range as described in the methods section and Table 1, for each sampled gas
343 | volume (five to seven values of increasing sample gas volumes correspond to the
344 | bars per block, respectively).

345 | For most situations, the very volatile compounds (bp. < 0 to 50 - 100 °C) labelled
346 | here as *Group 1* (black bars) seemed to be progressively lost as the sampled gas

347 volume increased, suggesting that the adsorbent is not strong enough to keep the
348 analyte adsorbed to the surface, independent of the concentration level.
349 Breakthrough for two of the evaluated very volatile compounds (diethyl ether and
350 pentafluoropyridine) in Tenax TA at low concentration considerably increased with
351 larger sample gas volumes (see Supp. A.5) indicating the limitations of this material
352 for *Group 1* volatiles even at nominal flow rate. Indeed, other studies also reported on
353 important losses of very volatile compounds such as acrolein due to breakthrough
354 with large sample volumes in Tenax TA (5 L, 100 mL/min air flow rate after liquid
355 spiking) while good recoveries were obtained for VOCs [33]. Similarly, using active
356 sampling with Tenax TA for monitoring VVOCs such as trichloroethene (TCE) and
357 1,1-dichloroethene (1,1-DCE) in soil vapor during controlled field experiments,
358 resulted in a bias in long duration samples. This effect was mostly related to the
359 combination of poor retention of these compounds by the sorbent material (low safe
360 sampling volumes) and long sampling periods [34].

361 In contrast to the relative recovery illustrated in Fig. 2, breakthrough of diethyl ether in
362 XAD-2 appeared less affected by increasing sample gas volumes (for
363 pentafluoropyridine and pentafluorobenzene though, recovery was barely affected,
364 and breakthrough did even not exceed 5%, see Supp. A.5 and A.6). Eventually, the
365 sorbent-analyte interaction in the second tube (used for assessment of breakthrough)
366 was already in its equilibrium state and the amount of compound further released
367 from the first tube with larger sample volumes, was not retained. Still, for low
368 concentrations XAD-2 seemed to better retain the *Group 1* volatiles with larger
369 sampled volumes (Fig. 2 B.0). In conjunction with the higher total recovery of XAD-2
370 vs. Tenax TA (Supp. A.6), this suggests two potential advantages of XAD-2: a
371 stronger adsorption particularly of the very volatile compounds, which is less affected
372 by increasing sample gas volumes but by increasing the concentration of the analyte.
373 The stronger binding of low concentrated analytes indicates that the XAD-2 isotherm
374 is not linear over the investigated range of concentrations.

375 Volatile compounds (bp. 50 - 100 to 240 - 260 °C) labelled here as *Group 2* (gray
376 bars) behaved only slightly different depending on the adsorbent. For Tenax TA,
377 recovery of volatile compounds improved with increasing sample gas volume while,
378 for XAD-2, these compounds were hardly affected with the exception of the very low
379 concentration range exhibiting the same pattern. Indeed, these differences dominate
380 the appearance of the *mean-normalized response 1* for the whole mixture in
381 Tenax TA as illustrated in Figs. 1 A.1, A.2 and A.3 at low sample gas volumes
382 compared to XAD-2 (Figs. 1 B.1 and B.2). In contrast, for *chlorinated VOCs and*
383 *SVOCs* (bp. 240 - 260 to 380 - 400 °C, white bars), the signal response was highly
384 reproducible (low %RSD values) and similar for both sorbents, i.e. not affected by the
385 sampled gas volume. However, total recoveries for *Group 3* in Tenax TA at low and
386 intermediate concentration range (Supp. A.6 and A.7) were considerably lower than
387 in XAD-2. Therefore, XAD-2 is the favorable material for fast adsorption favoring
388 volatile and semi volatile compounds (*Groups 2 and 3*) at regular flow rate and low
389 sample gas volumes.

390 Curiously, in the low concentration range of XAD-2 (Fig. 2 B.0), all compounds
391 behaved similar with increasing recovery at increasing sample gas volumes and
392 irrespective of their boiling point range. As suggested before, this appearance might
393 be related with the stronger analyte-surface interaction at low analyte concentration
394 (non-linear relationship between analyte concentration and adsorption forces) and
395 the consecutive arrival of analyte molecules to less occupied surface areas of the
396 sorption material in the rear of the tube when increasing sample gas volumes are
397 applied [25]. In any case, this exhibits a remarkable advantage for volatile profiling
398 aiming on a compromise for different kinds of compounds; they are all equally
399 favored by increasing sample gas volume not changing the compound pattern itself.
400 Unfortunately, at higher concentrations, volatility again interacts with the sampled
401 volume: in competition for an equally occupied surface area, very volatile compounds
402 will be more easily displaced than volatile and semi volatile compounds.

403 **3.2 Second regime of fast sampling: *sampling with a higher flow rate***

404 **3.2.1 Signal response at different collection times and in dependence on** 405 **compound volatility at high flow rate**

406 In the first regime, according to the US EPA Method TO-17, the recommended flow
407 of 100 mL/min [18] was used as a control, but very low sample gas volumes were
408 evaluated for fast sampling. For an orthogonal comparison with the second regime,
409 the recovery of volatiles was evaluated applying similar sample gas volumes
410 (between 300 - 1,800 mL), but this time using an uncommonly high flow rate to
411 reduce the collection time (between 0.3 - 3.6 min). Considering the well-known
412 influence of the sampling flow rate on breakthrough volumes and the recommended
413 range between 5 and 600 mL/min for Tenax GC (breakthrough volumes not
414 exceeding half the retention volumes) [12], a flow rate of 500 mL/min was selected
415 for this work. Indeed, this flow rate was the maximal applicable value before loss of
416 sorbent material driven by convection was experienced. Fig 3 A shows the mean-
417 *normalized response 1* of the standard mixture over 6 - 7 different sample gas
418 volumes at 500 mL/min using XAD-2 and Tenax TA. Signal response was evaluated
419 at two concentration ranges: A.0 and A.1 ~~equimolar~~ similar concentration at
420 intermediate level for both sorbents, and A.2 adjusted high level for Tenax TA only.

421 At higher flow rate, recovery had a different behavior compared to the nominal flow
422 rate (refer to Fig. 1). In XAD-2 (Fig. 3 A.0), a significantly higher signal response was
423 found at 300 mL (p -value < 0.05 of a paired t-test, two-tailed distribution, refer to
424 Table 4). However, above that value, higher sample gas volumes barely affected the
425 recovery any further. Though for Tenax TA (Fig. 3 A.1), signal responses were also
426 significantly lower above 700 mL (p -values < 0.05 of a paired t-test, two-tailed
427 distribution), the mean value was not at all substantially different and smaller sample
428 gas volumes seemed still insufficient for achieving considerably higher recoveries at
429 intermediate as well as high concentration range (Fig. 3 A.2). Therefore, if very low
430 sampling volumes should be applied for adsorption of volatile compounds, XAD-2

431 again might be a better option in terms of higher recovery and lower variability
432 compared to Tenax TA.

