Published in final edited form as:
Int J Environ Anal Chem. 2022 September 18; 102(19): 1–18. doi:10.1080/03067319.2022.2121163.

Method development for on-site monitoring of volatile organic compounds via portable TD-GC-MS: evaluation of the analytical performances of HAPSITE® ER instrumentation and thermal desorption sampling media

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Abstract

Determining worker exposure to hazardous volatile organic compounds (VOCs) in air at levels exceeding the Permissible Exposure Limits and Recommended Exposure Limits established by the U.S. federal agencies of Occupational Safety and Health Administration (OSHA) and the National Institute for Occupational Safety and Health (NIOSH), respectively, will continue to be an important part of environmental and occupational health risk assessments. The purpose of this work was to develop a reliable analytical method for rapid and on-site assessments of occupational VOC exposures using field-capable thermal desorption-gas chromatography-mass spectrometry (TD-GC-MS) instrumentation (i.e. the HAPSITE® ER). The experiments involved in this study included determining TD-GC-MS parameters suitable for efficient analyte separation and quantitation on the HAPSITE® ER, determinations of analyte mass loadings that cause mass spectrometer detector saturations, generation of calibration curves, estimations of the limits of detection (LODs) and quantification (LOQs), as well as desorption efficiency and relative response factor repeatability. The LODs using Carbopack™ B and Tenax® TA sampling media were estimated and ranged from 0.2–1.9 ng and 0.045–0.3 ng, respectively. The LOQs using Carbopack™ B and Tenax TA sampling media were estimated and ranged from 1.0–6.3 ng and 0.2–1.1 ng, respectively. We have developed a reliable analytical method for chloroform,

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Disclosure statement
No potential conflict of interest was reported by the author(s).

Supplemental data for this article can be accessed online at https://doi.org/10.1080/03067319.2022.2121163.

benzene, trichloroethylene, and heptane using field-portable HAPSITE® ER instrumentation and Tenax® TA sorbent media. Reliable and accurate methods were developed for chloroform and trichloroethylene using Carbopack™ B sorbent media, however, this particular sorbent hadlow desorption efficiency and insufficient repeatability in relative response factors for many analytes. Our current and ongoing work in determining the uptake rates for analytes on Tenax® TA sorbent media will make the methods described herein applicable for on-site occupational VOC exposure assessments of chloroform, benzene, trichloroethylene, and heptane using either passive or active air sampling techniques.

Keywords

HAPSITE® ER; TD-GC-MS; gas chromatography; thermal desorption

1. Introduction

Airborne volatile organic compounds (VOCs) have long been known to negatively affect the environment and human health. The U.S. Clean Air Act Amendments of 1990 and their subsequent modifications by the U.S. Environmental Protection Agency (EPA) listed 187 hazardous air pollutants (HAPs) that are required to be monitored to protect public health [1,2]. A vast majority of these HAPs are VOCs that cover a broad range of chemical classes and cause significant acute and chronic health effects upon exposure, typically via inhalation, in a variety of indoor and outdoor environments [1,3,4]. For example, benzene is a particularly hazardous aromatic VOC since it is a known human carcinogen [5–7] and ubiquitous in air, mostly from anthropogenic sources such as fuel usage as well as from industries that produce petroleum and chemicals [8]. Exposure to other hazardous aromatic VOCs like toluene, ethylbenzene, xylenes, and mesitylene, which are also released via fuel usage, have been linked to sperm abnormalities, reduced foetal growth, cardiovascular disease, respiratory dysfunction, asthma, and other serious health effects [8,9]. Chlorinated VOCs like chloroform, trichloroethylene, and tetrachloroethylene are used in a variety of processes like extraction of pharmaceutical products, adhesives, pesticides, dry cleaning, and metal degreasing, and are either probable or known human carcinogens [10–13].

Since exposure to these types of VOCs can occur in a variety of occupational settings, U.S. federal agencies such as the Occupational Safety and Health Administration (OSHA) and the National Institute for Occupational Safety and Health (NIOSH) have established limits on a number of VOCs people can be exposed to in the workplace to maintain the safety and health of workers. Specifically, OSHA has established legally enforceable Permissible Exposure Limits (PELs) while NIOSH has established Recommended Exposure Limits (RELs) for many compounds [14,15]. Determining whether workers have been exposed to hazardous VOCs at levels exceeding PELs and RELs will continue to be an important part of occupational and environmental health risk assessments. A popular method for sampling and quantifying VOCs in air includes collection of analytes onto commercially available sorbent materials packed within thermal desorption (TD) tubes followed by subsequent analyses using benchtop thermal desorption – gas chromatography – mass spectrometry (TD-GC-MS) instrumentation [16–19]. The sampling process exploits the molecular interactions between VOCs in air and the sorbent material such that VOCs are physically adsorbed, concentrated, and retained onto the sorbent. TD tubes are then analysed with a GC-MS system in which TD tubes are heated under a flow of inert gas to thermally desorb the sampled VOCs and transfer them to an additional sorbent, or cold trap, housed within a GC-MS system. The cold trap is then rapidly heated under a flow of inert gas to transfer the sampled VOCs into a GC-MS system for separation and quantification. VOCs can be sampled onto TD tubes by two main techniques, each having their own inherent advantages and disadvantages [20,21]. The first is active air sampling (AAS), in which electronic pumps are used to pull air through the sorbent, while the second is passive air sampling (PAS), where analyte molecules are collected onto sorbents via diffusion [22]. Air sampling with TD tubes is highly advantageous because a variety of sorbent media are commercially available for certain applications and many sorbents offer quantitative retention of VOCs over a relatively large range of volatility [19,21]. Additionally, TD air sampling has been found to be less laborious and more sensitive than legacy air sampling techniques that involve charcoal tubes and solvent extraction [23,24]. For example, since analytes collected onto TD tubes can, in most cases, be completely transferred to the column of a TD-GC-MS instrument without problem, and since there are no solvent peaks involved in chromatographic analyses, lower limits of detection with better selectivity can be achieved [23,24]. Also, since the overall TD-GC-MS process is non-destructive to the sorbent media, TD tubes can be reconditioned and reused ~100 times [21,24], thereby minimising overall costs.

