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Comparison of two common adsorption materials for thermal desorption gas chromatography – mass spectrometry of biogenic volatile organic compounds☆

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ABSTRACT

Volatile organic compounds (VOCs) are commonly collected from gaseous samples by adsorption to materials such as the porous polymer Tenax TA. Adsorbed compounds are subsequently released from these materials by thermal desorption (TD) and separated then by gas chromatography (GC) with flame ionization (FID) or mass spectrometry (MS) detection. Tenax TA is known to be particularly suitable for non-polar to semipolar volatiles, however, many volatiles from environmental and biological samples possess a rather polar character. Therefore, we tested if the polymer XAD-2, which so far is widely used to adsorb organic compounds from aqueous and organic solvents, could provide a broader coverage for (semi)polar VOCs during gas-phase sampling. Mixtures of volatile compounds covering a wide range of volatility (bp. 20–256 °C) and different chemical classes were introduced by liquid spiking into sorbent tubes with one of the two porous polymers, Tenax TA or XAD-2, and analyzed by TD/GC–MS. At first, an *internal standard mixture* composed of 17 authentic standards was used to optimize desorption temperature with respect to sorbent degradation and loading time for calibration. Secondly, we tested the detectability of a *complex standard mixture* composed of 57 volatiles, most of them common constituents of the body odor of mammals. Moreover, the performance of XAD-2 compared with Tenax TA was assessed as limit of quantitation and linearity for the *internal standard mixture* and 33 compounds from the *complex standard mixture*. Volatiles were analyzed in a range between 0.01–~250 ng/tube depending on the compound and material. Lower limits of quantitation were between 0.01 and 3 ng ± <25% RSD ($R^2 > 0.9$). Interestingly, we found different kinetics for compound adsorption with XAD-2, and a partially better sensitivity in comparison with Tenax TA. For these analytes, XAD-2 might be recommended as an alternative of Tenax TA for TD/GC–MS analysis.

1. Introduction

Solid sorbents commonly used for sampling of volatile organic compounds (VOCs) can be classified into inorganic sorbents (silica gels or molecular sieves), carbon-based porous materials (activated charcoals or carbon blacks), and porous organic polymers (styrene-divinylbenzene copolymers, ethylvinylbenzene-divinylbenzene copolymers, polyphenylene oxides, and others) [1]. Tenax TA is a macroporous organic polymer basically composed of 2,6-diphenyl-*p*-phenylene oxide [2], which, according to a review by Dettmer

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et al., 2002 [3], efficiently adsorbs many non-polar compounds, such as hydrocarbons down to carbon number C_5 [4], pesticides [5], or biogenic VOCs [6]. However, Tenax TA achieved merely unsatisfactory recoveries for very volatile and polar compounds, such as acetic acid, isopropanol, and 1,2-ethanediol [7]. In spite of the known limitations, Tenax TA is extensively used nowadays as a general adsorbent due to its affinity for compounds with a wide range of boiling points from 60 to 300 °C [8] and its several advantages that make it appropriate for air sampling such as high breakthrough volumes of C_7–C_{26} VOCs, a good thermal stability, and hydrophobicity [2].

However, several studies have reported artifact formation in Tenax when it is exposed to very oxidant gases like ozone, nitrogen dioxide, nitrogen oxide, sulfur dioxide, and others [9–11]. Mostly, phenyl-substituted carbonyl compounds such as benzaldehyde, acetophenone, benzophenone and benzene acetaldehyde are formed as artifacts from oxidation of Tenax with ozone [2]. In general, artifact formation is common in thermal desorption from solid adsorbents, but can be accepted if the contaminations do not interfere with analysis of the sample compounds [1]. In addition, another disadvantage is the comparably high price of Tenax as one of the most commonly used sorbents for thermal desorption [12], and many researchers are interested in efficient but cheaper alternatives of this material.

According to Lopez et al. [13], polymeric resins of the Amberlite XAD type and Carbotrap materials are increasingly suggested as efficient alternatives for collection and concentration of volatiles. The most popular of these macroreticular polymers (a variety of porous polymers with regular crosslinking, so-called *reticulation*, creating high internal surface pores for efficient diffusion of the solutes to the polymer surface) on the market, are based on styrene crosslinked by divinylbenzene, such as XAD-2 and XAD-4 [14]. Thus, XAD-2 was shown to have superior sorption characteristics unperturbed by high humidity of gaseous samples [15,16]. For thermal desorption, these styrene polymers were considered incompatible to be used in combination with other common sorbents due to a low maximum desorption temperature (<220 °C) [13,17,18]. However, a study performed by López et al., 2007 [13] demonstrated the feasibility of two other new polydivinylbenzene copolymer resins commercially found as Bond Elut (styrene-linked) and LiChrolut (ethylvinylbenzene-linked) for gas-solid trapping followed by thermal desorption of seven nonpolar, volatile organic compounds with acceptable desorption properties, cleanliness and stability at 220 °C. Similar results to Tenax TA were obtained in terms of distribution coefficients, breakthrough volumes, and chromatographic performance, demonstrating the usability of both resins for the adsorption and subsequent thermal desorption of selected VOCs at low concentrations.

However, Lopez et al. [13] tested only a very limited range of compounds for this type of materials, while adsorption is known to be material- and substance-specific [19,20]. Moreover, recovery of substances from complex mixtures such as biogenic and environmental samples is dependent on parameters affecting the efficiency of the method such as extraction conditions or other sample preparation steps [19,21,22]. Therefore, in this study, we investigated the feasibility of Amberlite XAD-2, commonly used as a wetted resin for adsorption from solvents, for thermal desorption of a very broad range of compounds as cheaper alternative for the sampling of VOCs in comparison to the performance of Tenax TA. To our knowledge, a direct comparison of these two materials beyond their degradation products after N-oxide exposure [23] is not available so far in the literature.

With water as the mobile phase, the selectivity of the polymeric resin for organic compounds is directly related to the hydrophobic polystyrene surface, being increased as the hydrophobicity of the target molecule increases [24]. In contrast, in an initial study using liquid elution of compounds adsorbed to XAD collected from the body odors of common marmosets we could also detect many (semi)polar compounds (data not shown). However, no sufficient data for the efficiency of analysis of biogenic VOCs after adsorption to XAD-2 from air as the mobile phase with subsequent thermal desorption is available so far.

Therefore, considering the expected compound selectivity and the high pricing of Tenax TA contrasted to the lack of information about suitability of XAD-2 for thermal desorption GC–MS, we conducted experiments comparing the performance of the two adsorbents. Relative recovery after spiking, stability during thermal desorption, analytical interferences due to formation of artifacts (oxidative degradation), breakthrough values and sensitivity were all evaluated to assess the applicability of XAD-2 as an alternative adsorbent to Tenax TA for multicomponent analysis in complex samples.

2. Experimental

2.1. Materials and chemicals

Thermal desorption tubes were assembled in-house using empty and pre-cleaned TD glass tubes (6.35 mm OD/4 mm ID × 89 mm length), ¼ swage locks, stainless steel tension springs, and glass wool (silanized), all purchased from Supelco (Sigma-Aldrich, Taufkirchen, Germany). Tubes were filled with 200 mg Tenax Porous Polymer (matrix Tenax TA, 60–80 mesh) and, alternatively, with 400 mg Amberlite XAD-2 (Supelco/Sigma-Aldrich, Taufkirchen, Germany) considering the apparent density ("packing" density) of Tenax TA ($0.28\ g/cm^3$) [25] and XAD-2 ($0.62\ g/cm^3$) [26] for the 6 cm long heated region of the standard glass tubes. The tubes were assembled adhering to the guideline and related procedures for packing sorbent tubes established by the U.S. Environmental Protection Agency (EPA) in the *Compendium Method TO-17 Determination of Volatile Organic Compounds in Ambient Air Using Active Sampling onto Sorbent Tubes* [27]. Shortly before GC–MS analysis, swage locks were replaced with tube caps for the thermal desorption system TD-20 (Shimadzu Kyoto, Japan). In addition, TD tubes Tenax (¼″ × 3.5″ TD glass tube, Tenax TA 60/80) were purchased from Camsco-Restek GmbH (Bad Homburg vor der Höhe, Germany).

All thermal desorption tubes were equilibrated using a TD *Clean Cube* unit (SIM Scientific Instruments Manufacturer GmbH, Oberhausen, Germany) with a constant flow of 50 mL/min of nitrogen (≥ 99.999%). The equilibration started at 40 °C until reaching 200 °C and 250 °C for XAD-2 and Tenax TA, respectively, during a period of 152 min.

If not stated elsewise, 100 mL/min nitrogen from a nitrogen generator Nitrox UHPLCMS 18 (Domnick Hunter, Gateshead, UK) adjusted by a *CFC-14PM* multi-channel gas flow regulator for *GC-14A GC–MS* (Shimadzu, Kyoto Japan) was used for calibration.

A *BiVOC* pump (Umweltanalytik GmbH, Holbach, Germany) was used to sample air through the tubes.

Two mixtures of volatile compounds were prepared to assess the applicability of XAD-2 for multicomponent analysis in complex samples. At first, an *internal standard mixture* composed of 17 standards was used to optimize desorption temperatures and loading times for calibration. These compounds were selected providing stability during short-term storage (less than 24 h), a wide range of volatility, appropriate chromatographic separation and absence from ambient air to ensure a contamination-free analysis. Relative recoveries were assessed in dependence on the temperature of desorption, as well as linear ranges and lower limits of quantitation (LLOQs) using XAD-2 compared with Tenax TA. Secondly, a *complex standard mixture* composed of 57 volatiles was used to extent the evaluation of XAD-2 and determination of breakthrough values. These compounds were selected to be common constituents of body odors of mammals as identified in the literature and a yet unpublished study with common marmosets (M. Kücklich et al., manuscript in revision), and other common organic compounds, e.g. organic solvents of low boiling points (high speed of evaporation). In addition, chemical diversity, a broad volatility range, and compound availability was considered to assess methods compound coverage and confirm the suitability of the optimized parameters. Ordering details on all substances are listed in the supplementary section Supp. A.1. Additional solvents used for preparation of solutions, such as methanol (Rotisolv, as solvent) and diethyl ether (DEE) p.a. ≥ 99.5% were purchased from Carl Roth GmbH & Co. KG (Karlsruhe, Germany).