433 | In addition, the signal response was also evaluated in dependence on compound
434 volatility at high flow rate. Fig. 3 B represents the mean response over all compounds
435 within the corresponding boiling point range at each applied gas volume (six to seven
436 values corresponding to the bars per block, respectively) during the second regime
437 using XAD-2 (Fig. 3 B.0) in comparison to Tenax TA (Figs. 3 B.1 and B.2).

438 | Interestingly, for XAD-2 (Fig. 3 B.0) and Tenax TA (Fig. 3 B.1 and 2) the pattern of
439 recoveries seemed to be very similar to the ones obtained at low flow rates (for
440 similar compound concentration, refer to Fig. 2) for the three boiling point ranges. For
441 very volatile compounds (*Group 1*, black bars), the signal response was
442 progressively reduced for increasing sample gas volumes while, for volatile
443 compounds (*Group 2*, gray bars) and chlorinated volatile and semi-volatile
444 compounds (*Group 3*, white bars), the signal response seemed to be slightly
445 enhanced for volumes above 300 mL, but only scarcely further affected by the gas
446 volume sampled. Consequently, the higher mean recoveries observed at low sample
447 gas volumes (below ~ 500 mL) in XAD-2 (Fig. 3 B.0) seemed mostly related to the
448 already presented more efficient performance of this adsorbent for the group of very
449 volatile compounds.

450 | **3.2.2 Signal response at high flow rate versus low flow rate**

451 | In previous sections, the volatile profiles were evaluated per flow rate, concentration
452 and sorbent for intra-batch variability of the signal response. In contrast, in this
453 section, an *inter-batch* comparison of the signal response at low and high flow rate is
454 presented. Fig. 4 compares the differences between the two sampling flow rates at
455 | different gas volumes sampled. ~~Similar, $\frac{1}{2}$ intermediate-equimolar~~ concentration for
456 XAD-2 and Tenax TA (Figs. 4 A.0 and B.0, respectively) and high concentration level
457 (0.31 - 3.13 mM) of adjusted signal response for Tenax TA (Fig. 4 B.1) was used for
458 evaluation. (Note that this was avoided with XAD-2 due to saturation in GC-MS).

459 | At all concentrations, the recovery of volatiles was severely reduced by the higher
460 flow rate, irrespective of the kind of sorbent material (Tenax TA or XAD-2) and gas
461 volumes sampled. The estimation of total recoveries (using breakthrough values at
462 low concentration and the comparison between both adsorbents at nominal flow rate)
463 showed that neither Tenax TA (extensively used for volatile analysis) nor XAD-2
464 provided a 100% recovery for all evaluated compounds. For example, the overall
465 recoveries at intermediate concentration sampled at 100 mL/min regular flow rate,
466 were $87 \pm 10\%$, $n=70$ and $86 \pm 14\%$, $n=70$ for XAD-2 and Tenax TA, respectively.
467 The overall recovery at intermediate concentration in the first tube at 500 mL/min
468 compared to the first tube at 100 mL/min regular flow rate was reduced to
469 approximately $73 \pm 23\%$, $n=56$ for Tenax TA and $72 \pm 17\%$, $n=56$ for XAD-2 in
470 average for all detected analytes. At high concentration, Tenax TA also exhibited an
471 approximate $79 \pm 11\%$, $n=84$ at 500 mL/min compared to nominal flow rate (Fig.

472 4 B.1). (Note that the value corresponds to the mean recovery over all compounds in
473 the standard mixture; therefore, the standard deviation illustrates the extent of
474 different recovery among the target compounds.)

475 | We consider the recovery loss at higher flow rate to be a consequence of the
476 insufficient interaction time between the analytes and the sorbent at higher flow rates.
477 Indeed, previous studies in field sampling also reported significant differences in
478 breakthrough of volatile compounds (bp. >100 °C, vapor pressure < 2 - 3 kPa at
479 20 °C) at different flow rates and identical sampled volumes using Tenax TA [38].
480 Consequently, higher flow rates should only be considered if a considerable loss in
481 recovery can be accepted for the anticipated experiment.

482 | **3.4. Multivariate statistical analysis of fast sampling under both regimes**

483 | In previous sections, the signal response for a mixture of volatile compounds
484 dissolved in an aerosol sampled from a moving gas stream was used to describe the
485 performance of two sorbents under variation of selected and well-known factors, such
486 as sample flow rate, sampled gas volume and analyte concentration. These variables
487 were evaluated separately per sorbent material, and specific findings were already
488 described, e.g. based on the compounds' volatility. However, these factors might not
489 be independent of each other [9] and their evaluation in isolation might have left
490 uncovered other features and possible patterns of interaction [32]. Therefore, a
491 multivariate statistical analysis was applied to identify the influence of the predictors
492 and their interactions on the signal response, as well as to confirm the already
493 described patterns.

494 | A comparison of the full model containing all predictors with a model lacking the test
495 predictors confirmed that collection time and flow (which together determine the
496 sampled gas volume) as well as sorbent and retention time (as a proxy for volatility)
497 affected the *normalized signal response 1* (LRT: $\chi^2 = 166.82$, $df = 19$, $p < 0.0001$).
498 Table 5 summarizes the results of the linear mixed model estimates. In particular, a
499 significant three-way interaction (LRT: $\chi^2 = 26.88$, $df = 1$, $p < 0.001$) was found
500 among retention time (as a proxy for volatility), collection time (for the sampled gas
501 volume) and flow rate.

502 | To facilitate the interpretation of the three-way interaction we conducted separate
503 models for low and high flow. The linear mixed-model estimates for the model on low
504 flow rate are listed in Table 6.

505 | At low flow rate (first regime), the signal response increased by increasing sample
506 gas volumes (as collection time in the model) for *Group 1* (VVOCs) while it
507 marginally decreased for *Group 2* (VOCs) and *Group 3* (chlorinated VOCs and
508 SVOCs) (LRT: $\chi^2 = 4.98$, $df = 1$, $p = 0.026$). This pattern agreed with the mean-
509 *normalized response 1* of the complete set of volatiles (Fig. 1), on which the signal
510 response increased by increasing sample gas volumes, but it disagreed with the
511 already shown dependence on compound volatility in the first regime (Fig. 2). This
512 last may be related to a stronger contribution to the model of a higher number of

513 analytes from the *Group 2* (VOCs) and *Group 3* (chlorinated VOCs and SVOCs)
514 compared to the small *Group 1* (VOCs) as listed in Table 1.