Traditional monitoring for assessing occupational VOC exposure compliance typically involves AAS onto sorbent tubes followed by sample analyses at an off-site laboratory [25,26]. However, this approach is problematic because sample collection, storage, and shipment to an off-site location for analyses is not only costly, but the process can take days to weeks to complete, which ultimately impedes the ability to make proper interventions to mitigate the immediate health risks associated with VOC over-exposure [26]. To overcome these problems and to quickly determine occupational VOC exposure compliance, new methods coupling TD air sampling with field-capable TD-GC-MS instrumentation are needed. TD air sampling in combination with TD-GC-MS is an ideal tool for occupational VOC exposure assessment because (1) the process involves simple air sampling techniques that enable whole sample analysis, (2) GC-MS is considered the best analytical technique for identifying and measuring individual compounds in complex air matrices because of the superb selectivity and sensitivity afforded by the instrumentation [17,27], and, (3) field-portable instruments are commercially available, making on-site exposure assessments possible. One such instrument is the Hazardous-Air-Pollutants-On-Site (HAPSITE®), which was developed by Inficon® (Syracuse, NY), and has been used to detect hazardous materials such as chemical warfare agents and VOCs in operational environments [24,28–36]. A recently upgraded version of this instrument, the Hazardous-Air-Pollutants-On-Site-Extended-Response (HAPSITE® ER), now provides a thermal desorption sampling system for analysis of TD tubes in the field with ~10 minute run times [37].

The purpose of this work was to develop a reliable analytical method for rapid and on-site assessment of occupational VOC exposures using field-portable HAPSITE® ER instrumentation for ten analytes (Table 1), and to compare the analytical performance of Carbopack™ B and Tenax® TA sorbent media in the method development using a combination of acceptance criteria established by NIOSH [38] as well as the EPA [39–41] for benchtop TD-GC-MS instrumentation. Tenax® TA is a hydrophobic porous polymer that has been widely used for sampling VOCs [19,35,42]. Some desirable characteristics of Tenax® TA are that the analytical problems associated with environmental water during sampling (i.e. a reduction in analyte retention from the competition between water and analyte adsorption onto the active sites of the sorbent) are lessened compared to that of carbonaceous TD material, such as Carbopack™ B [19,35,43]. Tenax® TA also exhibits excellent desorption efficiency for many compounds [44]. However, researchers have claimed that Tenax® TA is unsuitable for sampling compounds with boiling points ranging from <100°C (i.e. <212°F) [42,45], and reports have claimed that the sorbent does not strongly retain benzene under ambient conditions [44]. Furthermore, benzene and benzene derivative artefacts have been reported to be potential analyte interferences in TD-GC-MS analyses when using Tenax® TA to sample VOCs [45,46]. Since chloroform and benzene have the lowest PELs and RELs of the analytes studied in this work (Table 1) and given the aforementioned shortcomings of the use of Tenax® TA described in the literature, our hypothesis was that Carbopack™ B would be a more suitable choice of sorbent and have comparatively better analytical performance for our research objectives.

To compare the analytical performance of these sorbents, the experiments involved in this study included determining TD-GC-MS methods suitable for efficient analyte separation and quantitation on the HAPSITE® ER, determinations of analyte mass loadings that cause mass spectrometer (MS) detector saturations, generation of calibration curves, estimations of the limits of detection (LODs) and quantification (LOQs), as well as desorption efficiency and relative response factor repeatability studies. The analytical method described herein will be useful for occupational VOC exposure assessments, which will enable rapid, on-site analyses to determine compliance with worker exposure and public health standards.

2. Experimental

2.1. Chemicals, materials, and instrumentation

A HAPSITE® ER portable TD-GC-MS instrument, a thermal desorber sampling system, tri-bed concentrators, and internal standard gas canisters containing bromopentafluorobenzene (BPFB) and 1,3,5-tris(trifluoromethyl)benzene (TRIS) at 5.43 ppmv and 10.36 ppmv in nitrogen (N_2), respectively, were purchased from Inficon® (Syracuse, NY). Since it has been shown that glass TD tubes are more appropriate for use on the HAPSITE® ER compared to stainless steel [37], custom glass TD tubes filled with Carbopack™ B (40/60 mesh) and Tenax® TA (35/60 mesh) sorbents (6.63 mm OD × 89 mm packed with 52 mm bed length) were purchased from Supelco (Bellefonte, PA). Ultra-high purity N_2 was purchased from Wright Brothers (Cincinnati, OH), and the cylinder was connected to the HAPSITE® ER to serve as the carrier gas. A calibration solution loading rig (CSLR), and a tube conditioner (TC-20) were purchased from Markes International® (Cincinnati, OH) and connected to an N_2 cylinder using appropriate fittings. For all experiments, the flow rate of N_2 at the CSLR was set to 50 ± 5 mL/min using a needle valve and measured with a DryCal® DC-Lite flow calibrator obtained from Brandt Instruments, Inc. (Prairieville, LA).

Tedlar® gas sampling bags (0.5 L with single polypropylene septum fitting) as well as brass Swagelok® fittings with polytetrafluoroethylene (PTFE) ferrules for use with ¼-inch OD TD tubes were acquired from SKC Inc. (Eighty Four, PA). Gas tight syringes (model #'s 1825, 1002, 1005, 1025 and 1050) were purchased from Hamilton Company (Reno, NV). Two gas standards containing multiple VOCs in N_2 were purchased from Scott™ Analysed Gases (Plumsteadville, PA). The first was a 19-compound standard that was used for the MS detector saturation study on Carbopack™ B sorbent (Table S1). Ten out of the 19 compounds in this standard were of interest, which included those listed in Table 1. The second gas standard solely contained the 10 analytes in Table 1 and was used for the MS detector saturation study using Tenax® TA. The 10-compound gas standard was also used to construct calibration curves, perform LOD and LOQ studies, and determine desorption efficiencies and recoveries for analytes collected on Carbopack™ B and Tenax® TA sorbents. Table 2 lists the analyte concentrations for the two gas standards, the quantitative ions (*m/z*) used for all analyses, and the internal standard used for each analyte.

All TD tubes were conditioned for 1.5 hours using a Markes International® TC-20, capped using Swagelok® fittings, and stored at room temperature prior to use. The conditioning temperatures for TD tubes containing Carbopack™ B and Tenax® TA sorbents were 350 and 310°C, respectively. Prior to any TD-GC-MS runs, the HAPSITE® ER was tuned using the default conditions and sequence from the manufacturer. For all TD-GC-MS runs on the HAPSITE® ER, a 100% polydimethylsiloxane column (15 m × 0.25 mm ID; 1.0 μm film thickness) was used, the N_2 carrier gas pressure was set to 88 kPa, and the scanning range was set to 45–300 *m/z* with filament delays and dwell times set to 45 seconds and 400 microseconds (μs), respectively. The column, membrane, valve oven, heated lines, and thermal desorber temperatures for a particular TD-GC-MS method were noted accordingly in the supplementary information section. The quantitative ions for TRIS and BPFB internal standards for all analyses were 213 and 117 *m/z*, respectively. Data were analysed using the ER IQ software package (version 2.40.002) as well as the AMDIS and NIST MS spectral libraries provided by Inficon®.

