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# Porous Silica Spheres as Indoor Air Pollutant Scavengers

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## Abstract

Porous silica spheres were investigated for their effectiveness in removing typical indoor air pollutants, such as aromatic and carbonyl-containing volatile organic compounds (VOCs), and compared to the commercially available polymer styrene-divinylbenzene (XAD-4). The silica spheres and the XAD-4 resin were coated on denuder sampling devices and their adsorption efficiencies for VOCs evaluated using an indoor air simulation chamber. Real indoor sampling was also undertaken to evaluate the affinity of the silica adsorbents for a variety of indoor VOCs. The silica sphere adsorbents were found to have a high affinity for polar carbonyls and found to be more efficient than the XAD-4 resin at adsorbing carbonyls in an indoor environment.

## **Introduction**

In recent years indoor air pollution has become of major concern due to its well demonstrated effect on human health. The adverse health effects of indoor air pollution are expected to become more significant as lifestyles are predicted to become even more sedentary. In 2001, this was demonstrated in the national human activity pattern survey (NHAPS), where it was shown that US citizens typically spent 90 % of their time indoors<sup>1</sup>. Aldehydes in particular have adverse health effects (eye and lung irritation), and formaldehyde and acrolein are suspected carcinogens<sup>2-3</sup>. Changes in building design and improved energy efficiency, along with maximising insulation and minimising air exchange<sup>4</sup>, have led to increasingly airtight buildings<sup>5</sup>. Modern synthetic building materials, such as sealants, plastics and solvent-based coatings have further added to the problem of indoor air pollutants. Volatile organic compounds (VOCs), non-volatile organic compounds (NVOCs) and semi-volatile organic compounds (SVOCs) are of particular concern as indoor pollutants. VOCs are defined as organic compounds having a boiling point between 50 to 260 °C<sup>6</sup>. The relatively low boiling point of VOCs means they can easily release vapours into indoor air<sup>2</sup>. VOCs containing carbonyl moieties such as formaldehyde have been associated with health effects such as airway irritation, asthma and cancer at concentrations typically found indoors<sup>7, 8, 9</sup>.

There have been a variety of strategies employed for removing VOCs from indoor air environments. The most commonly used adsorbent is activated carbon. However there are numerous disadvantages associated with using activated carbon as an adsorbent, such as pore blocking, fire risk and regeneration problems<sup>10</sup>. The high specific surface area, controlled pore diameters and controlled morphology, for example spheres, rods and disks, of mesoporous silica makes them ideal candidates for adsorption applications. Indeed much research has recently

focused on using mesoporous materials for the adsorption of VOCs<sup>11,12,13</sup>. Zhao *et al.* have studied MCM-41 in comparison to activated carbon and hydrophobic zeolites for their effectiveness in the removal of VOCs. The study utilised temperature programmed desorption techniques to investigate the adsorption properties of MCM-41 and compared its performance to activated carbon and other hydrophobic zeolites. The study showed that MCM-41 was a highly efficient and competitive adsorbent for trapping a wide range of VOCs. There have also been several studies using either metal or functionalised mesoporous materials for the removal of VOCs<sup>14,15,16</sup>.

There are a variety of techniques available for sampling of indoor air pollutants and these can be classified into three main categories: (i) active sampling, which is based on the controlled passing of a gas through a suitable cartridge or container filled with an adsorbent<sup>17,18</sup>; the desired components of the gas are retained in the container due to chemical or physical adsorption, (ii) passive sampling, which is based on the free flow of analyte molecules from a sampling medium to a collecting medium; devices are usually cartridge like in design and based on diffusion through a well defined barrier<sup>19,20,21,22</sup>, and (iii) denudation sampling which is a combination of active sampling where the gas is forced through a tube and the diffusion of analytes from the gas to the surface of the tube coated with a suitable adsorbent<sup>23,24</sup>. A more detailed description of denuder sampling devices is presented below.

Denuders have been widely used as a means to minimise sampling artefacts during partitioning studies<sup>25-26</sup>, and provide an ideal platform on which to coat high surface area sorbents for gas flow testing. Designs include parallel plates, capillary tube bundles, glass honeycomb configurations and cylindrical annular denuders<sup>24, 27</sup>. The purpose of these designs is to

maximise the surface area of the denuder and subsequently provide maximum available surface area for the adsorbent material, in order to trap gas phase pollutants more efficiently by diffusion from polluted air streams. Annular denuders in particular have been used in several partitioning studies, both in ambient air and simulation chamber experiments<sup>25-28</sup>. They are comprised of several coaxial glass tubes, separated by an annular space of 1-2 mm through which the air flows<sup>25</sup>. Under laminar flow conditions the annular denuder (coated with a suitable adsorbent) traps gases by diffusion and acts as a suitable support for the silica or XAD-4 materials.