515 | Nevertheless, at higher flow rate (second regime) and in agreement with the results
516 already shown in Fig. 3, boiling point and sample gas volume significantly interacted
517 in their effect on the signal response (LRT: $\chi^2 = 8.16$, $df = 1$, $p = 0.004$). Table 7
518 describes the linear mixed model estimates for the model on high flow.

519 | In contrast to the behavior at nominal flow rate and in agreement with the already
520 shown data, at high flow rate the signal response decreased with increasing sample
521 gas volume for *Group 1* (VOCs) while only slight increases were observed for
522 *Groups 2* and *3* (volatile and semi volatile compounds).

523 | As an additional model output, only slightly higher signal responses were found for
524 XAD-2 than for Tenax TA at low and high, but not at intermediate concentration
525 (LRT: $\chi^2 = 65.01$, $df = 1$, $p < 0.001$) from a two-way interaction between sorbent
526 and concentration. In agreement with results from a previous work [25] this suggests
527 a less favorable sensitivity and linear range of the latter material. Thus, the model
528 outputs confirm most of the patterns and effects of the GC-MS signal response
529 already described in previous sections. Moreover, they describe the occurrence of
530 two-way and three-way interactions, explaining not only the dependence of the signal
531 response on different variables, but also how the complex interplay of the
532 experimental factors affect the target variable, i.e. the signal response.

533 | Within this context, it is evident from the data (Figs. 2 and 3 and the outcome of the
534 linear mixed model) that the signal response pattern we obtained from the standard
535 mixture changes in dependence on all three factors: concentration, sample volume
536 and collection flow rate. A linear correlation of the total recovery values obtained with
537 different collection volumes and flow, suggested that in general the response
538 patterns on XAD-2 with collection volumes up to 1,300 mL were more similar to each
539 other than with Tenax TA. Therefore, this material provides a remarkable advantage
540 anticipating fast sampling by higher flow rates. Regarding compound concentration,
541 for the same collection volume the best correlation between differently concentrated
542 standard mixtures was obtained for intermediate to low concentration at large
543 collection volumes. Here, the patterns between the different collection volumes again
544 were more similar with XAD-2 than with Tenax, which confirms a higher robustness
545 of XAD-2 also against fast sampling with lower collection volumes.

546 | Finally, we investigated whether chromatographic displacement (competitive
547 adsorption) could be the reason for the observed changes in response patterns of
548 our standard mixture. Competitive adsorption is the preferential adsorption of a
549 compound disfavoring other adsorbing compounds. The appearance depends on the
550 relative affinity of the different compounds to the adsorbing surface and on their
551 relative concentrations. Since it relates with adsorption homeostasis, low
552 concentration of the analytes (less occupied binding sites), a high sample flow (less
553 time for equilibration) and large collection volumes (more efficient transport to free

554 binding sites in the rear tube but before elution of the compound from the tube) can
555 be expected to reduce chromatographic displacement. Earlier data [25] already
556 suggested that chromatographic displacement at nominal flow does not play an
557 obvious role in our standard mixture since we found strict linearity for all compounds.

558 | However, when analyzing the ratios of total recovery between the two flow rates, the
559 volatile compounds diethyl ether, pentafluoropyridine, pentafluorobenzene, pyridine
560 and 3-methyl-2-butenyl acetate showed a stronger loss at high flow rate with large
561 collection volumes compared to the chlorinated compounds and least volatile
562 compounds in both materials. For higher concentrations at nominal flow rate, it were
563 again the less volatile compounds that were favored against the very volatile
564 compounds in positive interaction with large collection volumes. Consequently,
565 competitive adsorption might be discussed as a reason for this observation. Since
566 orthogonal experiments on the single analytes are not available though, our
567 experimental setup does not allow to finally establishing the occurrence of
568 chromatographic displacement. Still, the specific interaction with the adsorption
569 material only, not disturbed by interaction among the compounds, could also be
570 responsible for the observed behavior. The latter is supported indeed by the notion
571 that low concentration, a higher flow and large collection volumes below elution of the
572 target compounds were actually expected to *reduce* the effects of competitive
573 adsorption, i.e. in general improving the recovery of *all* compounds.

574 | **4. Conclusions**

575 The investigation of fast active sampling using two sampling regimes with Tenax TA
576 or XAD-2 revealed a relevant impact on the recovery of volatile compounds, in
577 dependence on several experimental factors and their potential interactions.

578 For Tenax TA, a significantly lower signal response at low sample gas volumes
579 showed, first, the limitation of this material for faster sampling at nominal flow rate
580 and, second, the necessity of longer interaction between the analyte and the surface;
581 the highest recovery was only found above ~ 700 - 800 mL gas volume sampled. In
582 contrast, for XAD-2, a different behavior was found depending on the concentration
583 range; only at low concentrations, the signal intensity increased significantly with
584 larger sample gas volumes while, at intermediate levels, the maximum recovery was
585 achieved already with low sample gas volumes. Given the better detection limits
586 compensating for the loss in low concentrated samples, XAD-2 indeed seems the
587 *better choice for fast adsorption at regular flow rate with low sample volumes*.

588 On the other hand, faster sampling by increasing the flow rate to 500 mL/min
589 severely reduced the relative recovery from the first desorption tube to approximately
590 | $73 \pm 23 \%$, $n=56$ for Tenax TA and $72 \pm 17\%$, $n=56$ for XAD-2 at **equimolar-similar**,
591 intermediate concentration, and $79 \pm 11 \%$, $n=84$ for Tenax TA at adjusted high
592 concentration. Consequently, *fast sampling by higher flow rates* is only reasonable if
593 a *high recovery loss* can be accepted for the study.

594 Despite the marked differences in terms of relative and total recovery at both flow
595 rates, the normalized signal response for analytes with different boiling points
596 resulted in similar patterns of recovery, an important advantage when semi-
597 quantitative analysis is required. Nevertheless, advantages of XAD-2 at standard flow
598 rate are not only a higher recovery for VVOCs and lower losses of the adsorbed
599 analyte by increasing the gas volumes sampled, but also the efficient adsorption of
600 VOCs and, in a lower degree, chlorinated VOCs and SVOCs even with low sample
601 volumes.

602 However, as already suggested earlier [19,20], a combination of adsorbents (multi-
603 bed sorbent tubes) might alternatively be recommendable to alleviate the observed
604 drawbacks in fast sampling, particularly if the nature of the target analytes is
605 unknown. Selecting a proper combination though would require further, detailed
606 testing similar to our experiments of more sorbents to identify suitable materials for
607 fast sampling. Obviously, the very volatile compounds are critical above all during
608 fast sampling so that further research could focus on these compounds. However,
609 the use of thermally less stable materials for multi-bed sorbents still needs careful
610 consideration, since complete release of SVOCs and chlorinated compounds, which
611 might commonly be found when sampling in the field, would also be desired.