2.2. MS detector saturation studies

ER IQ software indicates whenever a sample run on the HAPSITE® ER has saturated the MS detector by exhibiting red lines beneath the peak on the total ion chromatogram (TIC). If this occurs, the instrument automatically runs a default concentrator clean out method to heat and remove residual sample from the concentrator until a certain TIC count is reached. The following describes the procedure for determining the mass at which the analytes collected on Carbopack™ B sampling media saturated the MS detector on the HAPSITE® ER. Analyses were performed by examining one measurement of the MS detector response at various concentration levels. The results from this study formed the basis for choosing the relative analyte concentrations of the 10-compound gas standard such that linear mass ranges for all analytes could be determined when making future calibration curves without saturating the MS detector. A Tedlar® gas sampling bag was filled with N_2 then evacuated. This process was repeated four times to remove potential impurities. The bag was then connected to a cylinder containing the 19-compound gas standard and filled ~75% full.

Using gas tight syringes, different volumes of gas standard were withdrawn from the bag by piercing the septum. These volumes of gas standard were individually spiked onto various TD tubes using a Markes International® CSLR per the manufacturer's instructions. Table S2 describes the volumes and corresponding masses of gas standard injected onto tubes containing Carbopack™ B. Samples were analysed using the TD-GC-MS method described in Figure S1. A MS detector saturation study was also performed on analytes collected on Tenax® TA using a similar procedure to that described above, except the 10-compound gas standard was used, different volumes of gas standard were injected (Table S3), and TD tubes were analysed using the TD-GC-MS method described in Figure S2.

To calculate the theoretical mass of analyte injected onto TD tubes (m_x) in ng using a known injection volume (V) in mL, Equation (1) was used where C is the ppmv concentration of the individual component in the multi-component gas standard, R is the ideal gas constant (8,314.46 L Pa mol^{-1} K^{-1}), P is the pressure in Pa, M is the molar mass in g/mol, and T is the absolute temperature (K) [24]. All analyte masses were calculated assuming a pressure of 101,325 Pa and temperature of 293.2 K. Plots of the TIC maximum vs. analyte mass were made for each analyte on each sorbent (Figures S3 and S4) with one data point at each spike level. Red-circular data points were instances where ER IQ software reported a saturated MS signal while black-square data points indicate signals that were within a suitable magnitude of the MS detector. The approximate mass range of MS detector saturations for all analytes were indicated by the grey regions in Figures S3 and S4.

$$m_x = \frac{P \cdot V \cdot M \cdot C}{R \cdot T} \tag{1}$$

2.3. Calibration curves

To create calibration curves, seven media blanks were analysed to determine the baseline level for each analyte on each sorbent. The media blanks were then rerun to give the media blank baseline, and these results were averaged and used to blank correct the data. To make calibration standards, a Tedlar® gas sampling bag, previously filled with N_2 and evacuated to remove potential impurities, was filled with the 10-compound gas standard, then various volumes of standard gas were injected onto TD tubes in triplicate using the CSLR and gas tight syringes according to Tables 3 and 4 for Carbopack™ B and Tenax® TA sorbents, respectively. Standards with known analyte masses were analysed using the TD-GC-MS methods described in Figures S2 and S5.

Calibration curves were constructed by plotting area ratios on the y-axis and concentration ratios on the x-axis then fitting data to a linear equation. Equations (2) and (3) describe calculations of these quantities where A_x and m_x correspond to the area and mass of the analyte while A_{IS} and m_{IS} are the area and mass of the internal standard [40].

$$Area\ ratio\ = \frac{A_x}{A_{IS}}$$

(2)

$$\mathit{Concentration\ ratio} = \frac{m_x}{m_{IS}}$$

(3)

Values of m_{IS} in Equation (3) were calculated as ng masses. This was done by converting the volume of internal standard injected by the HAPSITE® ER from the internal standard canister (0.4 mL per discussions with Inficon®) during each TD-GC-MS analysis to a mass using Equation (1) assuming a temperature and pressure 293.2 K and 101,325 Pa. Therefore, concentration ratios rendered unitless quantities. Equation (4) was used to calculate and propagate uncertainties in the area ratios ($\delta(Arearatio)$) where δA_x and δA_{IS} are the uncertainties in the analyte areas and internal standard areas, and $\widetilde{Arearatio}$, $\widetilde{A_x}$, and $\widetilde{A_{IS}}$ are the average values of the area ratio, analyte area, and internal standard area, respectively [49].

$$\frac{\delta(\mathit{Area\ ratio}\ )}{\widetilde{\mathit{Area\ ratio}}} = \sqrt{\left(\frac{\delta A_x}{\widetilde{A_x}}\right)^2 + \left(\frac{\delta A_{IS}}{\widetilde{A_{IS}}}\right)^2}$$

(4)

Response factors (RF) for analytes (subscript x) and internal standards (subscript IS) were calculated using Equation (5) while relative response factors for analytes (RRF_x) were calculated via Equation (6) [39,40]. Calibrations were deemed acceptable if the relative standard deviation in the RRF_x (i.e. $\%RSD_{RRF_x}$) was ≤ 30% [39,40]. Additional acceptance criteria for calibrations are listed in Table S4 and included relative retention times (RRT), area responses of internal standard ($\%A_{IS}$), and retention time shifts of the internal standards (RT_{shift}) [39,40].

$$RF_x = \frac{A_x}{m_x}\ or\ RF_{IS} = \frac{A_{IS}}{m_{IS}}$$

(5)

$$RRF_x = \frac{A_x \cdot m_{IS}}{A_{IS} \cdot m_x}$$

(6)

2.4. Continuing calibration verifications (CCVs)

After initial calibration curves were made and prior to analysis of blanks or samples, continuing calibration verifications (CCVs) were run near the mid-point level of the multi-level calibration curve at the beginning of a TD-GC-MS sequence as well as after 10 runs to confirm that the HAPSITE® ER continued to generate results within acceptable agreement to the most current calibration curve [39,40]. Several quality assurance parameters were calculated from CCV data to evaluate the analytical performance of the instrument. These parameters and acceptance criteria [39,40] are listed in Table 5. The measured analyte mass of CCV standards in ng ($m_{x,CCV}$) was calculated via Equation (7) where DF is the dilution factor (which was 1 for all experiments) and $\overline{RRF}_x$ is the average relative response factor of the analyte from the most recent calibration [40].

$$m_{x,CCV} = \frac{A_x \cdot m_{IS} \cdot DF}{A_{IS} \cdot \overline{RRF}_x} \tag{7}$$