The given boiling points were retrieved in August 2016 from the web page of Carl Roth GmbH & Co. KG [28].

2.2. Flow resistance of pre-packed and in-house-packed sorbent tubes

Each sorbent tube was tested by measuring the maximum achievable flow sampling rate [L/min] when a pressure corresponding to the adjustment of the pump at 6 L air/3 min was applied to the sorbent tube (relative flow resistance of the tube). The sampling flow rates were measured in 60 sorbent tubes over all, i.e. 30 replicates per adsorbent material (Tenax TA and XAD-2). Additionally, commercially available Tenax TA tubes were measured separately to evaluate the in-house packing procedure.

2.3. Solvent selection for mixtures of volatile compounds

Initial optimization of thermal desorption was carried out with a mixture of 17 authentic standards (*internal standard mixture*). For this, four GC–MS grade solvents suitable for Tenax TA [29] were considered: diethyl ether (boiling point, bp. 35 °C), methanol (bp. 65 °C), ethyl acetate (bp. 77–78 °C) and cyclohexane (bp. 82 °C). The solvents were tested to meet two requirements: first, a high dissolving capacity for all target analytes and, second, a poor retention of the solvent by the adsorbent to avoid any interference of solvent and target signal. Therefore, the relative molar response of the solvents for EI-MS was considered. Relative molar response was assessed subjecting 0.1 μL methanol and 0.2 μL diethyl ether, ethyl acetate and cyclohexane, respectively, corresponding to ~2–2.5 μmol to GC–MS analysis using a *Trace GC Ultra* coupled with a *Finnigan MAT 95 XP* double focusing sector field mass spectrometer (Thermo Fisher Scientific, Bremen, Germany) (n = 3) equipped with an s/sl (split/splitless) injector (see below). In contrast to TD injection where the sample is concentrated on the trap stage, in s/sl injection the whole predefined portion of a sample is injected. Since electron impact ionization at 70 eV is known to produce highly reproducible spectra and ionization efficiencies across instruments, similar relative molar responses of the solvents are obtained with both instrumental set ups. In comparison, 1 μL of each solvent was injected into a thermal desorption tube at sampling conditions (100 mL/min nitrogen passed through each sorbent bed, XAD-2 and Tenax TA, during 13 min, n = 3).

2.4. Preparation of mixtures of volatile compounds

Stock solutions of authentic standards were prepared by weighing the pure standard material (amount calculated by density) directly added into amber glass vials containing the required amount of methanol to obtain 100 mM stock standard solutions. Secondary standard dilutions were prepared by mixing together the required volumes of the corresponding stock solutions in the required volume of methanol. This protocol was adapted from the recommended procedure for stock standard solutions described in the U.S. Environmental Protection Agency (EPA) *Method 8260C Volatile Organic Compounds by Gas Chromatography/Mass Spectrometry* (GC/MS) [30]. Compound concentrations of the diluted standard mixture were adjusted with respect to their molar responses. To avoid any recovery loss, solutions and mixtures were quickly prepared and immediately stored under cooling conditions (<4 °C).

Two mixtures of volatile compounds were used for evaluation as described in the following.

2.4.1. Internal standard mixture

A mix composed of 17 compounds as described in the supplementary section Supp. A.1 Section (was used to optimize the conditions of thermal desorption and assess the expected dynamic behavior of the *complex standard mixture* (see below) including sample loading time. Isobutanal, *trans*-2-hexenal and 2-hydroxybutyric acid were not included for several reasons. Isobutanal showed critical coelution in the total ion current (TIC) causing the peak of the selective mass traces m/z 43, 72, 41 to split strongly or even separate as the concentration decreased in both materials. In the case of *trans*-2-hexenal, the molar response in the mixture was considerably lower than the rest of compounds, so that the evaluation of linear range would have required a very high concentration of the analyte in the mixture. Finally, 2-hydroxy-butyric acid showed a very long tailing in both materials severely affecting quantitation at lower concentrations.

2.4.2. Complex standard mixture

57 authentic solid and liquid standards were prepared by dissolving appropriate amounts in methanol to reach a final concentration of 0.3 mM each. One μL of the *complex standard mixture* was injected into the adsorption tubes at a constant nitrogen flow of 100 mL/min passing through the sorbent bed for 13 min and assessed for detectability and chromatographic separation. Nine compounds, m-cresol, ethanol, 2-propanol, acetaldehyde, propanal, 2-propenal, dichloromethane, diethylamine and ethyl methanoate were not detected. 33 compounds with appropriate chromatographic separation were used in the following for evaluation of LLOQs, dynamic behavior and breakthrough values (see Section 3.5).

2.5. Sample loading time

In the US EPA method TO-17, 5 min are recommended to sweep vapors onto the sampling surface of the sorbent bed assuring satisfactory removal of the sample solvent from the adsorbent while quantitatively retaining the analytes. However, it was noted that this approach might not work appropriately for groups of compounds with a wide range of boiling points [27]. Since in this project, XAD-2 should be tested for compounds featuring broad range of volatility (see below), we determined the required period of sampling time to obtain an optimal (highest) signal response for both, Tenax TA and XAD-2. The required loading time was determined after injecting 1 μL of the 0.3 mM *internal standard mixture* to a tube with 100 mL/min nitrogen passing through the sorbent bed during variable periods of time (between 3 and 13 min). Relative recovery was assessed based on normalization of the respective signal responses to the response obtained after 5 min sweeping.

2.6. LLOQ, relative recoveries and breakthrough of the compounds

Linearity and LLOQs were evaluated including at least five calibration levels. LLOQ was defined as the minimum compound amount producing a signal response with an RSD < 25% and a coefficient of determination $R^2 < 0.9$ according to the linear regression of the concentration series.

Breakthrough is an important property in the evaluation of sorbent materials [31]. Breakthrough was defined as the percentage of VOC (mass of analyte) that can be determined in the back tube of two sorbent tubes connected in series during sampling [32,33]. 33 substances from the *complex standard mixture* were used to evaluate compound breakthrough in both adsorbents, Tenax TA and XAD-2. Two desorption tubes were connected in series for each replicate analysis and 1 μL of standard mix each at three concentration levels covering the linear range was loaded onto the sorbent tubes (100 mL/min nitrogen, 13 min, n = 3). The breakthrough values were expressed as the mass fraction of the analyte in the back tube to the total mass of analyte found in both sample tubes (ng/tube).

Relative recoveries of the *internal standard mixture* were determined at three concentration levels: low (1–40 μM), medium (4–123 μM) and high (333 μM) depending on the compounds molar response, and three desorption temperatures (190, 220 and 250 °C, 3 replicates) to assess the effect of deviations from the maximum recommended desorption temperature of 200 °C for XAD-2 [17,34]. Response was normalized to the signal at 250 °C. (Note: Identification of artifact formation beyond naphthalene, ethylbenzene and benzoic acid [35] is not available in the literature and is presented therefore in the supplementary section (Supp. A.2). This information is useful considering that analysis of compounds also appearing as artifacts upon thermal degradation may be hampered when using XAD-2.)

2.7. TD-GC–MS instrumental parameters

A *GCMS-TQ8040* system composed of a gas chromatograph *GC-2010 Plus* coupled to a *TQ-8040* triple quadrupole mass spectrometer (Shimadzu, Kyoto, Japan) was used for analysis of all samples. The samples were introduced into the instrument by a thermal desorption system *TD-20* (Shimadzu, Kyoto, Japan) set to a purge flow rate of 60 mL/min and the following temperatures: valve 250 °C, trap cool −19 °C, trap heat 250 °C, interface 260 °C, block 190 °C for XAD-2 and 250 °C for Tenax TA (if not stated elsewise), and sample transfer line 260 °C.

For chromatographic separation, two GC columns were connected with each other: *Rxi-1* ms, 30 m × 0.25 mm ID, 0.25 μm df, and SGE Analytical Science *BPX50,* 2 m × 0.15 mm ID, 0.15 df (Restek GmbH, Bad Homburg vor der Höhe, Germany). In the GC, a split ratio of 10 was applied with helium 5.0 (alphagaz Air Liquide, Düsseldorf, Germany) as carrier gas at a column flow of 1.55 mL/min at a linear velocity of 35 cm/s. The initial GC oven temperature was 50 °C for 0.5 min, afterwards the temperature was increased by 10 °C/min to 250 °C for 19.5 min, and kept at a maximum of 250 °C for 5 min. The electron impact (EI) ionization source operated at 70 eV and 200 °C and the interface temperature was set to 250 °C. Q3 scan was used as acquisition mode at a speed of 1428 amu/s for *m*/*z* 30–300. A system check was performed on regular basis with at least two blanks of conditioned tubes in every batch to monitor the appearance and intensity of any artifacts.

The molar response of each tested solvent for calibration was analyzed using a *Trace GC Ultra* coupled with a *MAT 95 XP* double focusing sector field mass spectrometer (Thermo Electron, Bremen, Germany) with liquid injection mode. For chromatographic separation, a capillary column *SLB*®*-5 ms* of 30 m length, 0.25 mm ID, 0.25 μm df (Sigma-Aldrich, Taufkirchen, Germany) was used. Injection temperature was set to 230 °C, the split ratio to 300. The EI source operated at 70 eV and 230 °C with a scan range of *m*/*z* 30–150 at a scan rate of 0.4 s/d. The multiplier gain was set −0.1 relative to the tuning result.