612 As a last comment, we would like to mention that although EPA method TO 17A
613 approved the loading of liquid mixtures of volatiles in a stream of carrier gas (e.g.
614 nitrogen) to be the optimal method to resemble the air sampling process, sampling
615 vapors instead of loading volatile mixtures and, probably more important, variation in
616 the environmental conditions (e.g., composition of the gaseous sample, humidity and
617 ambient temperature) might also impact the results and conclusions presented here
618 when it comes to real measurements in the field. Assessment of these parameters is
619 an ongoing project in our lab. Our results should provide a valid basis now for further
620 research on other influential factors with the final goal of establishing efficient, fast
621 sampling of volatiles under field conditions.

622

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635 **Appendix A. Supplementary data**

636 Supplementary data associated with this article can be found in the online version.

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740
741
742

743 **Figure Captions**

744

745 **Fig. 1.** Mean-normalized response 1 of the standard mixture over 5 - 7 different
746 sample gas volumes at 100 mL/min sampling flow rate using Tenax TA (A) and XAD-
747 2 (B). Different concentration ranges (Table 2) were used for the evaluation of signal
748 response variability: A.0 and B.0, adjusted-response low level concentration; A.1 and
749 B.1, adjusted-response intermediate level concentration; A.2 and B.2, equimolar-high
750 level concentration; and A.3, adjusted-response high level concentration, Tenax TA
751 only. Normalized response 1 refers to the areas of each compound under different
752 sampling conditions normalized to the mean area of this particular compound within
753 the sample batch of that specific sorbent. Consequently, the normalized response
754 values do not allow for quantitative comparison between the sorbents, i.e. between
755 the different experiments A.0 - B.2. Normalized response 1 was calculated as the
756 mean for all analytes (14 compounds) per sample volume illustrating the extent of
757 different (high deviation) or similar (low deviation) behavior of the analytes. Triplicate
758 or quadruplicate ($n = 3 - 4$) sample tubes were loaded per collection time, flow rate,
759 sorbent material and concentration level, respectively.

760 **Fig. 2.** Mean-normalized signal response 1 of 14 volatiles classified in three boiling
761 point ranges (three blocks: black for Group 1, gray for Group 2 or white for Group 3)
762 over five to seven levels of increasing sample gas volumes (corresponding to the
763 number of bars per block, respectively) at 100 mL/min sampling flow rate using
764 Tenax TA and XAD-2. Three concentration ranges were used for the evaluation of
765 signal response variability: A.0 and B.0, in the lower range of the calibration range;
766 A.1 and B.1, in the middle of the linear range (response-adjusted); A.2 and B.2,
767 equimolar-similar concentration, high level; and A.3, high level (response adjusted for
768 Tenax TA only). Normalized response 1 refers to the areas of each compound under
769 different sampling conditions normalized to the mean area of this particular
770 compound within the sample batch of that specific sorbent; therefore, it does not
771 compare between sorbents. Normalized response 1 was calculated here as the mean
772 for the analytes per group and sample volume. Triplicate or quadruplicate ($n = 3 - 4$)
773 sample tubes were loaded per collection time, flow rate, sorbent material and
774 concentration level, respectively.

775 **Fig. 3. (A)** Mean-normalized response 1 of the standard mixture over 6 - 7 different
776 sample gas volumes at 500 mL/min using XAD-2 and Tenax TA. Signal response
777 was evaluated at two concentration ranges: A.0 and A.1, equimolar-similar
778 concentration, intermediate level (0.32 - 0.35 mM) for both sorbents, respectively,
779 and A.2, adjusted high level (0.31 - 3.13 mM) only for Tenax TA. (B) Mean-
780 normalized signal response 1 of volatiles classified in three boiling point ranges
781 (three blocks: black for Group 1, gray for Group 2 and white for Group 3), at six to
782 seven different sample gas volumes (corresponding to the bars per block,
783 respectively) and 500 mL/min sampling flow rate. B.0 and B.1: equimolar-similar,
784 intermediate concentration range (0.32 - 0.35 mM) using XAD-2 and Tenax TA,

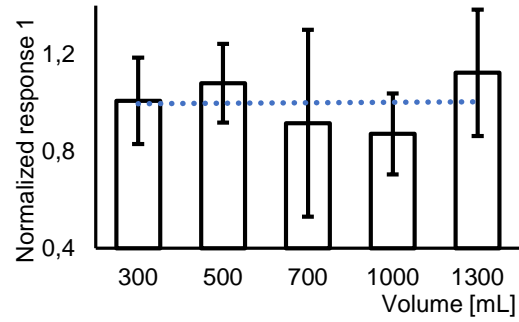
785 respectively, and **B.2**: adjusted response concentration range (0.31 - 3.13 mM) using
786 Tenax TA. *Normalized response 1* refers to the areas of each compound under
787 different sampling conditions normalized to the mean area of this particular
788 compound within the sample batch of that specific sorbent. Consequently, the values
789 do not compare between the sorbents. *Normalized response 1* was calculated as the
790 mean of all analytes (14 compounds) per sample volume (Figs. **3 A**) or as the mean
791 of the analytes per group and sample volume (Figs. **3 B**). Quadruplicate ($n = 4$) tubes
792 were loaded per collection time, flow rate, sorbent material and concentration level.

793 | **Fig. 4.** Mean-normalized signal response 2 for the two sampling flow rates, 100 and
794 500 mL/min, with 4 - 6 different sample gas volume values at two concentration
795 | levels. **A.0** and **B.0**: similar, intermediate ~~equimolar~~ concentration for XAD-2 and
796 Tenax TA, respectively; **B.1**: high concentration level for Tenax TA only. *Normalized*
797 *response 2* refers to the areas of each compound under different sampling conditions
798 and two flow rates, normalized to the mean area of each particular compound across
799 the data sets for both sampling flow rates. *Normalized response 2* was calculated as
800 the mean of all analytes (14 compounds) per sample volume. Triplicate or
801 quadruplicate ($n = 3 - 4$) sample tubes were loaded per collection time, flow rate,
802 sorbent material and concentration level, respectively.