2.5. Estimations of limits of detection (LODs) and limits of quantification (LOQs)

LODs and LOQs for the analytes collected on each sorbent were estimated using the same standard preparation procedure described in the calibration curve section, except smaller volumes of gas standard were used, and injections were made in duplicate. Additionally, two media blank samples were analysed for each sorbent. The TD-GC-MS methods used for determining LODs and LOQs on Carbopack™ B and Tenax® TA sorbents are shown in Figure S2 and S5. Tables S5–S7 show the volumes and corresponding masses that were used for the LOD and LOQ studies on each sorbent. In most cases, the masses of analytes used in the LOD and LOQ studies were lower than the lowest standard used for the calibration curve. For this reason, LODs and LOQs reported herein are estimated values. Plots of raw area counts vs. analyte mass (ng) were made, and from this data, and Equations (8) and (9) were used to calculate the estimated LODs where $SE(y)$ is the standard error in the linear regression, s is the slope, B is the average signal of the media blank, and b is the y-intercept [38,50,51]. LODs were reported as the larger value obtained between Equations 8 and 9. Plots of area ratio vs. concentration ratio were also made, and the percent recovery was calculated at each level. LOQs were reported as the larger value obtained from Equation 10 or the mass above which the percent recovery was at least 75% [38].

$$LOD = \frac{3 \cdot SE(y)}{s} \tag{8}$$

$$LOD = \frac{3 \cdot SE(y) + B - b}{s} \tag{9}$$

$$LOQ = 3.33 \cdot LOD \tag{10}$$

2.6. Desorption efficiency and relative response factor (RRF) repeatability studies

Desorption efficiency and relative response factor repeatability studies were performed for analytes collected on Carbopack™ B and Tenax® TA sorbents at three different spike levels by spiking tubes with a known mass of analyte, analysing the spiked tubes using an appropriate method (see Figures S2 and S5) followed by the analysis of an empty tube without any sorbent, then re-analysing the spiked tubes. The spike levels used for studies on Carbopack™ B sorbent were 1.00, 3.00, and 12.50 mL volumes, while those for studies on Tenax® TA sorbent were 0.75, 2.00, and 5.00 mL volumes (see Tables 3 and 4 for corresponding analyte masses). Six replicates were analysed at each spike level. Analytes were deemed to be adequately desorbed from sorbent media if the criteria in Table 6 were met where the percent desorption efficiency and percent repeatability in the relative response factors values were >95% [39] and 100 ±20%, respectively.

3. Results and discussion

3.1. MS detector saturation studies

The mass ranges of MS detector saturation for each analyte on each sorbent are summarised in Table 7. The analytes with the lowest mass range of MS detector saturation were ethylbenzene, *p*-xylene, *o*-xylene, and mesitylene. The saturation ranges for trichloroethylene and tetrachloroethylene were observed to be quite large in comparison to the other compounds. Based on these data, it would not be recommended to analyse compounds near the low end of the mass ranges reported in Table 7 for each analyte to avoid MS detector saturation on the HAPSITE® ER.

3.2. Calibration curves

From calibration curves using TRIS (Figure 1(a–c)) and BPFB (Figure 1(b–d)) as internal standards, the slopes, y-intercepts, as well as values of $\overline{RRF}_x$ and $\%RSD_{RRF}$ for all analytes were calculated and are summarised in Tables 8 and 9 for Carbopack™ B and Tenax® TA sorbents, respectively. All of the calibration curves using Tenax® TA sorbent (Figure 1 (c, d) were acceptable because the $\%RSD_{RRF}$ values for all analytes were < 30% and the criteria listed in Table S4 were satisfied [39,40]. These results suggest that Tenax® TA is a suitable sorbent for our research goals despite the potential shortcomings highlighted in the introduction for using Tenax® TA as a sorbent for sampling lower boiling point compounds. Applying the same acceptance criteria to the calibration curves created using Carbopack™ B sorbent revealed acceptable calibrations for chloroform, benzene, trichloroethylene, heptane, toluene, tetrachloroethylene, and ethylbenzene. However, calibration data for *p*-xylene, *o*-xylene, and mesitylene using Carbopack™ B were unacceptable because of values > 30 $\%RSD_{RRF}$ (Table 8). The calibration curves in Figure 1 were used for the desorption efficiency and relative response factor repeatability studies on Tenax® TA, and LOD/LOQ studies on Carbopack™ B. The calibration curves used for desorption efficiency and relative response factor repeatability studies on Carbopack™ B (Figure S6 and Table S8) and the LOD/LOQ studies on Tenax® TA (Figure S7 and Table S9) are shown in the supplemental information section.

3.3. Continuing calibration verifications (CCVs)

With respect to the LOD/LOQ, desorption efficiency, and relative response factor repeatability studies on Carbopack™ B and Tenax® TA sorbents described in the next sections, the acceptance criteria from CCV data for some of the analytes were, in some cases, outside of the ranges described in Table 5. Table 10 represents instances in which the acceptance criteria of CCV data were met, indicated by 'Y', or failed, indicated by 'N', for the analytes. Tables S10 and S11 provide summaries of all CCV data in this work. The lack of precision for the compounds in Table 10 is likely due to the relatively slow mass scan time of the HAPSITE® ER compared to bench top instrumentation, resulting in attenuation or elimination of detection capabilities of VOCs with high boiling points [24].

3.4. Estimations of limits of detection (LODs) and limits of quantification (LOQs)

The LODs and LOQs of each analyte on each sorbent were estimated. Plots of raw area counts vs analyte mass (ng) using Carbopack™ B and Tenax® TA sorbents are presented in Figure S8. The slopes, y-intercepts, and values of $SE(y)$, and $\%RSD_{RRF}$ were calculated from these data for each sorbent (Tables S12 and S13) and were used to estimate the LODs and LOQs. Plots of area ratio vs. concentration ratio were made for each analyte for each sorbent (Figure S9) and percent recoveries were calculated at each spike level (Table S14).

The estimated LODs and LOQs for each analyte on each sorbent are summarised in Table 11. The estimated LODs using Carbopack™ B and Tenax® TA sampling media ranged from 0.2–1.9 ng and 0.045–0.3 ng, respectively. The estimated LOQs using Carbopack™ B and Tenax TA sampling media ranged from 1.0–6.3 ng and 0.2–1.1 ng, respectively. Consistent with the design limitations of a portable system the HAPSITE® ER has lower sensitivity, lower resolution and easier saturation compared to benchtop TD-GC-MS instrumentation [24]. Rodriguez-Navas and co-workers previously measured VOCs from several municipal solid waste streams by active sampling onto Tenax® TA and Carboxen™ 1000 sorbents followed by analyses on bench top TD-GC-MS instrumentation [52]. Ninety-three compounds were analysed in this study including the 10 compounds in the present study. The LODs measured for 93 compounds in Rodriguez-Navas and co-workers' study ranged from ~1 to ~4 pg. Comparing this data to the estimated LODs in the present study reveal that the estimated LODs determined on the HAPSITE® ER using Carbopack™ B sorbent were ~200 to 500 times higher than that of the benchtop instrumentation used in Rodriguez-Navas and co-workers study. Furthermore, the estimated LODs using Tenax® TA sorbent in the present study were ~40 to ~100 times higher than that of the benchtop instrumentation.