2.8. Data evaluation

Three selective mass traces were considered for the assessment of peak areas (refer to Tables 3 and 4). One quantitation ion and two confirming selective ions were used for identification; presence and relative intensity of the *m*/*z* were considered for identification of the corresponding compound before integration. *GCMS solution* software version 4.20 was used as data evaluation program for peak picking and integration. Unpaired two-sample Student's *t*-tests and tests on normal distribution (Lilliefors test) were carried out applying the software R, version 3.1.1 [36]. For all other calculations, Microsoft Excel 2013 was used (Microsoft, Redmont, USA).

3. Results and discussion

3.1. The flow resistance of pre-packed and in-house packed sorbent tubes

According to the EPA Method TO-17 for the *Determination of Volatile Organic Compounds in Ambient Air Using Active Sampling Onto Sorbent Tubes* [27], compression of the sorbent bed can lead to excessive tube impedance [1]. Therefore, we assessed the maximum achievable flow sampling rate of our in-house packed tubes when the pump was set to 2 L/min; Table 1 shows the average effective sampling flow rates obtained for each sorbent (32 replicates for XAD-2 and 31 for Tenax TA). Large differences in the maximum sampling rate (i.e. flow resistance) were found between both sorbent materials: a higher flow rate of 1.15 L/min was achieved with XAD-2 compared with the lower flow rate of 0.69 L/min for Tenax TA. The higher flow rate with XAD-2 was likely related to the particle size which was two to three times higher for XAD-2 (590 μm [26]) than Tenax TA (60/80 mesh [25], ∼250–180 μm) resulting in a lower packing density. Thus, the use of 20/40 mesh Tenax (∼850–425 μm) would probably produce a flow resistance similar to the used XAD-2 material. However, the flow rate of 100 mL/min used for our investigations could be easily adjusted with both materials.

In addition, Table 1 shows a comparison between pre-packed and in-house packed Tenax tubes. The differences between pre-packed and in-house packed tubes are suggested to be produced by unintentional compression or inhomogeneous filling of the bed of the in-house packed tubes. Another hint for that is the smaller standard deviation of the commercial tubes. However, recovery and repeatability of the volatiles were satisfactory with both, pre-packed and in-house packed, since we obtained an overall RSD less than 20% (for Tenax TA 12% and 9% and for XAD-2 15% and 9% average and median RSD, respectively, for replicate analysis of the mix of 17 compounds) confirming that the higher impedance of the in-house packed tubes did not disturb the quality of our outcomes.

3.2. Solvent selection: methanol as solvent for the standard compounds

The molar response of analytes with respect to a particular analytical method can be very different. Therefore, for comparison of compound amounts based on signal responses, a calibration or consideration of the relative molar response of a substance is required, which is the ratio of the response of the analyte to the response of a reference compound normalized to the same molar amount, usually 1 mol of each substance. We initially analyzed the relative molar response of all prospective solvents, i.e. the signal response (TIC, total ion current) produced by the same amount of each solvent [37]; we wanted to determine the signal response ratio without the effect of possible retention/recovery of the solvent by the adsorbent. For this, a similar molar amount of each tested sol-

Table 1
Maximum flow rate of sorbent tubes filled with the two materials XAD-2 and Tenax TA, respectively.

Testing	Adsorbent	Assembly	Average Mass [mg]	n	Flow Sampling Rate [L/min]
Material	XAD-2	In-house packed	400	32	1.15 ± 0.09
	Tenax TA	Pre-packed and in-house packed	190	31	0.69 ± 0.16
Packing	Tenax	Pre-packed	–	9	0.89 ± 0.05
	TA	In-house packed	190	22	0.61 ± 0.10

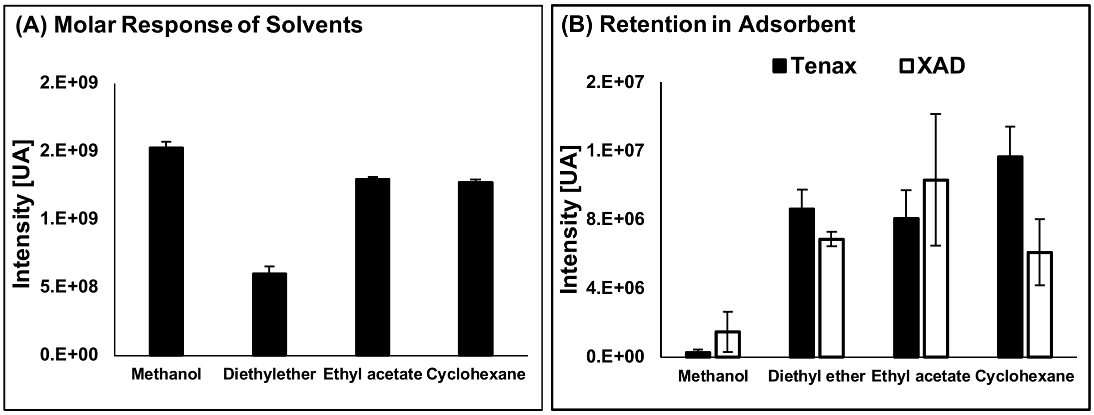

Fig. 1. (A) Molar response of each solvent to achieve the signal response corresponding to 5 μmol by variable volumes of injection. Analysis was performed by GC–MS after liquid injection. (B) Retention in the adsorbent by signal response for tested solvents after loading in sorbent tubes of Tenax TA and XAD-2. Analysis was performed by GC–MS after thermal desorption.

vent was introduced to GC–MS analysis by liquid injection and the signal responses were compared with those obtained after thermal desorption. Fig. 1A shows the relative molar responses of the four selected solvents based on the TIC. Methanol showed the highest, while diethyl ether had the lowest molar response amongst the tested solvents.

In comparison, Fig. 1B presents the signal responses after loading volumes of 1 μL of each solvent onto the adsorption tubes. It is evident that methanol is poorly retained by both sorbents concluded from the lower signal intensity compared with the other solvents. Comparing boiling points and chemical nature, poor retention of methanol could be related to its polarity since both Tenax and XAD-2 preferentially adsorb non-polar and moderately polar compounds with boiling points starting from 40 and 60 °C, respectively. In contrast, diethyl ether was retained the most considering its relative molar response in GC–MS. In conclusion, methanol was selected as solvent for our standard mixtures in the following investigations.

3.3. *Optimization of the sampling time*

In the US EPA method TO-17, it was noted that the otherwise recommended 5 min for sweeping the vapors onto the sampling surface of the sorbent to satisfactorily eliminating the solvent while quantitatively retaining the analytes, might be not appropriate for groups of compounds with a wide range of boiling points [27] as anticipated in our investigation. Therefore, we evaluated variations in the signal response of volatile compounds in the *internal standard mixture* due to different loading times (3, 5, 7, 10 and 13 min) and assessed the relative response normalized to the response after 5 min. Fig. 2 (A and B) shows the different behavior of the *internal standard mixture* when adsorbed onto Tenax TA and XAD-2, respectively. While response of the Tenax TA samples was not affected by the loading time, for XAD-2 an increased loading time seemed to improve the recovery of volatiles, possibly due to longer interaction time with the surface and arrival at less occupied surface areas. Channeling due to the bigger particle size of XAD-2 was excluded as a reason because we found no dependency of the signal response on the sampling flow rate (data not shown). In addition, a previous evaluation with Tenax TA for longer loading times between 13 and 23 min showed higher signal responses at 18 and 23 min, but was also characterized by a higher variance of the data (Supp. A.3). Consequently, 13 min was selected to improve the adsorption conditions for XAD-2 without apparent compromise for Tenax TA. However, these findings need to be considered comparing the molar response (sensitivity) that can be obtained using both materials. Also, if used for preparation of multi-sorbent tubes involving these two materials, XAD-2 might be considered therefore to be placed in front of the sampling direction.

3.4. *The effect of desorption temperature on signal response*

We assessed if a reduced desorption temperature to avoid artifact formation influences the recovery of our target analytes and therefore, the feasibility of our optimized thermal desorption protocol. Fig. 3 shows the signal intensities for each analyte (*internal standard mixture*) after desorption at different temperatures at three concentration levels for both materials, Tenax TA and XAD-2, A and B, compared with the value from Tenax at 250 °C; Table 2 lists average signal ratios and paired *t*-test p-values (two-tailed distribution) between the adsorbent/desorption temperature combinations.

For Tenax TA, the evaluation of the samples for all concentration levels showed that on average the overall response ratio was similar between all three temperatures. However, very volatile compounds (bp. <50–100 °C) such as diethyl ether and, to a lesser extent, isobutanal, had a higher signal response at desorption temperatures < 250 °C for the two lower concentration levels. This effect might be possibly related to higher losses through the split valve at higher temperatures. Consequently, the split ratio may be subject to further optimization for higher desorption temperatures. On the other hand, volatile compounds (bp. 50–100 to 240–260 °C) showed slightly lower responses as desorption temperatures decreased, e.g. the chlorinated compounds. Indeed, 2,4,5-trichlorophenol, 4-chlorophenol and 3,4-dichlorophenol seem to respond particularly better to

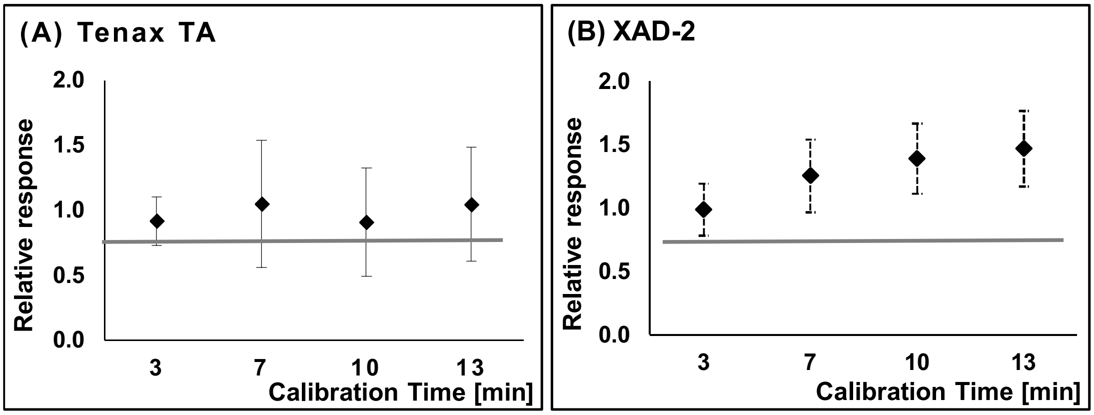

Fig. 2. Relative recovery after 3, 7, 10 and 13 min sweeping time normalized to the signal response after 5 min sweeping time for Tenax TA (A) and XAD-2 (B). A significant effect of loading time over signal response was found with XAD-2, but not Tenax TA. Thirteen minutes was finally selected as loading time to improve the adsorption of the compounds by XAD-2 without apparent effect for Tenax TA.