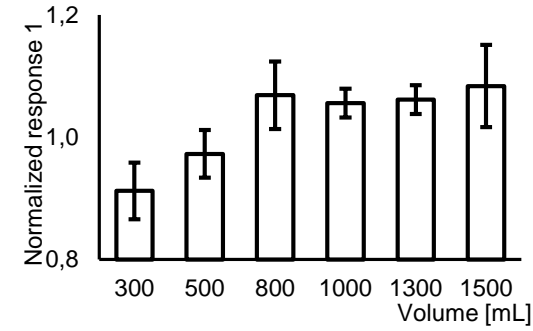
803

Figure

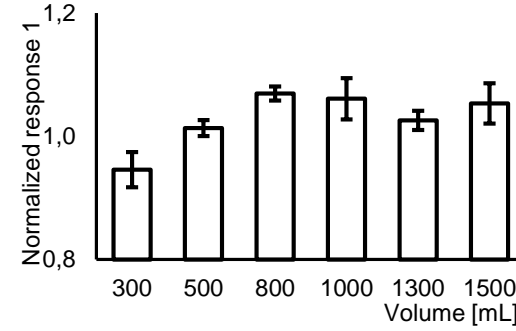
A.0 Tenax TA, 0.004-0.12 mM, $n=3$



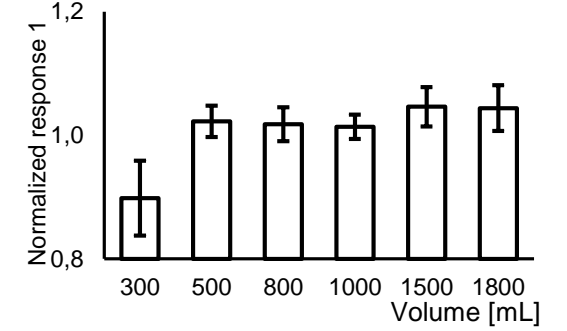
A.1 Tenax TA, 0.09-0.96 mM, $n=4$



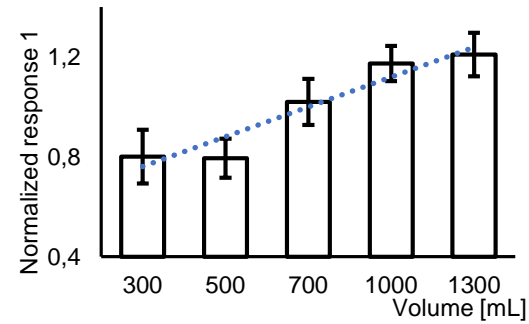
A.2 Tenax TA, 0.96-1.22 mM, $n=4$



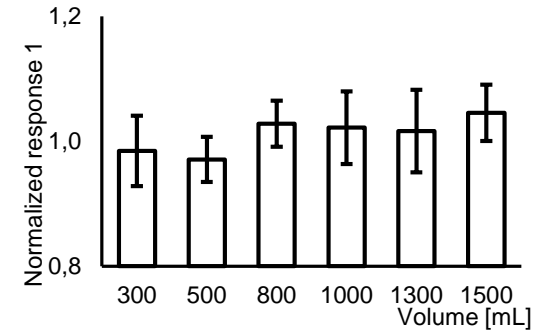
A.3 Tenax TA, 0.31-3.13 mM, $n=4$



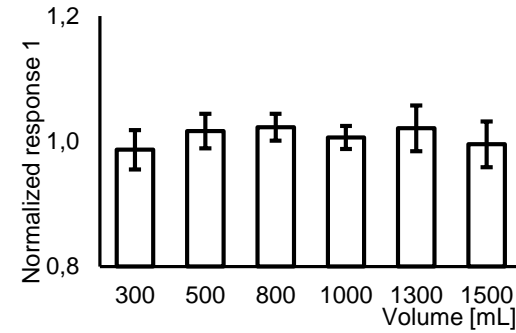
B.0 XAD-2, 0.004-0.12 mM, $n=3$

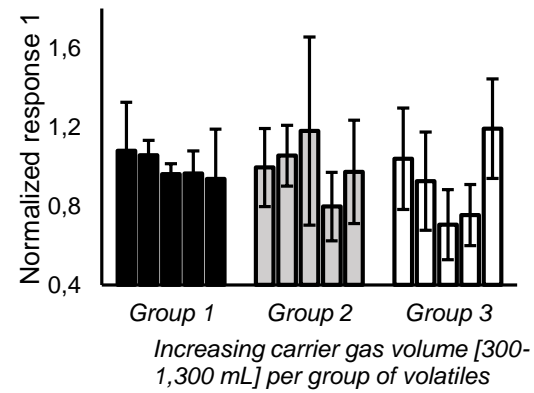
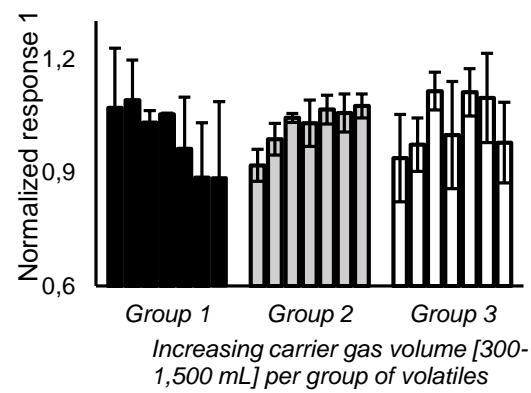
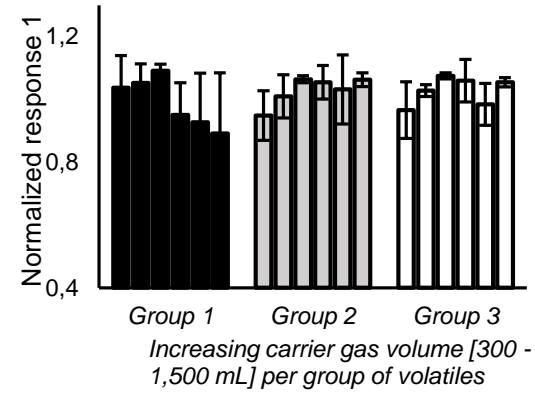
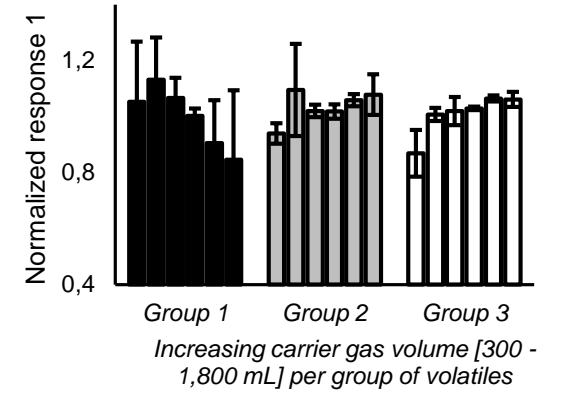
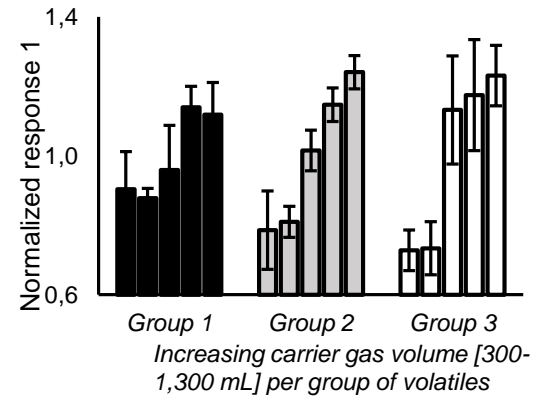
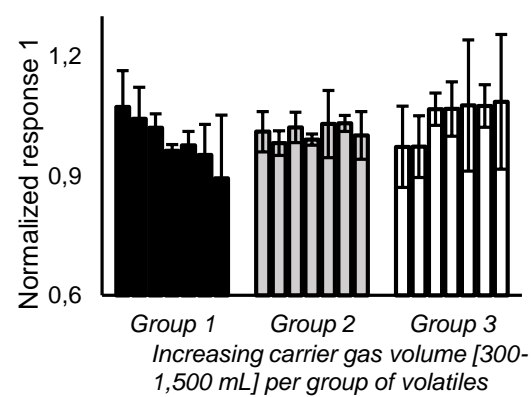
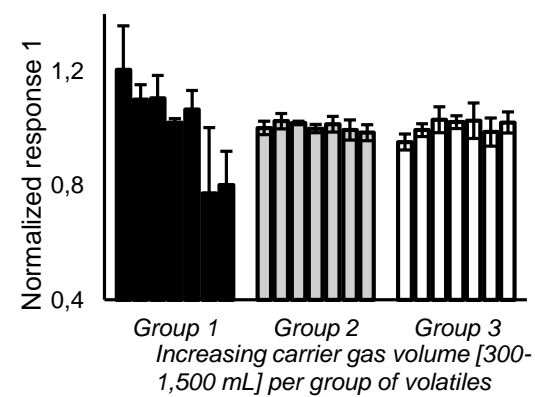