3.5. Desorption efficiency and relative response factor (RRF) repeatability studies

Desorption efficiency and relative response factor repeatability studies were performed for each sorbent on the HAPSITE® ER to compare analytical performances. Ethylbenzene, *p*-xylene, *o*-xylene, and mesitylene did not desorb well from Carbopack™ B sorbent since the percent desorption efficiency values for these compounds were well below 95% for many analytes (Table 12). These results explain why the calibration curves for these compounds generated from Carbopack™ B sorbent had $\%RSD_{RRF}$ values near or > 30%. On the contrary, the percent desorption efficiency values for all compounds using Tenax® TA were >95%

(Table 12), thus exhibiting efficient analyte desorption from the media. As highlighted in the Introduction, Tenax® TA has been noted to exhibit efficient analyte desorption [44]. Results for the relative response factor repeatability study at each spike level for each sorbent are summarised in Table 13.

3.6. Determining the method viability for analytes

Considering the acceptance criteria described in Tables 5 and 6, accurate and reliable measurements for chloroform and trichloroethylene could be made on the HAPSITE® ER using Carbopack® B sorbent. For many of the analytes collected on this sorbent, the CCV criteria were not met (Table 10) and/or the $\%Rep.RRF$ values were outside the acceptance range of 100 ±20% (Table 13). However, the method described herein is viable for the analysis of chloroform, benzene, trichloroethylene, and heptane on the HAPSITE® ER using Tenax® TA sorbent since the CCV criteria were satisfied for these compounds for all experiments (Table 10), and the $\%Rep._{RRF}$ values were within the acceptance window of 100 ±20% (Table 13).

4. Conclusions

Despite reported concerns of using Tenax® TA as a sorbent to sample benzene and other low boiling point VOCs in air, we have developed a reliable analytical method for the rapid and on-site assessment of occupational exposures to chloroform, benzene, trichloroethylene, and heptane using field-portable HAPSITE® ER instrumentation and Tenax® TA sorbent media. Though reliable and accurate methods were developed for chloroform, and trichloroethylene using Carbopack™ B sorbent media, the data suggest that this sorbent does not perform better than Tenax® TA for our set of analytes because of low desorption efficiency and insufficient repeatability in relative response factors for many of the analytes. Generally speaking, the less volatile compounds performed more poorly for both sorbents.

The methods developed herein using HAPSITE® ER instrumentation and Tenax® TA are significant since (1) they enable the detection of chloroform and benzene, which have the lowest PELs and RELs of all analytes investigated, (2) they are highly reliable since the acceptance criteria established by U.S. federal agencies such as NIOSH and the EPA were satisfied for these analytes, and (3) the field-portable capabilities and short run times (~10 minute/sample) afforded by the instrumentation allow the user to make timely interventions to mitigate the immediate health risks associated with over-exposure to these compounds without having to ship samples to an off-site location. Our current and on-going work in determining the uptake rates for analytes on Tenax® TA sorbent packed within glass TD tubes, which has been shown to be a more appropriate tube material than stainless steel for use on the HAPSITE® ER [37], will make the methods described herein applicable for occupational VOC exposure assessments of chloroform, benzene, trichloroethylene, and heptane using either PAS and AAS techniques. Going forward, field evaluation with side-by-side samples analyzed in a laboratory would further validate the method for worker exposure assessment.

Alternative acceptance criteria may be applied to the data in this work to increase the number of compounds applicable for the method if the user is willing to sacrifice, to a reasonable extent, the accuracy, precision, and bias of the data. For example, if the acceptance criteria of $\%D_{RRF}$, $\%B$, and $\%P$ from CCV data were expanded to ±40%, ±40%, and ±30%, respectively, and if the $\%Rep._{RRF}$ value criteria were expanded to 100 ±30%, the methods described herein would be viable for the detection and measurement of all ten analytes using Tenax® TA sorbent (Tables S15, S16, and S17). Quantitative sample analyses should not proceed for analytes that fail to meet the user-defined acceptance criteria. However, since the TD-GC-MS instrumentation offers excellent selectivity and significantly reduces the risk of false positives as compared to GC-FID, it is reasonable to continue analyses for analytes that fail the acceptance criteria with an understanding that the results could be used as estimated values for screening purposes [53].

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

The authors gratefully acknowledge Ronnee Andrews and Ryan LeBouf for reviewing the draft manuscript, as well as Peter B. Shaw for statistical data analyses. The Oak Ridge Institute for Science and Education (ORISE) is also gratefully acknowledged for supporting this work.

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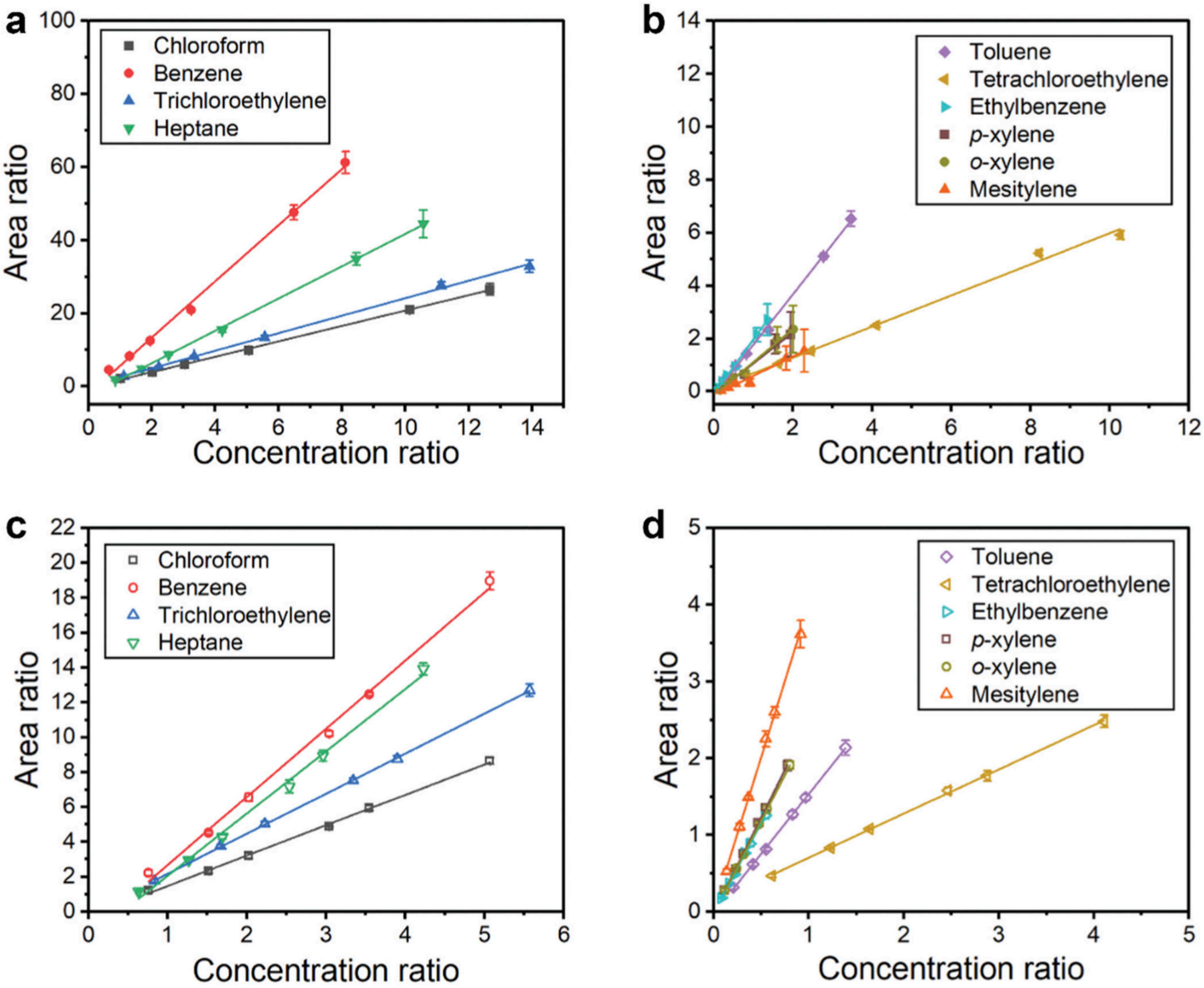