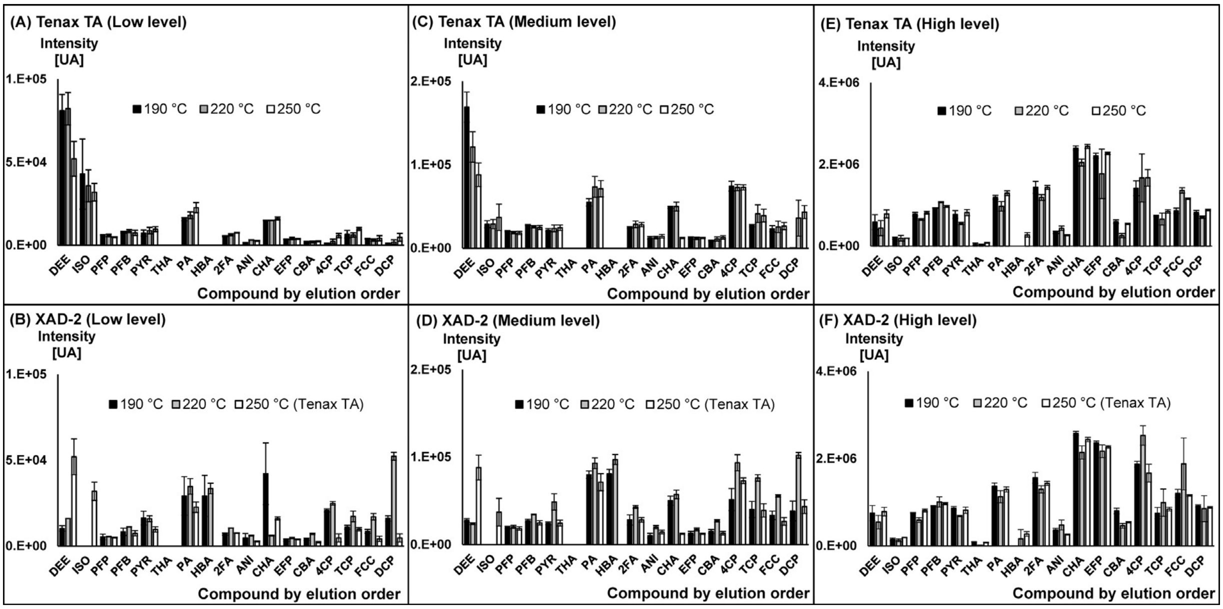

Fig. 3. Signal response of standard compounds after spiking 1 μL of standard solution at three concentration levels adjusted to their molar responses: low (1–40 μM), medium (4–123 μM) and high (333 μM) onto a sorbent bed of Tenax TA (A, C and E) or XAD-2 (B, D and F), respectively, and subsequent thermal desorption at 190, 220, and 250 °C, respectively (n = 3). Abbreviations: DEE, diethyl ether; ISO, isobutanal; PFP, pentafluoropyridine; PFB, pentafluorobenzene; PYR, pyridine; THA, trans-2-hexenal; PA, 3-methyl-2-butenyl acetate; HBA, 2-hydroxy-butyric acid; 2FA, 2-fluoroaniline; ANI, aniline; CHA, cyclohexyl acetate; EFP, ethyl pentafluorobenzoate; CBA, 2-chlorobenzaldehyde; 4CP, 4-chlorophenol; TCP, 2,4,5-trichlorophenol; FCC, 4-methoxybenzyl acetate; and DCP, 3,4-dichlorophenol.

Table 2

Ratio of signal intensity at different temperatures [average intensity at tested temperature/average intensity at highest temperature ± standard deviation] and p-value (paired *t*-test, two-tailed distribution) for all detected compounds of the *internal standard mixture* spiked to Tenax TA and XAD-2, respectively, at low, medium and high concentration levels (1–40, 4–123 and 333 μM, respectively). If the value is higher 1, the parameter set leads to higher responses, if below one, response is decreased.

Concentration level	Tenax TA [190 °C/250 °C]	Tenax TA [220 °C/250 °C]	XAD-2/Tenax [190 °C/250 °C]	XAD-2/Tenax [220 °C/250 °C]
Low[a] (1–40 μM)	0.8 ± 0.3 (p = 0.02)	0.9 ± 0.2 (p = 0.05)	1.6 ± 0.9 (p = 0.06)	1.7 ± 1.0 (p = 0.013)
Medium[a] (4–123 μM)	0.9 ± 0.14 (p = 0.07)	1.0 ± 0.08 (p = 0.78)	1.0 ± 0.2 (p = 0.85)	1.6 ± 0.4 (p < 0.01)
High (333 μM)	0.9 ± 0.17 (p = 0.013)	0.8 ± 0.3 (p < 0.01)	1.1 ± 0.17 (p = 0.05)	1.0 ± 0.4 (p = 0.76)

[a] At low and medium concentrations, DEE, ISO and 4CP were not considered due to the different behavior of these compounds at low concentrations that might possibly obscure the general trend as discussed in the manuscript Sections 3.6 and 3.7.

higher desorption temperatures with Tenax TA indicating irreversible adsorption when the temperature decreases.

For XAD-2, at lower concentration levels, a higher desorption temperature (220 °C) generally resulted in higher signal responses. Indeed, a response ratio of 1.6 ± 0.8 ($p < 0.01$) of 220 °C compared to 190 °C was determined. Similar to the observation with Tenax TA, this effect was particularly strong for the compounds with higher boiling points in the *internal standard mixture*, and also the chlorinated compounds performed particularly well with XAD-2. Unfortunately, XAD-2 was not tested at 250 °C because the signal background originating from thermal material breakdown was too high compared to the one obtained at 190 °C or even 220 °C (Supp. A.2). Consequently, though 200 °C was recommended as maximal temperature for thermal desorption [17], we suggest 220 °C for

XAD-2 as optimal compromise between material degradation and compound recovery losses by irreversible adsorption which in turn may create active sites within the adsorption material. Therefore, when the application of XAD-2 is anticipated, refreshment by solvent cleaning might be recommended from time to time. However, based on the literature recommendation and since we experienced a higher general background by a factor of 2.3 for the median signal responses of 12 identified degradation products ($n = 4$) at 220 °C, we kept a desorption temperature of 190 °C for XAD-2 in our experiments.

For both, Tenax TA and XAD-2, a decrease of desorption temperature from 250 °C to 220 °C or 190 °C had only little effect on the signal intensity for our *internal standard mixture* (average intensity loss by a factor of 0.92 in comparison to desorption at 250 °C). When comparing the recovery of XAD-2 with Tenax TA at the high concentration level (Fig. 3F and Table 2; Supp. A.4), most of the compounds showed similar recoveries with ratios between 1.0 up to 1.1 to the reference value from Tenax at 250 °C (XAD-2_250 °C/Tenax_250 °C = 1.2 ± 0.3, $p = 0.07$); only the chlorinated compounds still provided a consistently higher response with XAD-2 at 220 °C than with Tenax TA in agreement with [38]. However, at the two lower concentration levels, XAD-2 on average provided higher signal responses compared to Tenax at 250 °C (1.6 and 1.7 fold-change, $p < 0.05$, for XAD-2_190 °C and XAD-2_220 °C, respectively). Consequently, a desorption temperature decrease can be well accepted for volatile analysis by thermal desorption with XAD-2. For Tenax, however, adjustment of desorption temperature produces a selective effect with respect to the volatility of the analyzed compounds complicating the selection of optimal conditions for multi-component mixtures. In contrast, XAD-2 seems to be a better choice for analyses of multi-component mixtures featuring a broad range of boiling points as anticipated here: at a desorption temperature of 220 °C, it performed better than Tenax at 250 °C for low concentrated compounds.

3.5. *Comparison of sensitivity between thermal desorption from XAD-2 and Tenax TA*

An important parameter of method comparison is the sensitivity that can be achieved with a new method and if better LLOQs can be obtained. Thus, while XAD-2 after liquid extraction provided average LODs in comparison to other materials [39], it was shown before to provide superior LODs among the XAD resins in comparison with activated carbon/florisil for thermal desorption of environmentally important halogenated and small aromatic hydrocarbons [38]. Tables 3 and 4 show now the comparison of LLOQs for the compounds of the *internal standard mixture* and the biogenic VOCs of the *complex standard mixture* for Tenax TA and XAD-2.