Here we report the adsorption efficiency of silica spheres (SSPH), for various VOCs observed in indoor environments. The packing ability, concentration of surface hydroxyl groups and the easily modified surface chemistry of the spheres coated on denuder tubes were examined and compared to the commercially available polymer resin XAD-4. A denuder sampler was utilised in this study as it can accommodate high flow rates and the results are extremely reproducible, which is advantageous when comparing the adsorption capacities of two compounds. Air from a simulation chamber containing a mixture of VOCs was pumped through the SSPH or XAD-4 coated denuder tubes in order to evaluate the adsorption efficiency of both materials. The denuder sampler was utilised in this study as Ambient indoor air samples were also taken using the same procedure for the purposes of an on site test of both materials.

## **Experimental**

### **Sample preparation**

Porous silica spheres were prepared based on the method previously described by Keane *et al.*<sup>29</sup> and Shimura *et al.*<sup>30</sup>. Tetraethylorthosilicate (TEOS) was used as the silica source and cetyltrimethylammonium bromide (CTAB) acted as the structure directing agent for pore

formation and methanol (MeOH) was used as a co-solvent. CTAB (1.2 g) was dissolved in deionised water (88 ml) and methanol (MeOH, 500 ml); the solution was stirred for 2 h. Ammonia hydroxide (32 ml, 32.66 % w/w NH<sub>3</sub> in H<sub>2</sub>O) and TEOS (8 ml) were then added to the solution, the temperature was maintained at room temperature and the mixture was stirred for 24 h. The silica precipitate was separated by centrifugation and dried at room temperature. Calcination of the surfactant template was performed at 550 °C for 8 h.

### **Materials characterisation**

The surface areas of the calcined micro/mesoporous silica materials were measured using nitrogen adsorption/desorption isotherms at 77 K on a Micromeritics Gemini 2375 volumetric analyser. Each sample was degassed for 5 h at 473 K prior to a measurement. The Brunauer, Emmett and Teller (BET) model was used to determine the surface area of the material from N<sub>2</sub> adsorption/desorption isotherms<sup>31</sup>. The average pore size distribution of the calcined silicas was calculated using the Barrett-Joyner-Halanda (BJH) model from a 60 point BET surface area plot<sup>32</sup>. Adsorption isotherms were used to calculate mean pore diameters and distributions. Scanning electron microscopy (SEM) analysis of the adsorbents to identify their morphologies was conducted on a JEOL 5510 SEM. The powder samples were placed on carbon tape and then adhered to a brass stub before being placed into the SEM chamber. Particle size distributions (PaSD) were measured using a Malven particle sizer. D10 is defined as the particle diameter at 10 % of the cumulative particle size distribution; D90 is defined as the particle diameter at 90 % of the cumulative particle size distribution. D90/10 is defined as the ratio of the D90 value to the D10 value and used as a measure of the monodispersivity of the samples.

## Trapping efficiency experiments

The design and operating principles of the atmospheric simulation chamber are similar to those described in detail elsewhere<sup>33-35</sup>. The atmospheric simulation chamber is rectangular in shape and has a volume of *ca.* 6500 L. The chamber was operated at atmospheric pressure using purified air (Zander KMA 75), and the temperature and amount of water vapour in the chamber were monitored by a dewpoint meter (Vaisala DM70). Experiments were typically performed at  $295 \pm 2$  K and at a dewpoint temperature of  $223 \pm 5$  K. Between experiments the chamber was cleaned by flushing with purified air at a flow rate of  $150 \text{ L min}^{-1}$  for a minimum of 6 h. The carbonyls, aromatic aldehydes and aromatic hydrocarbons were introduced into the chamber using a glass impinger system in which pre-weighed amounts of each VOC were slowly heated in a gentle flow of purified air. The volatilised compounds were allowed to mix in the chamber for at least 1 h prior to sampling. The two adsorbent materials under investigation in this study were microporous SSPH and the XAD-4 resin, a styrene-divinylbenzene polymer, both of which were applied to the denuder tubes using a standard coating procedure<sup>25</sup>. The annular denuder (University Research Glassware, Chapel Hill, NC) consisted of five concentric glass tubes, 242 mm in length, separated by a space of 1 mm. The trapping efficiency of each adsorbent was determined by first sampling air upstream of the denuder tube and subsequently sampling the breakthrough of carbonyls, aldehydes or aromatic hydrocarbons at the exit of the denuder tube. In the case of the carbonyls and aromatic aldehydes this measurement involved the use of two impingers, connected in series, containing 10 mL of a  $0.25 \text{ g L}^{-1}$  solution of *O*-2,3,4,5-pentafluorobenzyl hydroxylamine (PFBHA) in deionised water to derivatise the carbonyls *in-situ*<sup>36</sup>. Yu *et al.*<sup>37</sup>, found that reacting carbonyls with this reagent coupled with gas chromatography mass spectrometry (GC-MS) provided a much better alternative to other methods available for the measurement of carbonyl-containing VOCs. Sampling using this