B.1 XAD-2, 0.09-0.96 mM, $n=4$

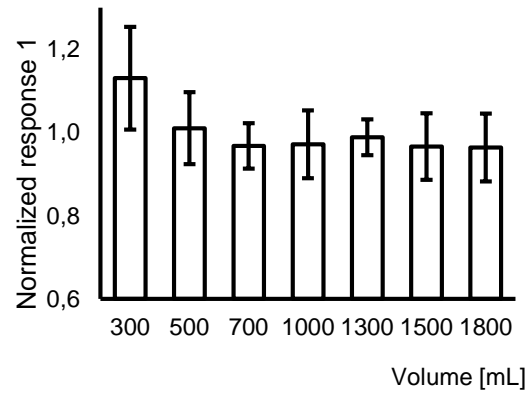


B.2 XAD-2, 0.96-1.22 mM, $n=4$

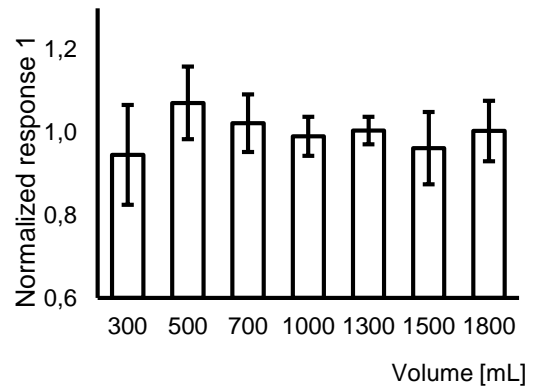


A.0 Tenax TA, 0.004-0.12 mM, $n=3$ **A.1** Tenax TA, 0.09-0.96 mM, $n=4$ **A.2** Tenax TA, 0.96-1.22 mM, $n=4$ **A.3** Tenax TA, 0.31-3.13 mM, $n=4$ **B.0** XAD-2, 0.004-0.12 mM, $n=3$ **B.1** XAD-2, 0.09-0.96 mM, $n=4$ **B.2** XAD-2, 0.96-1.22 mM, $n=4$ 