3.5.1. *Internal standard mixture*

LLOQs were estimated based on the evaluation of linearity (5–7 calibration levels, slope, intercept, coefficient of determination, RSD ± <25% for all levels in linear range and $R^2 > 0.9$), and expressed in units of mass [ng analyte per tube] in 1 μL injected. Similar LLOQs were obtained for ten compounds with both sorbent materials, suggesting that XAD-2 indeed is a competitive alternative to Tenax TA rather than complementing the selectivity of this standard material. Four substances, diethyl ether, pyridine, aniline and 4-methoxybenzyl acetate, however, showed particularly better LLOQs in XAD-2 than in Tenax TA, which produced a higher relative standard deviation at the lowest detected concentration level. Thus, XAD-2 showed lower variation in signal response of replicate analysis even at low concentrations (e.g. an average 11 ± 9% RSD at the lowest quantified concentration) compared to the results after desorption from Tenax TA (20 ± 9% RSD). This variability might be related to the comparably long sweeping time applied during calibration or compound degradation due the higher desorption temperature applied to Tenax TA. Furthermore, incomplete desorption could contribute to the observed variance considering the enhanced responses at higher temperatures for this material. Albeit, the average slope (m) obtained by linear regression for every component of the *internal standard mixture* had very similar values between both materials ($m = 1.08 \pm 0.14$ for Tenax TA and 1.06 ± 0.08 for XAD-2). Surprisingly, LLOQs did not show any dependency on the compounds boiling point and/or polarity based on log *P* (not shown). However, a low overall sensitivity of the chlorinated compounds, i.e. 2,4,5-trichlorophenol, 4-chlorophenol and 3,4-dichlorophenol was expected due to bad chromatographic performance (long tailing) [40] and recovery loss (irreversible adsorption) [41] commonly found in analysis of underivatized phenols by gas chromatography.

3.5.2. *Complex standard mixture*

As *proof of concept*, we assessed method coverage, chromatographic separation and intensity pattern for 57 compounds of our *complex standard mixture* (Fig. 4). Nine compounds were not detected from both, Tenax TA and XAD-2 (see Section 2.4). These nine undetected compounds, e.g. acetaldehyde, ethyl methanoate, 2-propanol, and 2-pentanone, are representatives of each considered chemical class with particularly low molecular weights (<90 g/mol), high volatility (bp. <100 °C), and medium and high polar nature. This would be in agreement with Hayward et al. [16] who found adsorption to XAD-2 generally improved with low vapor pressures and large molecular size. In addition, it suggests that the response of a compound is related not only to recovery losses by evaporation before and during spiking (a potentially problematic procedure for very volatile compounds), but, eventually, also by incomplete or, in turn, irreversible adsorption of polar compounds in the sorbent materials Tenax TA and XAD-2 which, according to our results, both can be used for sampling of nonpolar and moderately polar analytes. Consequently, in contrast to what we originally aimed for, XAD-2 did not provide a substantially different substance coverage compared to Tenax TA.

Moreover, the general intensity pattern obtained with the 48 detected compounds was similar between XAD-2 and Tenax TA (Pearson correlation coefficient $r = 0.85$, XAD_190 °C/Tenax_250 °C average fold-change 1.5, median fold-change 1.1, $p = 0.09$ in a paired two-tailed *t*-test) and confirmed our finding that indeed these two materials perform rather similar in terms of compound selectivity and recovery at higher concentrations. However, similar to the *internal standard mixture*, different molar responses for specific target compounds were also found in the *complex standard mixture*, such as a higher molar response for heptanoic acid in Tenax TA, or dimethylformamide, dihydromyrcenol, and benzoic acid ethyl ester in XAD-2; acetoin was only detected with XAD-2. Data from an initial study in our lab, Kücklich et al. (manuscript under revision) indicates that XAD-2 might favor carbonyls in contrast to Tenax TA which in turn might provide better sensitivities with specific hydroxyls. Thus, approximately 30% of all analyzed compounds within our two mixtures of 17 and 33 compounds provided better LLOQs after thermal desorption from XAD-2, 25% for Tenax TA (Tables 3 and 4). Eventually, in addition to its superior sorption characteristics [15], this effect could at least partially be caused by a more instant release of the corresponding compounds from XAD-2 upon thermal desorption, indicated by the longer sample interaction time required for this material during adsorption.

We compared the general signal abundance of 48 detected compounds in dependence on their chemical character (Fig. 5). All chemical classes considered here were covered by both Tenax TA and XAD-2, and a distinguishable trend based on their functional grouping was hardly found. For both adsorbents, higher signal intensities might be expected for the less polar compounds because

Table 3
LLOQs and slope (m) and intercept (b) of the linear calibration model obtained by linear regression (PLS) for the compounds of the *internal standard mixture* and 33 compounds of the *complex standard mixture* spiked onto Tenax TA after thermal desorption at 250 °C and analyzed by GCMS-TQ8040. Values in bold indicate better LLOQ compared with XAD-2. Abbreviations are explained in the footnote.

No.	Compound	R. t. [min]	*m/z*	n	LLOQ [ng/tube]	Highest tested concentration [ng/tube]	m	b	R^2	%RSD
Internal Standard Mixture										
1	Diethyl ether	2.4	31 (74,59)	5	3.05	247.07	0.91	5.80	0.94	15
2	Pentafluoropyridine	2.6	169 (100,124)	6	0.23	56.35	1.04	6.26	1.00	9
3	Pentafluorobenzene	2.8	168 (99,137)	6	0.23	56.02	1.03	6.37	1.00	8
4	Pyridine	3.5	79 (52,39)	5	0.33	26.37	0.95	6.21	1.00	12
5	3-Methyl-2-butenyl acetate	5.6	43 (68,86)	6	0.53	128.17	0.97	6.33	0.99	15
6	2-Fluoroaniline	6.0	111 (84,64)	6	0.15	37.04	1.12	6.56	1.00	12
7	Aniline	6.3	93 (66,39)	5	0.38	31.04	1.10	6.16	0.99	16
8	Cyclohexyl acetate	7.3	43 (82,67)	6	0.20	47.40	0.95	6.55	1.00	10
9	Ethyl pentafluorobenzoate	7.6	195 (240,212)	6	0.10	24.01	1.02	6.59	1.00	7
10	2-Chlorobenzaldehyde	8.4	139 (111,75)	6	0.19	46.86	0.99	5.82	0.98	14
11	4-Chlorophenol	9.6	128 (130,65)	5	1.59	128.56	1.31	6.45	0.97	11
12	2,4,5-Trichlorophenol	12.0	196 (97,132)	6	0.81	197.45	1.21	6.32	1.00	14
13	4-Methoxybenzyl acetate	12.6	121 (180,91)	5	0.74	60.07	1.27	6.77	1.00	16
14	3,4-Dichlorophenol	12.6	162 (99,63)	6	0.67	163.00	1.30	6.41	0.99	14
15	Isobutanal	n.a.								
16	*trans*-2-Hexenal	n.a.								
17	2-Hydroxy-butyric acid	n.a.								
Complex Standard Mixture										
1	Acetic acid, methyl ester	2.4	74 (43,59)	3	0.91	8.23	0.72	5.54	0.94	10
2	2,3-Butanedione	2.5	86 (43,42)	3	1.06	9.57	0.48	5.60	0.93	12
3	Chloroform	2.7	83 (85,47)	7	0.01	13.26	0.71	6.16	0.96	13
4	Cyclohexane	3.0	56 (84,69)	3	1.04	9.35	0.80	5.99	0.99	6
5	Triethylamine	3.1	86 (101,58)	5	0.14	11.24	0.91	6.73	1.00	13
6	Furan, 2-ethyl-	3.1	81 (96,53)	5	0.13	10.68	1.05	6.71	0.98	15
7	Butanoic acid, methyl ester	3.2	74 (87,43)	5	**0.14**	11.35	0.75	6.15	0.97	8
8	Pyridine	3.4	79 (52,39)	5	0.33	26.37	0.95	6.21	1.00	12
9	Formamide, *N,N*-dimethyl-	3.7	73 (44,30)	2	2.71	8.12	1.73	6.88	1.00	15
10	Butanoic acid, ethyl ester	4.0	88 (101,71)	5	0.16	12.91	0.99	5.63	1.00	15
11	Acetic acid, butyl ester	4.1	43 (73,61)	5	0.16	12.91	0.75	6.61	0.94	12
12	3-Heptanone	5.0	114 (85,57)	3	**1.41**	12.69	1.04	6.04	1.00	9
13	Xylene	5.2	91 (106,77)	6	0.05	11.80	0.88	6.87	0.98	15
14	Acetic acid, pentyl ester	5.3	43 (70,55)	5	**0.01**	14.47	0.61	6.32	0.85	17
15	n-Nonane	5.4	43 (85,57)	5	**0.01**	14.24	0.52	6.17	0.89	14
16	Hexanoic acid, methyl ester	5.5	74 (99,87)	7	**0.01**	14.47	0.94	6.75	0.99	6
17	Aniline	6.1	93 (66,39)	5	0.38	31.04	1.10	6.16	0.99	16
18	Phenol	6.3	94 (66,39)	5	**0.13**	10.46	0.66	6.05	0.87	15
19	Octanal	6.6	41 (84,69)	3	1.58	14.25	0.96	6.43	1.00	6
20	Acetic acid, hexyl ester	6.8	43 (84,56)	5	**0.20**	16.02	1.01	7.06	0.97	16
21	Heptanoic acid	7.7	60 (87,73)	3	1.61	14.47	1.12	6.66	0.99	13
22	2-Nonanone	7.9	58 (71,142)	5	**0.20**	15.80	1.01	7.03	1.00	7
23	1,6-Octadien-3-ol, 3,7-dimethyl-	8.1	71 (121,93)	3	1.90	17.14	1.05	6.67	1.00	4
24	2-Butenedioic acid (Z)-, diethyl ester	8.9	99 (127,82)	7	**0.02**	19.13	0.99	7.04	1.00	12
25	Benzoic acid, ethyl ester	9.1	105 (150,122)	5	0.21	16.69	0.72	6.77	0.94	11
26	Octanoic acid	9.1	60 (101,73)	5	**0.20**	16.02	0.82	6.22	0.97	22
27	2-Butenedioic acid (E)-, diethyl ester	9.2	127 (99,55)	5	**0.24**	19.13	1.25	7.04	1.00	16
28	Octanoic acid, ethyl ester	9.5	88 (127,101)	6	0.08	19.14	1.05	6.98	1.00	8
29	Benzaldehyde, 4-methoxy-	10.2	135 (136,107)	2	5.04	15.13	1.55	7.09	1.00	11
30	Undecanal	11.1	41 (126,96)	5	**0.23**	18.92	0.84	6.36	1.00	17
31	Benzamide, *N,N*-dimethyl-	11.7	105 (148,77)	5	0.20	16.58	0.95	6.64	0.99	11
32	Alpha-Ionone	12.8	121 (136,192)	5	0.26	21.37	0.88	6.71	0.99	6
33	Beta-Ionone	13.5	177 (192,135)	5	0.26	21.37	1.02	7.07	1.00	7
Average					**0.64**	**37.31**	**0.98**	**6.45**	**0.98**	**12**
Median					**0.23**	**16.69**	**0.99**	**6.43**	**0.99**	**12**

No. = designated ID number in the internal standard mixture and in the complex standard mixture, respectively. R.t. = retention time, *m/z* (quantitation ion and confirmation ions), n = number of levels in linear range, m = slope in linear regression model, b = intercept in linear regression model, R^2 = coefficient of determination, LLOQ = lower limit of quantitation and n.a. (not analyzed).