Figure 1.

Calibration curves for analytes collected on (a and b) Carbopack™ B, and (c and d) Tenax® TA sorbents. TRIS was used an internal standard in plots (a) and (c) while BPFB was used as the internal standard in plots (b) and (d).

Table 1.

Molecular weights, boiling points, OSHA PELs, and NIOSH RELs for the 10 analytes.

Analyte	**Molecular weight (g/mol) [47]**	**Boiling point (°C) [48]**	**OSHA PEL (ppmv) [14,15]**	**NIOSH REL (ppmv) [14,15]**
Chloroform	119.4	61.2	2	2
Benzene	78.1	80.1	1	0.1
Trichloroethylene	131.4	86.8	100	25
Heptane	100.2	98.4	500	85
Toluene	92.1	110.6	200	100
Tetrachloroethylene	165.8	121.2	100	50
Ethylbenzene	106.2	136.2	100	100
p-xylene	106.2	138.3	100	100
o-xylene	106.2	144.4	100	100
Mesitylene	120.2	164.7	100	100

Table 2.

Concentrations of analytes within the 19-compound and 10-compound gas standards, and quantitative ions (*m/z*) used for all analyses. All compounds are balanced in N_2 and have ± 5% analytical uncertainty.

Analyte	**Concentrations in 19-compound gas standard (ppmv)**	**Concentrations in 10-compound gas standard (ppmv)**	**Quantitative ion (*m/z*)**	**Internal standard used**
Chloroform	1.03	5.20	83	TRIS
Benzene	1.00	5.09	78	TRIS
Trichloroethylene	0.97	5.19	132	TRIS
Heptane	1.02	5.17	71	TRIS
Toluene	1.00	3.08	91	BPFB
Tetrachloroethylene	1.00	5.07	166	BPFB
Ethylbenzene	0.98	1.05	91	BPFB
p-xylene	0.94	1.50	91	BPFB
o-xylene	1.02	1.55	91	BPFB
Mesitylene	0.99	1.56	105	BPFB

Table 3.

Volumes and masses of compounds injected onto TD tubes containing Carbopack™ B sorbent for generating calibration curves.

		Injection volume (mL)						
Analyte	**Concentration in gas standard (ppmv)**	**1.00**	**2.00**	**3.00**	**5.00**	**10.0**	**12.5**	
Chloroform	5.20	25.8	51.6	77.4	129	258	323	Analyte mass (ng)
Benzene	5.09	16.5	33.0	49.6	82.6	165	207	
Trichloroethylene	5.19	28.3	56.7	85.0	142	283	354	
Heptane	5.17	21.5	43.1	64.6	108	215	269	
Toluene	3.08	11.8	23.6	35.4	59.0	118	147	
Tetrachloroethylene	5.07	34.9	69.9	105	175	349	437	
Ethylbenzene	1.05	4.64	9.27	13.9	23.2	46.3	57.9	
p-xylene	1.50	6.62	13.2	19.9	33.1	66.2	82.8	
o-xylene	1.55	6.84	13.7	20.5	34.2	68.4	85.5	
Mesitylene	1.56	7.79	15.6	23.4	39.0	77.9	97.4	

Table 4.

Volumes and masses of compounds injected onto TD tubes containing Tenax® TA sorbent for generating calibration curves.

		Injection volume (mL)						
Analyte	**Concentration in gas standard (ppmv)**	**0.75**	**1.50**	**2.00**	**3.00**	**3.50**	**5.00**	
Chloroform	5.20	19.4	38.7	51.6	77.4	90.3	129	Analyte mass (ng)
Benzene	5.09	12.4	24.8	33.0	49.6	57.8	82.6	
Trichloroethylene	5.19	21.3	42.5	56.7	85.0	99.2	142	
Heptane	5.17	16.1	32.3	43.1	64.6	75.4	108	
Toluene	3.08	8.84	17.7	23.6	35.4	41.3	59.0	
Tetrachloroethylene	5.07	26.2	52.4	69.9	105	122	175	
Ethylbenzene	1.05	3.48	6.95	9.27	13.9	16.2	23.2	
p-xylene	1.50	4.97	9.93	13.2	19.9	23.2	33.1	
o-xylene	1.55	5.13	10.3	13.7	20.5	23.9	34.2	
Mesitylene	1.56	5.85	11.7	15.6	23.4	27.3	39.0	

Table 5.

Equations, symbol definitions, and acceptance criteria for CCVs.