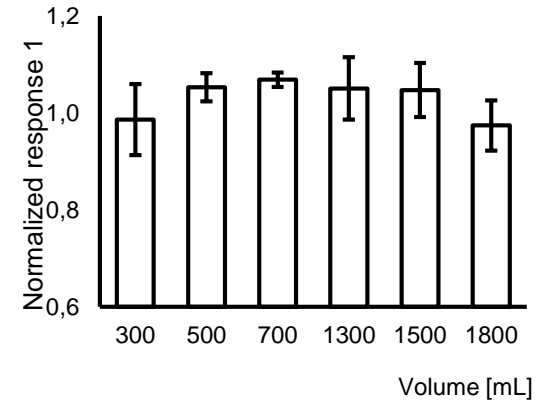
A.0 XAD-2, 0.32-0.35 mM, $n=4$,



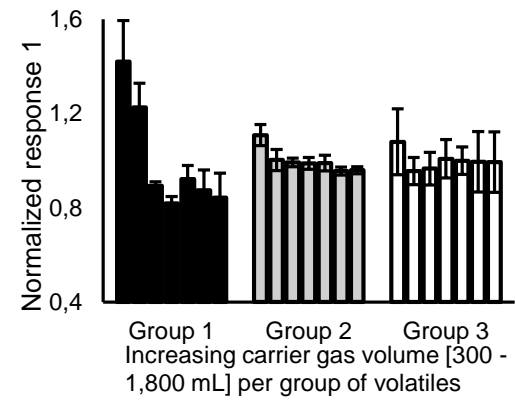
A.1 Tenax TA, 0.32-0.35 mM, $n=4$



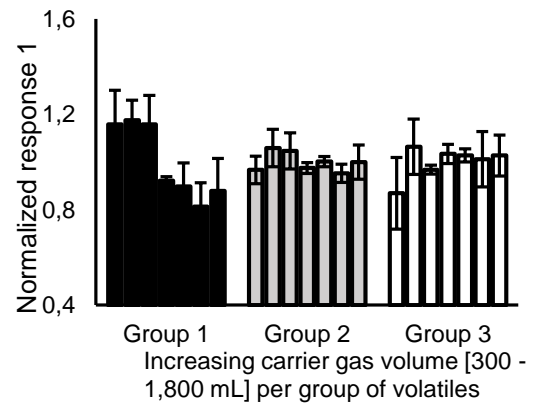
A.2 Tenax TA, 0.31-3.13 mM, $n=4$



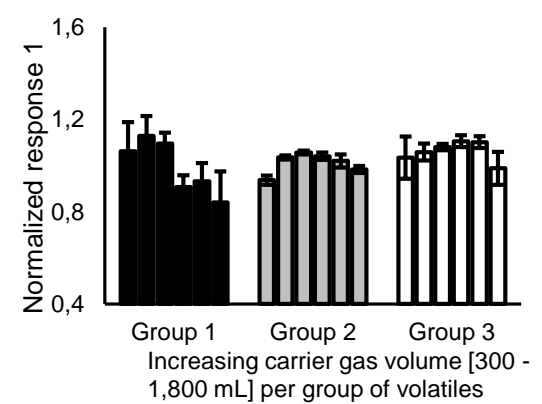
B.0 XAD-2, 0.32-0.35 mM, $n=4$

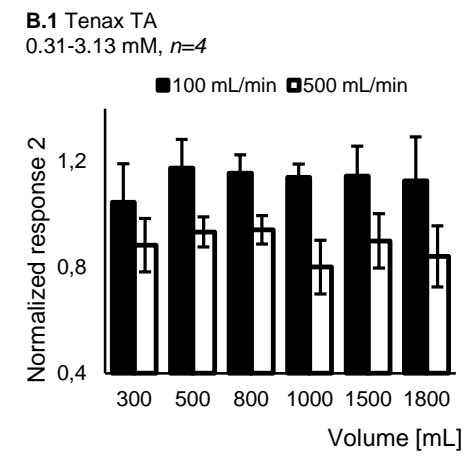
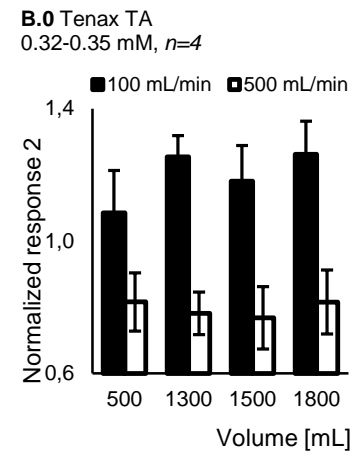
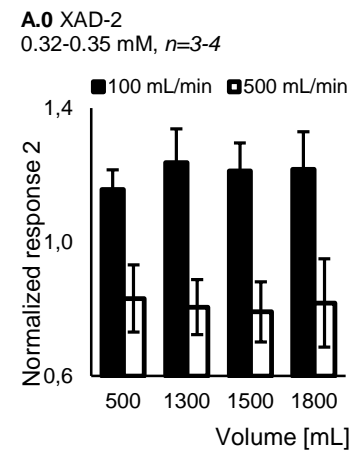


B.1 Tenax TA, 0.32-0.35 mM, $n=4$



B.2 Tenax TA, 0.31-3.13 mM, $n=4$





1 **Table 1.** Composition of the standard mixture (14 compounds) organized by
 2 ascending elution order at five concentration levels covering the linear range of
 3 Tenax TA.
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No.	Compound	Concentration range [mM]					Predicted b.p. (°C) ^c	Group (No.)
		low (0.004- 0.12)	Intermediate ^a (0.32-0.35)	intermediate (0.09-0.96)	high ^a (0.96- 1.22)	high (0.31- 3.13)		
1	Diethyl ether	0.12	0.34	0.96	1.07	8.78 ^b	33.2 ± 3.0	1
2	Pentafluoropyridine	0.01	0.32	0.18	0.96	0.91	100.1 ± 35.0	
3	Pentafluorobenzene	0.01	0.33	0.11	1.03	0.88	85.5 ± 35.0	
4	Pyridine	0.01	0.33	0.22	1.04	0.87	115.3 ± 0.0	2
5	3-Methyl-2-butenyl acetate	0.04	0.34	0.35	1.03	0.99	149.7 ± 9.0	
6	2-Fluoroaniline	0.01	0.35	0.18	1.06	1.03	182.5 ± 0.0	
7	Aniline	0.01	0.34	0.45 ^d	1.02 ^d	0.99 ^d	184.4 ± 0.0	
8	Cyclohexyl acetate	0.01	0.35	0.17	1.01	0.90	173.0 ± 0.0	
9	Ethyl pentafluorobenzoate	0.004	0.34	0.11	0.98 ^d	0.31	240.9 ± 40.0	3
10	2-Chlorobenzaldehyde	0.01	0.32	0.34	0.98	1.03	211.9 ± 0.0	
11	4-Chlorophenol	0.04	0.32	0.26	1.22	2.96	220.0 ± 0.0	
12	2,4,5-Trichlorophenol	0.04	0.32	0.17	1.03	3.01	254.8 ± 35.0	
13	4-Methoxybenzyl acetate	0.01	0.34	0.22	1.00	1.08	251.4 ± 15.0	
14	3,4-Dichlorophenol	0.04	0.33	0.27	1.00	3.13	247.1 ± 20.0	not included
n.a.	Isobutanal	0.01	0.35	0.09	1.05	0.95	67.1 ± 8.0	
n.a.	<i>trans</i> -2-Hexenal	0.01	0.32	0.11	1.05	1.01	146.5 ± 0.0	
n.a.	2-Hydroxy-butyric acid	0.04	0.33	0.11	1.01	1.02	238.3 ± 13.0	
	Minimal	0.004	0.32	0.09	0.96	0.31		
	Maximal	0.12	0.35	0.96	1.22	3.13		

"No." = designated ID number for each compound, "n.a." = not analyzed.

^a **Equimolar-Similar** concentration range for mixture of volatiles.

^b Diethyl ether only was used at a concentration of 8.8 mM.

^c Predicted boiling points at standard pressure (760 Torr) were retrieved from SciFinder - CAS.

^d Concentration in saturation (for aniline) or higher than the evaluated linear range (ethyl pentafluorobenzoate).

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15 | **Table 2.** Experimental set up for the evaluation of fast sampling under two regimes:
 16 | low sample volume at regular flow rate (first approach, *ISV*), and at high flow rate
 17 | (second approach, *hFR*).

Sampling regime	Sorbent (s)	Concentration range [mM]	Volume range [L]	Flow rate [mL/min]	Collection time range [min]
ISV: low sample volume at regular flow rate	Tenax TA, XAD-2	low (0.004-0.12)	0.3 - 1.3	100	3 - 13
	Tenax TA, XAD-2	intermediate (0.09-0.96)	0.3 - 1.5	100	3 - 15
	Tenax TA, XAD-2	high (0.96-1.22)	0.3 - 1.5	100	3 - 15
hFR: high flow¹ rate	Tenax TA, XAD-2	intermediate ² (0.32-0.35)	0.5 - 1.8	100 / 500	5 - 18 / 1.0 - 3.6
	Tenax TA	high ³ (0.31-3.13)	0.3 - 1.8	100 / 500	3 - 18 / 0.6 - 3.6

¹Low concentration range was not evaluated due to poor detection of the compounds.

²Equimolar-³Similar concentration range for mixture of volatiles.

³The high, adjusted concentration level was introduced to the experimental setup only for Tenax TA. In the high concentration range (0.31-3.13 mM), diethyl ether only was used at a concentration of 8.8 mM. Three to four tubes were loaded per collection time, flow rate, sorbent material and concentration level ($n = 3 - 4$).