[*] Linear regression data shown was calculated in the range between 0.01–~250 ng/tube depending on the compound.

of the adsorption properties of the sorbent materials: less polar compounds with ester, aldehyde, and ketone functional groups could adsorb stronger than the more polar compounds with alcohol and carboxylic acid functional groups. However, in partial agreement with our pilot study with volatile samples from common marmosets we could well quantify several (semi)polar compounds and almost similar signal intensities were obtained for all chemical classes without apparent differences between both adsorbents except for better sensitivity of XAD-2 at lower concentrations. This suggests that the signal response may be determined rather by detector responsiveness than by large differences in the recovery.

3.6. *Relative recoveries and compound breakthrough*

In adsorption sampling, the breakthrough of compounds, i.e. when a compound travels through the tube and leaves again already during the sampling process itself, is an undesirable appearance. Within this context, breakthrough values below 5% [27] are usually considered to provide optimum conditions of performance.

Table 4
LLOQs and slope (m) and intercept (b) of the linear calibration model obtained by linear regression (PLS) for the compounds of the *internal standard mixture* and 33 compounds of the *complex standard mixture* spiked onto XAD-2 after thermal desorption at 190 °C and analyzed by GCMS-TQ8040. Values in bold indicate better LLOQ compared with Tenax TA. Abbreviations are explained in the footnote.

No.	Compound	R. t. [min]	*m/z*	n	LLOQ [ng/tube]	Highest tested concentration [ng/tube]	m	b	R^2	%RSD
Internal Standard Mixture										
1	Diethyl ether	2.4	74 (31,59)	6	**1.02**	247.07	1.03	5.53	0.98	10
2	Pentafluoropyridine	2.6	169 (100,124)	6	0.23	56.35	1.13	6.42	1.00	8
3	Pentafluorobenzene	2.8	168 (99,137)	6	0.23	56.02	1.06	6.48	1.00	5
4	Pyridine	3.5	79 (52,39)	6	**0.11**	26.37	0.90	6.22	0.98	11
5	3-Methyl-2-butenyl acetate	5.6	43 (68,86)	6	0.53	128.17	1.09	6.48	1.00	13
6	2-Fluoroaniline	6.0	111 (84,64)	6	0.15	37.04	1.14	6.42	1.00	9
7	Aniline	6.3	93 (66,39)	6	**0.13**	31.04	0.98	5.95	0.98	11
8	Cyclohexyl acetate	7.3	43 (82,67)	5	0.20	47.40	1.01	6.71	0.97	20
9	Ethyl pentafluorobenzoate	7.6	195 (240,212)	6	0.10	24.01	1.11	6.79	1.00	9
10	2-Chlorobenzaldehyde	8.4	139 (111,75)	6	0.19	46.86	0.92	5.91	0.99	15
11	4-Chlorophenol	9.6	128 (130,65)	5	1.59	128.56	1.13	6.38	0.99	7
12	2,4,5-Trichlorophenol	12.0	196 (97,132)	6	0.81	197.45	1.17	6.31	1.00	10
13	4-Methoxybenzyl acetate	12.6	121 (180,91)	6	**0.25**	60.07	1.14	6.66	1.00	13
14	3,4-Dichlorophenol	12.6	162 (99,63)	6	0.67	163.00	1.06	6.24	0.99	10
15	Isobutanal	n.a.								
16	*trans*-2-Hexenal	n.a.								
17	2-Hydroxy-butyric acid	n.a.								
Complex Standard Mixture										
1	Acetic acid, methyl ester	2.4	74 (43,59)	5	**0.10**	8.23	0.42	5.21	0.94	12
2	2,3-Butanedione	2.5	86 (43,42)	5	**0.12**	9.57	0.21	4.99	0.80	18
3	Chloroform	2.7	83 (85,47)	7	0.01	9.57	0.87	6.42	0.99	13
4	Cyclohexane	3.0	84 (56,69)	5	**0.12**	9.35	0.72	5.85	0.97	15
5	Triethylamine	3.1	86 (101,58)	5	0.14	11.24	0.88	6.49	0.96	18
6	Furan, 2-ethyl-	3.1	81 (96,53)	5	0.13	10.68	0.77	6.26	0.95	15
7	Butanoic acid, methyl ester	3.2	74 (87,43)	3	1.26	11.35	0.89	6.32	1.00	6
8	Pyridine	3.4	79 (52,39)	6	**0.11**	26.37	0.90	6.22	0.98	11
9	Formamide, *N,N*-dimethyl-	3.6	73 (44,30)	3	**0.90**	8.12	1.04	6.36	1.00	22
10	Butanoic acid, ethyl ester	4.0	88 (101,71)	6	**0.05**	12.91	0.85	6.16	0.99	10
11	Acetic acid, butyl ester	4.1	43 (73,61)	5	0.16	12.91	0.80	6.70	0.97	19
12	3-Heptanone	5.0	85 (57,114)	2	4.23	12.69	0.96	6.41	1.00	11
13	Xylene	5.2	91 (106,77)	6	0.05	11.80	0.92	6.91	0.99	9
14	Acetic acid, pentyl ester	5.3	43 (70,55)	4	0.54	14.47	1.09	7.07	0.99	12
15	n-Nonane	5.4	57 (85,43)	6	0.06	14.24	0.62	6.26	0.95	21
16	Hexanoic acid, methyl ester	5.5	74 (99,87)	6	0.06	14.47	0.99	6.85	1.00	13
17	Aniline	6.2	93 (66,39)	6	**0.13**	31.04	0.98	5.95	0.98	11
18	Phenol	6.3	94 (66,39)	4	0.39	10.46	0.70	6.29	0.88	18
19	Octanal	6.6	41 (84,69)	4	**0.53**	14.25	0.88	6.01	0.99	12
20	Acetic acid, hexyl ester	6.8	43 (84,56)	4	0.59	16.02	0.95	6.99	0.98	14
21	Heptanoic acid	7.7	60 (87,73)	3	1.61	14.47	1.25	6.77	1.00	27
22	2-Nonanone	7.9	58 (71,142)	4	0.59	15.80	0.91	6.22	0.94	18
23	1,6-Octadien-3-ol, 3,7-dimethyl-	8.2	93 (121,71)	6	**0.07**	17.14	0.83	6.22	0.99	14
24	2-Butenedioic acid (Z)-, diethyl ester	8.9	99 (127,82)	6	0.08	19.13	0.90	6.95	0.99	13
25	Benzoic acid, ethyl ester	9.1	150 (105,122)	7	**0.01**	16.69	0.72	5.95	0.96	9
26	Octanoic acid	9.1	60 (101,73)	2	5.34	16.02	1.12	6.65	1.00	26
27	2-Butenedioic acid (E)-, diethyl ester	9.2	127 (99,55)	4	0.71	19.13	0.99	6.76	0.98	17
28	Octanoic acid, ethyl ester	9.6	88 (127,101)	6	0.08	19.14	0.96	6.88	1.00	10
29	Benzaldehyde, 4-methoxy-	10.2	135 (136,107)	4	**0.56**	15.13	0.83	6.53	0.95	14
30	Undecanal	11.1	96 (126,41)	4	0.70	18.92	0.63	5.51	0.90	22
31	Benzamide, *N,N*-dimethyl-	11.7	105 (148,77)	5	0.20	16.58	0.77	6.65	0.87	13
32	Alpha-Ionone	12.8	121 (136,192)	7	**0.02**	21.37	0.52	6.17	0.92	10
33	Beta-Ionone	13.5	177 (192,135)	7	**0.02**	21.37	0.67	6.53	0.97	15
Average					**0.55**	**37.23**	**0.90**	**6.34**	**0.97**	**14**
Median					**0.19**	**16.69**	**0.92**	**6.38**	**0.99**	**13**

*Linear regression data shown was calculated in the range between 0.01–∼250 ng/tube depending on the compound.
No.= designated ID number in the internal standard mixture and in the complex standard mixture, respectively. R.t. = retention time, *m/z* (quantitation ion and confirmation ions), n = number of levels in linear range, m = slope in linear regression model, b = intercept in linear regression model, R^2 = coefficient of determination, LLOQ = lower limit of quantitation and n.a. (not analyzed).

Wong et al. [32] determined breakthrough values not only during air sampling but also during injection of standards in desorption tubes to evaluate possible leaking from the sorbent tube at calibration conditions. Breakthrough values for volatile compounds were determined by connecting two desorption tubes in series, sampling at different flow rates and/or different sample volumes, then calculating the mass fraction between the tubes [32,33].

The adsorption of a compound to an adsorbent is a specific interaction, a.o. dependent on the concentration of this compound in the gas phase (sorption isotherm). Therefore, in this study, breakthrough values of Tenax TA and XAD-2 (Tables 5 and 6, respectively) were evaluated loading different concentrations of the *complex standard mixture* with 33 selected compounds. As a result, none of the analyzed compounds showed consistent breakthrough at all concentrations, however, with Tenax TA four and with XAD-2 fourteen compounds (eleven of which in the lowest concentration level) were detected in the back tube at least at one concentration level.