Parameter	Equation	Acceptance criteria	Symbol definitions
Percent difference in the RRF ($\%D_{RRF}$)	$\%D_{RRF} = 100 \times \frac{RRF_{x,CCV} - \overline{RRF}_x}{\overline{RRF}_x}$	± 30%	$RRF_{x,CCV}$ = RRF of analyte in the CCV standard $m_{x,CCV\#1}$ = Measured analyte mass of CCV standard spike #1 (ng) $m_{x,CCV\#2}$ = Measured analyte mass of CCV standard spike #2 (ng) $\overline{m}_{x,CCV} =$ Average of $m_{x,CCV\#1}$ and $m_{x,CCV\#2}$(ng)
Analytical bias (%B)	$\%B = 100 \times \frac{m_{x,CCV} - m_x}{m_x}$	± 30%	
Analytical precision (%P)	$\%P = 100 \times \frac{\lvert m_{x,CCV\#1} - m_{x,CCV\#2} \rvert}{x,CCV}$	≤20%	

Table 6.

Parameters, equations, symbol definitions, and acceptance criteria for desorption efficiency and relative response factor repeatability studies on Carbopack™ B and tenax® TA sorbents.

Parameter	Equation	Acceptance criteria	Symbol definitions
Percent desorption efficiency ($\%Desorptionefficiency$)	$\%Desorptionefficiency = 100 \times 1 - \frac{P \cdot A_{x,\,spike\#1rerun}}{P.A._{x,spike\#1}}$	>95%	$P.A._{x,spike\#1}$ = peak area of analyte measured after the initial spike of standard onto TD tube $P.A.^{\mathrm{x,spike\#1}rerun}$ = peak area of analyte measured after rerunning the initially spiked TD tube
Percent repeatability in the Relative Response Factor ($\%Rep._{RRF}$)	$\%Rep._{RRF} = 100 \times \frac{m_{x,\,meas.}}{m_x}$	100 ± 20%	$m_{x,meas.}$ = Measured mass of spiked analyte (calculated via Equation 7 in main text) m_x = Theoretical mass of analyte (calculated via Equation 1 in main text)

Table 7.

Results summary of MS detector saturation study on Carbopack™ B and Tenax® TA sorbents.

	~ Mass range of MS detector saturation (ng)	
Analyte	**Carbopack™ B**	**Tenax® TA**
Chloroform	512–767	645–710
Benzene	325–487	248–289
Trichloroethylene	>795	>850
Heptane	425–637	431–484
Toluene	230–306	118–147
Tetrachloroethylene	>1033	611–699
Ethylbenzene	86.5–130	104–116
p-xylene	124–207	99.3–116
o-xylene	135–225	103–120
Mesitylene	148–247	39.0–58.5

Table 8.

Summary of the slopes, y-intercepts, $\%RSD_{RF_x}$, and $\%RSD_{RRF}$ values from the analyte calibration data in Figure 1(a,b) using Carbopack™ B sorbent.

Analyte	**Slope**	**y-intercept**	$\overline{RRF}_x$	$\%RSD_{RRF_x}$
Chloroform [a]	2.11 ± 0.02	−0.31 ± 0.15	2.03	3.93
Benzene [a]	7.68 ± 0.13	−1.99 ± 0.58	6.84	7.54
Trichloroethylene [a]	2.40 ± 0.04	0.18 ± 0.35	2.44	3.63
Heptane [a]	4.42 ± 0.12	−2.47 ± 0.73	3.42	22.5
Toluene [b]	1.90 ± 0.02	−0.14 ± 0.04	1.75	8.38
Tetrachloroethylene [b]	0.59 ± 0.01	0.10 ± 0.07	0.63	5.69
Ethylbenzene [b]	2.06 ± 0.12	−0.10 ± 0.10	1.72	21.5
p-xylene [b]	1.17 ± 0.12	−0.12 ± 0.14	0.92	33.4
o-xylene [b]	1.25 ± 0.13	−0.15 ± 0.15	0.95	33.4
Mesitylene [b]	0.73 ± 0.11	−0.15 ± 0.14	0.48	51.1

[a and b] represent the use of TRIS or BPFB as the internal standard, respectively.

$\%RSD_{RF_{TRIS}} = 5.66$ and $\%RSD_{RF_{BPFB}} = 2.54$.

Table 9.

Summary of the slopes, y-intercepts, $\%RSD_{RF_x}$, and $\%RSD_{RRF}$ values from the analyte calibration data in Figure 1(c,d) using Tenax® TA sorbent.

Analyte	Slope	y-intercept	$\overline{RRF}_x$	$\%RSD_{RRF_x}$
Chloroform [a]	1.74 ± 0.02	−0.28 ± 0.07	1.61	4.81
Benzene [a]	6.11 ± 0.10	−1.25 ± 0.19	5.14	9.17
Trichloroethylene [a]	2.30 ± 0.03	−0.13 ± 0.09	2.23	3.76
Heptane [a]	3.57 ± 0.07	−1.52 ± 0.19	2.64	18.8
Toluene [b]	1.56 ± 0.03	−0.03 ± 0.03	1.51	4.98
Tetrachloroethylene [b]	0.58 ± 0.01	0.12 ± 0.02	0.66	8.56
Ethylbenzene [b]	2.34 ± 0.04	−0.02 ± 0.01	2.26	4.62
p-xylene [b]	2.49 ± 0.04	−0.02 ± 0.02	2.43	4.51
o-xylene [b]	2.39 ± 0.03	−0.01 ± 0.02	2.35	4.02
Mesitylene [b]	3.98 ± 0.09	0.01 ± 0.05	4.00	4.66

[a and b] represent the use of TRIS or BPFB as the internal standard, respectively.

$\%RSD_{RF_{TRIS}} = 4.37$ and $\%RSD_{RF_{BPFB}} = 8.04$.

Table 10.

Summary of the instances in which CCV data either met, indicated by ‘Y’, or failed, indicated by ‘N’ the acceptance criteria described in Table 5.

	Carbopack™ B						Tenax® TA					
	LOD/LOQ study			Desorption efficiency and relative response factor repeatability study			LOD/LOQ study			Desorption efficiency and relative response factor repeatability study		
Analyte	**%DRRF**	**%**	**%P**	**%DRRR**	**%B**	**%**	**%D_{RRF}**	**%B**	**%P**	**%D_{RRF}**	**%B**	**%P**
Chloroform	Y	Y	Y	Y	Y	Y	Y	Y	Y	Y	Y	Y
Benzene	Y	Y	Y	Y	Y	Y	Y	Y	Y	Y	Y	Y
Trichloroethylene	Y	Y	Y	Y	Y	Y	Y	Y	Y	Y	Y	Y
Heptane	N	N	Y	-	-	-	Y	Y	Y	Y	Y	Y
Toluene	Y	Y	Y	-	-	-	Y	Y	N	Y	Y	N
Tetrachloroethylene	N	N	Y	N	N	N	Y	Y	Y	Y	Y	N
Ethylbenzene	Y	Y	Y	-	-	-	Y	Y	N	N	N	N
p-xylene	-	-	-	-	-	-	Y	Y	N	N	N	N
o-xylene	-	-	-	-	-	-	Y	Y	N	N	N	N
Mesitylene	-	-	-	-	-	-	Y	Y	N	Y	Y	N

[‘-’] Denotes instances where the calibration curve was unacceptable.