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Table 3. *p*-Values of t-tests (paired, two-tailed distribution) between the mean-normalized signal response 1 (mean of 11 compounds, 3 - 4 replicates) for 5 - 7 different sampled gas volumes at 100 mL/min sampling flow rate compared to the maximum evaluated sampled gas volume (denoted as Ref. within each row) per concentration range in Tenax TA and XAD-2.

Material	Concentration range [mM]	Volume [mL]						
		300	500	700 - 800	1,000	1,300	1,500	1,800
Tenax TA	0.004-0.12	0.71	0.69	0.81	<0.05	Ref.		
	0.09-0.96	<0.05	<0.05	0.21	0.10	0.18	Ref.	
	0.96-1.22	<0.05	<0.05	0.20	0.48	<0.05	Ref.	
	0.31-3.13	<0.05	0.20	0.12	<0.05	<0.05*	0.57	Ref.
XAD-2	0.004-0.12	<0.05	<0.05	<0.05	0.24	Ref.		
	0.09-0.96	<0.05	<0.05	<0.05	<0.05	<0.05	Ref.	
	0.96-1.22	0.61	0.20	0.12	0.36	0.19	Ref.	

For both materials, the "very volatile compound" diethyl ether, showed a reversed behavior compared with all other substances, while aniline and 2-chlorobenzaldehyde showed a very low reproducibility. Therefore, these three were not included in the comparison.

*The measurements at 1.3 L were prepared in a different batch for analysis.

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29 **Table 4.** *p*-Values obtained from t-test comparisons (paired, two-tailed distribution) of
 30 mean-normalized signal response 1 of 11 detected volatiles (3 - 4 replicates) for 6 - 7
 31 different sampled gas volumes at 500 mL/min sampling flow rate compared to the
 32 **maximum evaluated sampled gas volume** (denoted as Ref. within each row) per
 33 concentration range in Tenax TA and XAD-2.

Material	Concentration range [mM]	Volume [mL]						
		300	500	700 - 800	1,000	1,300	1,500	1,800
XAD-2	0.32-0.35	<0.05	0.48	0.38	0.36	0.57	0.36	Ref.
Tenax TA	0.32-0.35	0.06	0.64	1.00	<0.05	<0.05	<0.05	Ref.
	0.31-3.13	1.00	<0.05	<0.05	0.14	<0.05	<0.05	Ref.

For both materials, a "very volatile compound", diethyl ether, showed a reversed behavior compared to all other substances. In addition, aniline and 2-chlorobenzaldehyde showed very low reproducibility. Therefore, all three were excluded from the comparison.

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36 **Table 5.** Linear mixed model estimates for the main model (full data set). Reference
 37 levels for factorial predictors were "high" (flow, concentration), "Tenax TA" (sorbent)
 38 and "adjusted" (response type). Estimates depict effects of levels in parentheses
 39 relative to these reference levels. Continuous predictors were z-transformed, non-
 40 significant interactions were removed from the model.

Predictor	Estimate	SE	t	<i>p</i> -value
Intercept	0.532	0.160	3.334	¹
Retention time (as a proxy for volatility)	0.275	0.045	6.123	¹
Collection time (for sampled gas volume)	-0.174	0.080	-2.183	¹
Flow (low)	0.673	0.109	6.189	¹
Sorbent (XAD-2)	-0.421	0.036	-11.580	¹
Concentration (low)	-0.256	0.262	-0.979	¹
Concentration (intermediate)	-0.140	0.180	-0.781	¹
Response type (<u>equimolar similar concentration</u>)	0.106	0.179	0.590	0.562
Retention time : collection time	0.239	0.046	5.219	¹
Retention time : flow (low)	-0.137	0.049	-2.808	¹
Collection time : flow (low)	0.208	0.079	2.654	¹
Sorbent : concentration				< 0.001
(XAD-2) : (low)	0.566	0.194	2.919	
(XAD-2) : (intermediate)	0.431	0.041	10.423	
Retention time : collection time : flow (low)	-0.232	0.044	-5.306	< 0.001

¹ *p*-value not shown because of a limited interpretation in terms comprised in higher-order interactions

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44 **Table 6.** Linear mixed model estimates for the model on low flow. Reference levels
 45 for factorial predictors: "Tenax TA" (sorbent), "high" (concentration) and "adjusted"
 46 (response type). Estimates depict effects of levels in parentheses relative to these
 47 reference levels. Continuous predictors were z-transformed.

Predictor	Estimate	SE	T	p-value
Intercept	0.999	0.131	7.653	¹
Retention time (as a proxy for volatility)	0.001	0.006	0.220	¹
Collection time (as sampled gas volume)	0.032	0.029	1.107	¹
Sorbent (XAD-2)	-0.419	0.037	-11.281	¹
Concentration (low)	-0.059	0.226	-0.261	¹
Concentration (intermediate)	-0.003	0.144	-0.023	¹
Response type (<u>equimolar similar concentration</u>)	0.240	0.144	1.672	0.129
Retention time : collection time	-0.052	0.017	-2.997	0.026
Sorbent : concentration				< 0.001
(XAD-2) : (low)	0.588	0.212	2.775	
(XAD-2) : (intermediate)	0.425	0.048	8.914	

¹ p-value not shown because of a limited interpretation in terms comprised in higher-order interactions

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50 **Table 7.** Linear mixed model estimates for the model on high flow. Reference levels
 51 for factorial predictors were "Tenax TA" (sorbent) and "high" (concentration).
 52 Estimates depict effects of levels in parentheses relative to these reference levels.
 53 Continuous predictors were z-transformed.

Predictor	Estimate	SE	T	p-value
Intercept	1.005	0.020	49.865	¹
Retention time (as a proxy for volatility)	0.002	0.007	0.303	¹
Collection time (as sampled gas volume)	-0.032	0.018	-1.770	¹
Sorbent (XAD-2)	0.020	0.029	0.678	0.498
Concentration (intermediate)	-0.058	0.029	-2.040	0.051
Retention time : collection time	0.049	0.015	3.205	0.004

¹ p-value not shown because of a limited interpretation in terms comprised in higher-order interactions

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Electronic Supplementary Material (online publication only)

[Click here to download Electronic Supplementary Material \(online publication only\): Supp_Marcillo_Rev_191216.docx](#)

CRediT statements

Conceptualization	AM and CB
Methodology	AM and CB
Software	na
Validation	AM
Formal analysis	AM and BS
Investigation	AM
Resources	AW and CB
Data Curation	AM and CB
Writing - Original Draft	AM
Writing - Review & Editing	BS, AW and CB
Visualization	AM, BS and CB
Supervision	AW and CB
Project administration	AM and CB
Funding acquisition	AW and CB

Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:



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