Breakthrough of acetic acid methyl ester (both materials), cyclohexane and triethylamine (Tenax TA only) and chloroform and hexanoic acid methyl ester (XAD-2 only) was observed at higher

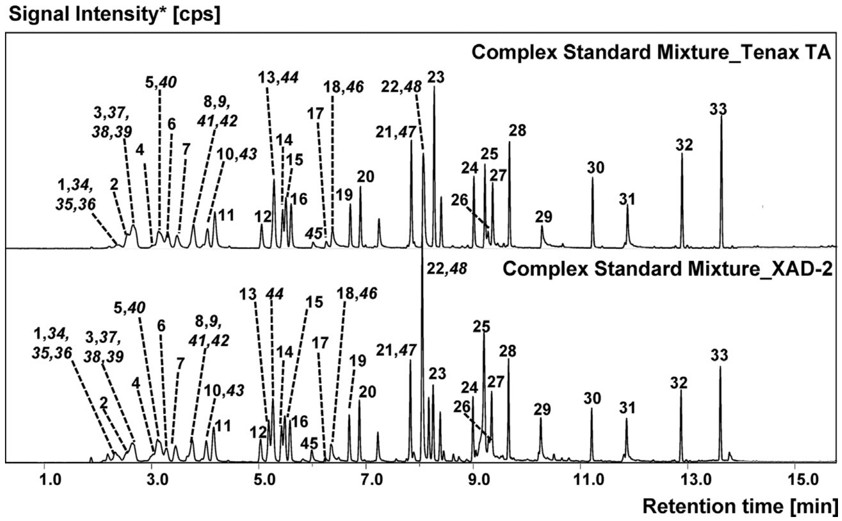

Fig. 4. Intensity pattern of the *complex standard mixture* of 57 (48 detected) compounds after spiking in Tenax TA and XAD-2 tubes and desorption at optimized temperatures (250 and 190 °C, respectively). 33 selected compounds (identified from 1 to 33) are described in Tables 3 and 4. Additionally detected compounds (*assigned number for identification*) are the following: acetone (*34*), diethyl ether (*35*), 2-pentanone (*36*), 2-butanol (*37*), ethyl acetate (*38*), *n*-hexane (*39*); acetoin (*40*), formamide, *N*, *N*-dimethyl- (*41*), toluene (*42*), propanoic acid, 2-oxo-ethyl ester (*43*), 2-heptanol (*44*), benzaldehyde (*45*), hexanoic acid (46), 7-octen-2-ol, 2,6-dimethyl- (*47*), benzoic acid, methyl ester (*48*). Nine compounds, m-cresol, ethanol, 2-propanol, acetaldehyde, propanal, 2-propenal, dichloromethane, diethylamine and ethyl methanoate were not detected.

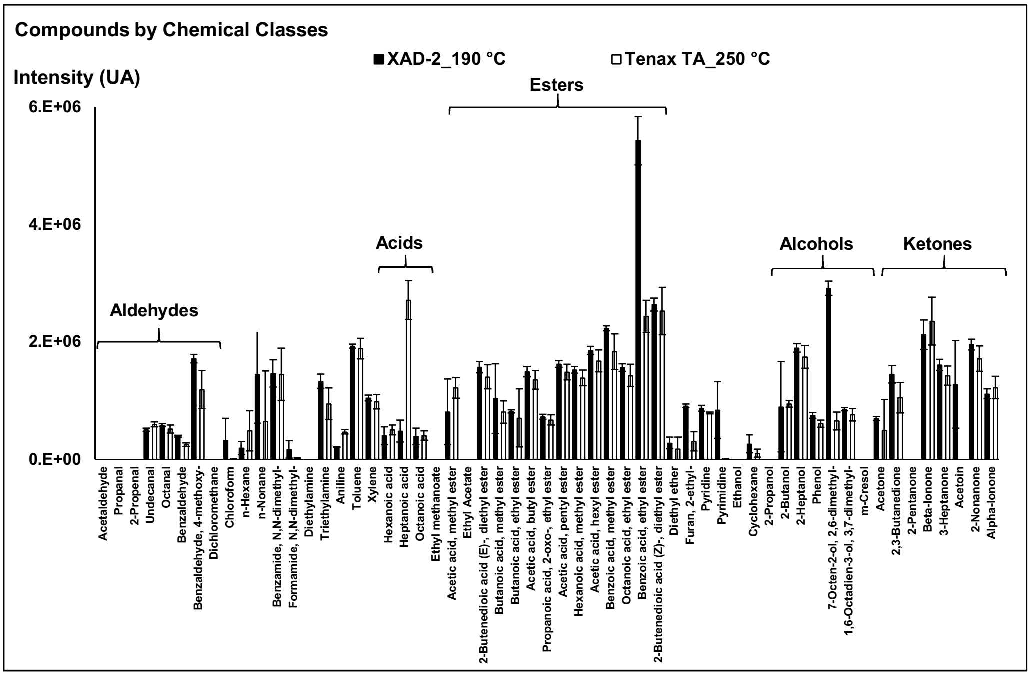

Fig. 5. Comparison of molar responses of 48 detected compounds classified by chemical classes using both materials, Tenax TA and XAD-2. Nine compounds were not detected (see Section 2.4).

concentration levels and might therefore be related to saturation of the adsorbent, i.e. the shrinking availability of free adsorption sites with progressing occupation by the target molecules. Since breakthrough at the high concentration level was not a general appearance but mainly restricted to these compounds, we suggest the occurrence of competitive adsorption within the compound mixture for this level to be responsible for the observed effect.

The situation of breakthrough at low concentration level but not at higher concentrations is different and requires that the adsorption at very low partial pressures is considerably more efficient than at increasing partial pressures. For a moving gas volume through the adsorbent (active sampling), a compounds partial pressure in the gas phase decreases in dependency on the adsorption efficiency for this particular compound from the moment when the sample comes in contact with the adsorbent till it leaves the tube again.

Adsorbed particles do not have a fixed binding site but move along the surface of the adsorbent and enable the occupation of binding sites the adsorbate binds particularly tight to (usually defects in the non-perfect structure of the sorbent polymer scaffold, previously reported for XAD-2 [42]). Such particularly active binding sites could provide a very high initial adsorption efficiency and be occupied very efficiently but compound-selective. It can be assumed that these binding sites have an average amount and distribution in the material, so that this particularly efficient adsorption will continue up to a certain, fixed threshold till the favored binding sites are occupied. After saturation of these

Table 5

Breakthrough of 33 volatile compounds from the *complex standard mixture* at three concentration levels (1 μL of standard mix injected, 100 mL/min nitrogen flow during 13 min) in Tenax TA. Rel. Rec. is the relative recovery calculated as the percentage of the mass of VOC (ng/tube) detected in the back tube to the total mass of analyte detected in both tubes. If the mass of a compound is below the limit of quantitation, <l.q. is used (coefficient of determination $R^2 > 0.98$ and RSD < 25%). If the relative recovery is less than 5% (US EPA method TO-17), <5 is used. If the compound is not detected, n.d. is used. An asterisk is added when a value could not be determined (the compound was not detected or was lower the limit of quantitation). %RSD^1 is the relative standard deviation obtained in triplicate analyses in the first desorption tube. %RSD^2 is the relative standard deviation obtained in triplicate analyses in the back tube.

No.	Compound	High level (111 μM)			Medium level (12 μM)			Low level (1.4 μM)		
		Rel. Rec [%]	RSD^1 [%]	RSD^2 [%]	Rel. Rec. [%]	RSD^1 [%]	RSD^2 [%]	Rel. Rec. [%]	RSD^1 [%]	RSD^2 [%]
1	Acetic acid, methyl ester	26.6	3.5	19.8	<l.q.	16.3	*	<l.q.	20.0	*
2	2,3-Butanedione	<l.q.	4.4	*	<l.q.	14.8	*	<l.q.	44.0	*
3	Chloroform	<5	0.6	76.7	8.9	16.4	35.8	14.0	5.5	21.5
4	Cyclohexane	28.4	5.7	5.9	<l.q.	25.1	*	n.d.	*	*
5	Triethylamine	14.4	16.0	18.0	<l.q.	5.3	*	<l.q.	19.6	*
6	Furan, 2-ethyl-	<l.q.	6.2	*	<l.q.	14.0	*	<l.q.	9.9	*
7	Butanoic acid, methyl ester	<l.q.	3.9	*	<l.q.	13.8	*	<l.q.	8.7	*
8	Pyridine	n.d.	4.3	*	<l.q.	12.7	*	n.d.	56.6	*
9	Formamide, *N,N*-dimethyl-	n.d.	*	*	n.d.	*	*	n.d.	*	*
10	Butanoic acid, ethyl ester	n.d.	6.1	*	<l.q.	24.0	*	n.d.	12.5	*
11	Acetic acid, butyl ester	<l.q.	1.0	*	<l.q.	10.2	*	<l.q.	28.4	*
12	3-Heptanone	<l.q.	*	*	<l.q.	*	*	n.d.	*	*
13	Xylene	<l.q.	4.3	*	<l.q.	7.2	*	<l.q.	16.5	*
14	Acetic acid, pentyl ester	<l.q.	3.1	*	<l.q.	4.9	*	<l.q.	55.3	*
15	n-Nonane	n.d.	4.6	*	n.d.	9.4	*	n.d.	40.6	*
16	Hexanoic acid, methyl ester	<l.q.	4.2	*	<5	5.6	62.4	<l.q.	13.9	*
17	Aniline	<l.q.	8.3	*	<l.q.	14.0	*	n.d.	18.7	*
18	Phenol	<5	6.8	63.7	27.6	8.3	39.1	<l.q.	13.3	*
19	Octanal	n.d.	5.2	*	n.d.	4.9	*	n.d.	*	*
20	Acetic acid, hexyl ester	<l.q.	3.3	*	<l.q.	6.8	*	<l.q.	13.7	*
21	Heptanoic acid	n.d.	12.9	*	n.d.	16.6	*	n.d.	32.6	*
22	2-Nonanone	<l.q.	2.9	*	<l.q.	3.9	*	<l.q.	13.3	*
23	1,6-Octadien-3-ol, 3,7-dimethyl-	<l.q.	3.8	*	<l.q.	5.4	*	<l.q.	19.4	*
24	2-Butenedioic acid (Z)-, diethylester	<l.q.	5.5	*	<l.q.	13.2	*	n.d.	9.1	*
25	Benzoic acid, ethyl ester	<l.q.	2.6	*	19.9	25.7	87.4	<l.q.	11.4	*
26	Octanoic acid	<5	16.1	81.6	17.4	23.7	110.2	<l.q.	13.1	*
27	2-Butenedioic acid (E)-, diethylester	<l.q.	4.7	*	<l.q.	22.8	*	<l.q.	32.1	*
28	Octanoic acid, ethyl ester	<l.q.	4.3	*	<l.q.	5.7	*	<l.q.	17.1	*
29	Benzaldehyde, 4-methoxy-	n.d.	7.0	*	n.d.	35.3	*	n.d.	68.5	*
30	Undecanal	<5	17.9	47.7	12.5	25.6	73.9	<l.q.	22.3	*
31	Benzamide, *N,N*-dimethyl-	n.d.	10.0	*	n.d.	4.0	*	<l.q.	17.5	*
32	Alpha-Ionone	<l.q.	5.5	*	<l.q.	6.6	*	<l.q.	10.4	*
33	Beta-Ionone	<l.q.	4.5	*	<l.q.	3.0	*	<l.q.	9.8	*