Table 11.

Summary of the estimated analyte LODs, and LOQs from Carbopack™ B and Tenax® TA sorbents.

Analyte	Carbopack™ B		Tenax® TA	
	LOD (ng)	LOQ (ng)	LOD (ng)	LOQ (ng)
Chloroform	[a] 0.2	[a] 1.3	[a] 0.3	[c] 0.9
Benzene	[a] 0.3	[c] 1.0	[a] 0.2	[c] 0.6
Trichloroethylene	[a] 0.5	[c] 1.7	[a] 0.3	[c] 1.0
Heptane	[b] 1.9	[c] 6.3	[b] 0.2	[c] 0.8
Toluene	[b] 0.6	[c] 1.9	[a] 0.1	[c] 0.3
Tetrachloroethylene	[b] 0.7	[c] 2.2	[a] 0.1	[c] 0.3
Ethylbenzene	[b] 1.2	[c] 3.8	[b] 0.3	[c] 1.1
p-xylene	-	-	[b] 4.5×10^{-2}	[c] 0.2
o-xylene	-	-	[b] 0.1	[c] 0.2
Mesitylene	-	-	[b] 0.3	[c] 0.9

[a, b, and c] represent the use of Equations (8–10), respectively while

[d] denotes the mass above which percent recovery was at least 75%.

'-' indicates an acceptable calibration curve could not be generated for the experiment.

Table 12.

Summary of the desorption efficiency studies. Average *%Desorption efficiency* values for Carbopack™ B and Tenax® TA sorbents at various spike levels (n =6 for each spike level).

	***%Desorption efficiency* on Carbopack™ B**			***%Desorption efficiency* on Tenax® TA**		
Analyte	**1.00 mL spike**	**3.00 mL spike**	**12.5 mL spike**	**0.75 mL spike**	**2.00 mL spike**	**5.00 mL spike**
Chloroform	99.9 ± 0.1	100.0 ± 0.0	100.0 ± 0.0	100.0 ± 0.1	100.0 ± 0.0	100.0 ± 0.0
Benzene	99.9 ± 0.1	99.9 ± 0.0	100.0 ± 0.0	99.8 ± 0.2	99.9 ± 0.0	100.0 ± 0.1
Trichloroethylene	100.0 ± 0.1	99.9 ± 0.0	100.0 ± 0.0	100.0 ± 0.0	100.0 ± 0.0	0100.0 ± 0.0
Heptane	[a] 94.1 ± 2.8	[a] 97.0 ± 1.4	[a] 99.6 ± 0.3	99.9 ± 0.0	100.0 ± 0.0	0100.0 ± 0.0
Toluene	[a] 97.8 ± 2.0	[a] 98.9 ± 0.8	[a] 99.9 ± 0.1	[a] 99.8 ± 0.1	[a] 99.9 ± 0.0	[a] 100.0 ± 0.0
Tetrachloroethylene	[a] 99.7 ± 0.3	[a] 99.9 ± 0.0	[a] 100.0 ± 0.0	[a] 99.9 ± 0.0	[a]100.0 ± 0.0	[a] 100.0 ± 0.0
Ethylbenzene	[a] 81 ± 4.8	[a] 86 ± 7.6	[a] 94.2 ± 2.2	[a] 99.9 ± 2.0	[a] 99.6 ± 0.0	[a] 100.0 ± 0.2
p-xylene	[a] 73 ± 9.0	[a] 74 ± 9.3	[a] 85 ± 6.4	[a] 99.5 ± 1.0	[a] 99.7 ± 0.1	[a] 99.9 ± 0.0
o-xylene	[a] 68 ± 8.2	[a] 75 ± 9.2	[a] 90 ± 6.4	[a] 100.0 ± 0.0	[a] 100.0 ± 0.0	[a] 100.0 ± 0.0
Mesitylene	[a] 58 ± 13	[a] 67 ± 12	[a] 81 ± 11	[a] 99.6 ± 0.1	[a] 99.9 ± 0.0	[a] 100.0 ± 0.0

[a] Denotes CCV criteria were not met when performing the desorption efficiency study. Refer to Tables 3 and 4 for the corresponding masses at each spike level.

Table 13.

Summary of the relative response factor repeatability studies. Average percent %Rep.RRF values for Carbopack™ B and Tenax® TA sorbents at various spike levels. (n =6 for each spike level).

	%Rep.RRF on Carbopack™ B			**%Rep.RRF on Tenax® TA**		
Analyte	**1.00 mL spike**	**3.00 mL spike**	**12.5 mL spike**	**0.75 mL spike**	**2.00 mL spike**	**5.00 mL spike**
Chloroform	92.6 ± 7.44	92.5 ± 4.17	115 ± 4.02	101 ± 6.37	103 ± 5.97	104 ± 2.37
Benzene	83.4 ± 7.52	91.9 ± 4.04	134 ± 7.48	95.1 ± 7.30	99.2 ± 5.32	107 ± 4.03
Trichloroethylene	86.4 ± 7.11	95.9 ± 3.25	109 ± 6.84	95.3 ± 5.24	103 ± 2.76	106 ± 2.86
Heptane	[a] 55.6 ± 11.8	[a] 88.9 ± 5.86	[a] 166 ± 12.7	82.1 ± 7.92	99.5 ± 3.74	118 ± 2.81
Toluene	[a] 91.0 ± 13.4	[a] 104 ± 4.76	[a] 142 ± 12.0	[a] 95.1 ± 8.04	[a] 102 ± 7.86	[a] 100 ± 3.68
Tetrachloroethylene	[a] 102 ± 13.1	[a] 106 ± 6.51	[a] 99.1 ± 5.06	[a] 94.1 ± 5.78	[a] 98.5 ± 3.96	[a] 93.6 ± 2.64
Ethylbenzene	-	-	-	[a] 91.9 ± 5.94	[a] 104 ± 8.15	[a] 103 ± 2.70
p-xylene	-	-	-	[a] 91.9 ± 7.78	[a] 106 ± 8.16	[a] 105 ± 2.11
o-xylene	-	-	-	[a] 92.4 ± 7.42	[a] 104 ± 8.18	[a] 104 ± 5.58
Mesitylene	-	-	-	[a] 84.3 ± 7.04	[a] 102 ± 6.67	[a] 104 ± 4.19

‘-’ Denotes instances where the calibration curve was unacceptable.

[a] Denotes CCV criteria were not met when performing the relative response factor repeatability study. Refer to Table 3 and Table 4 for the corresponding masses at each spike level.