especially efficient binding sites, subsequently delivered sample is adsorbed with slightly decreased efficiency over a comparably long time scale so that the small fraction of sample amount which was not bound can reach the back tube which still has free tight-binding sites.

This effect could explain the observed results since the bound amount of the compound stays constant but the fraction of the whole sample in the back tube would be higher for low concentrated compounds. Also, the fact that only one material was affected (this effect was mostly restricted to XAD-2) and the observed compound selectivity of breakthrough at low concentration level would support this hypothesis. Moreover, since the response from the freshly packed back tube exhibited a high variance among triplicate analyses, we repeated our breakthrough experiment with higher replication using several times reused tubes instead of new ones. In this experiment, we did not observe any breakthrough with XAD-2, but lower signal responses at the lower concentration levels along with better overall variances (data not shown). We conclude from this that after a few cycles of usage and equilibration these particularly active sites might become inactivated by time and though adsorption and desorption might be slightly less efficient, the reproducibility of the whole process is enhanced.

Eventually, a reduced flow rate enabling improved interaction between adsorbate and surface or a shorter sweeping time resulting in a smaller sample volume not exceeding the breakthrough volume, might be recommended for those compounds [27]. We clearly showed, however, that for XAD-2 the overall intensity was actually enhanced with the sweeping time (i.e. sample volume) and was constant for Tenax TA up to 13 min. Consequently, adsorption to XAD-2 still seems to require a longer interaction time or, accordingly, a longer time to travel to adsorption sites to achieve successful retention of a higher fraction of the compound amount in the first tube (particularly when dealing with a set of compounds featuring this broad range of volatility).

4. Conclusion

For the first time, we present comprehensive data on the performance of XAD-2 in comparison with Tenax TA for adsorption of volatile compounds from gaseous samples followed by thermal desorption and analyzed by GC–MS, based on results obtained with 17 standard compounds and 57 common target analytes. In conclusion, XAD-2 showed comparable achievements to the well-known adsorbent Tenax TA; it appears to not complement or broaden the applicability of this air sampling technique. Both materials had an overall similar compound coverage with few specific differences.

In detail, with respect to sensitivity, we found that XAD-2 selectively provided lower limits of quantitation in comparison with Tenax TA. Moreover, decreasing the desorption temperature of XAD-2 to 220 °C due to thermal material breakdown at higher temperatures did not compromise the signal response in target analysis; in fact, the sensitivity (LLOQ) of 17 volatile compounds in the *internal standard mixture* and 33 substances of the *complex standard mixture* could be improved by an average factor of 1.7 even without significantly compromising reproducibility (average %RSD = 15 ± 5). In particular, the use of XAD-2 might improve the

Table 6
Breakthrough of 33 volatile compounds from the *complex standard mixture* at three concentration levels (1 μL of standard mix injected, 100 mL/min nitrogen flow during 13 min) in XAD-2. Rel. Rec. is the relative recovery calculated as the percentage of the mass of VOC (ng/tube) detected in the back tube to the total mass of analyte detected in both tubes. If the mass of a compound is below the limit of quantitation, <l.q. is used (coefficient of determination $R^2 > 0.98$ and RSD < 25%). If the relative recovery is less than 5% (US EPA method TO-17), <5 is used. If the compound is not detected, n.d. is used. An asterisk is added when a value could not be determined (the compound was not detected or was lower the limit of quantitation). %RSD^1 is the relative standard deviation obtained in triplicate analyses in the first desorption tube. %RSD^2 is the relative standard deviation obtained in triplicate analyses in the back tube.

No.	Compound	High level (111 μM)			Medium level (12 μM)			Low level (1.4 μM)		
		Rel. Rec [%]	RSD^1 [%]	RSD^2 [%]	Rel. Rec. [%]	RSD^1 [%]	RSD^2 [%]	Rel. Rec. [%]	RSD^1 [%]	RSD^2 [%]
1	Acetic acid, methyl ester	18.4	15.2	21.8	<l.q.	6.1	*	<l.q.	24.2	*
2	2,3-Butanedione	<l.q.	1.7	*	<l.q.	18.2	*	<l.q.	9.3	*
3	Chloroform	8.7	1.7	48.8	9.7	27.4	20.1	<l.q.	20.0	*
4	Cyclohexane	<l.q.	6.4	*	<l.q.	22.7	*	42.9	20.1	14.8
5	Triethylamine	<l.q.	7.3	*	<l.q.	21.8	*	<l.q.	14.2	*
6	Furan, 2-ethyl-	<l.q.	17.6	*	<l.q.	33.0	*	<l.q.	10.9	*
7	Butanoic acid, methyl ester	n.d.	*	*	n.d.	*	*	n.d.	*	*
8	Pyridine	<l.q.	10.9	*	<l.q.	11.5	*	<l.q.	14.3	*
9	Formamide, *N,N*-dimethyl-	<l.q.	*	*	n.d.	*	*	n.d.	*	*
10	Butanoic acid, ethyl ester	<l.q.	8.0	*	n.d.	12.0	*	n.d.	11.8	*
11	Acetic acid, butyl ester	<l.q.	8.6	*	<l.q.	9.7	*	56.0	28.2	8.5
12	3-Heptanone	n.d.	*	*	n.d.	*	*	n.d.	*	*
13	Xylene	<5	6.9	82.1	22.4	19.6	105.1	72.6	4.9	105.6
14	Acetic acid, pentyl ester	<l.q.	8.1	*	<l.q.	18.1	*	77.7	*	45.8
15	n-Nonane	n.d.	9.0	*	<l.q.	5.8	*	31.9	26.9	17.5
16	Hexanoic acid, methyl ester	14.7	10.1	0.9	<l.q.	25.2	*	<l.q.	14.9	*
17	Aniline	<l.q.	21.5	*	<l.q.	23.8	*	<l.q.	30.0	*
18	Phenol	<l.q.	25.1	*	44.4	25.0	75.6	54.3	*	10.5
19	Octanal	<l.q.	16.5	*	<l.q.	11.6	*	<l.q.	*	*
20	Acetic acid, hexyl ester	<l.q.	8.1	*	<l.q.	13.9	*	45.7	*	59.9
21	Heptanoic acid	n.d.	*	*	n.d.	*	*	n.d.	*	*
22	2-Nonanone	n.d.	10.0	*	n.d.	27.0	*	n.d.	*	*
23	1,6-Octadien-3-ol, 3,7-dimethyl-	<l.q.	6.8	*	<l.q.	15.0	*	39.8	8.0	5.3
24	2-Butenedioic acid (*Z*)-, diethylester	<l.q.	10.7	*	<l.q.	22.1	*	<l.q.	5.0	*
25	Benzoic acid, ethyl ester	n.d.	11.0	*	n.d.	12.0	*	n.d.	4.0	*
26	Octanoic acid	n.d.	*	*	n.d.	*	*	n.d.	*	*
27	2-Butenedioic acid (*E*)-, diethylester	<l.q.	11.8	*	<l.q.	24.4	*	<l.q.	*	*
28	Octanoic acid, ethyl ester	<l.q.	8.1	*	<l.q.	16.0	*	<l.q.	14.0	*
29	Benzaldehyde, 4-methoxy-	n.d.	20.0	*	n.d.	20.0	*	n.d.	*	*
30	Undecanal	<l.q.	16.0	*	<l.q.	22.0	*	<l.q.	*	*
31	Benzamide, *N,N*-dimethyl-	n.d.	15.0	*	n.d.	15.0	*	80.7	37.0	63.2
32	Alpha-Ionone	<l.q.	6.0	*	<l.q.	16.0	*	8.7	33.0	67.6
33	Beta-Ionone	n.d.	6.6	*	<l.q.	15.4	*	19.2	29.0	92.8

outcome from analysis of chlorinated substances. Though it seems to require a longer compound interaction time, thermal desorption analysis with XAD-2 was comparably sensitive and more robust compared with Tenax TA (smaller variance at low concentration levels of many compounds). Consequently, XAD-2 can be well used as a cheaper and at least equally effective alternative to Tenax TA, even favorable when it comes to analysis of low amounts of compounds in a multiple-component mixture featuring very different boiling points.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.chroma.2017.07.005.

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