technique proceeded for 50 min at a flow rate of 10 L min<sup>-1</sup> from the pump through the tube and an additional flow of 1 L min<sup>-1</sup> from the tube exit through the impinger system. The impinger solutions were replaced every 10 min to monitor the change in trapping efficiency with time. These solutions were then left to react for 24 h before extraction into n-hexane (2 ml) and dried using sodium sulfate in preparation for GC-MS analysis. The analytical method has been described in detail in previous publications<sup>34-35</sup>. The aromatic hydrocarbons, benzene, toluene, *p*-xylene and 1,3,5-trimethylbenzene, were monitored using a gas chromatograph (Varian 3800) with flame ionisation detection (GC-FID) connected directly to the denuder tube inlet and outlet via a 6 port gas sampling valve (Valco). Sampling was carried out over a 120 min period, with a sample being injected every 8 min.

### **Indoor air sampling**

The indoor air sampling was carried out in a typical wet chemistry laboratory to ensure maximum exposure to a variety of VOCs. Two identical denuders were coated, as described above, with SSPH or XAD-4 resin. Sampling was carried out at 10 L min<sup>-1</sup> for a period of 24 h. The adsorbed material was then extracted in 10 ml of methanol and reacted with PFBHA (0.0025 g). These solutions were then left for 24 h before they were reduced to almost complete dryness and reconstituted in 2 ml of hexane and dried using sodium sulfate in preparation for GC-MS analysis.

### **GC-MS analysis**

A Varian GC-MS system (Saturn 2000) equipped with a split/split-less injector (Varian 1079) was used for chemical analysis. The chromatographic column used was a Chrompack CP-Sil-8CB (5 % phenyl, 95 % dimethylpolysiloxane), 30 m in length, with an internal diameter of 0.25

mm. The derivatives were analysed using the following column oven temperature program: 60°C held for 1 min and then ramped from 60 to 100 °C at 5 °C min<sup>-1</sup>, from 100 to 280 °C at 10 °C min<sup>-1</sup> and from 280 to 310 °C at 30 °C min<sup>-1</sup>. The temperature was then held at 310 °C for 5 min. The injector temperature was held at 280 °C for 1 min and then ramped to 310 °C at 50 °C min<sup>-1</sup>. EI mass spectra were acquired over a mass range *m/z* 60- 650 amu. When analysing the PFBHA derivatives, reconstructed ion chromatograms were used. The *m/z* 181 ion EI fragment was used in most cases for quantification of the derivatised carbonyls<sup>37,36</sup>. Three groups of carbonyls were investigated; small carbonyls (acetaldehyde, acetone, butanal, valeraldehyde and hexanal), dicarbonyls (glyoxal, methylglyoxal) and aromatic aldehydes (benzaldehyde, *p*-tolualdehyde), these compounds were studied as they are known to be common indoor air pollutants<sup>38</sup>. As more than one isomer can be formed for asymmetric carbonyls, as both *Z*- and *E*- oximes are possible. For example acetone reacts with PFBHA to yield one oxime whereas acetaldehyde can form two isomers. Asymmetric dicarbonyls such as methylglyoxal can form up to four isomers. If a dicarbonyl contains a double bond with the carbonyl moieties on either side, a total of eight oximes are possible. This is because the compound can exist in a *cis* and a *trans* form, each of which can form four isomers. Therefore several derivatized compounds have multiple peaks when analyzed by gas chromatography. The structures, molecular masses of oximes, retention times and ions used for quantification by GCMS are given in Table 1.

**Table 1** Structures, retention times, oxime molecular masses and ions used for quantification of carbonyls using GC-MS in trapping efficiency tests.

## GC-FID analysis

The concentrations of the aromatic hydrocarbons, benzene, toluene, *p*-xylene and 1,3,5-trimethylbenzene, were monitored using a gas chromatograph (Varian 3800) with flame ionisation detection (GC-FID) connected directly to the chamber via a 6 port gas sampling valve (Valco). The valve is fitted with a 1 cm<sup>3</sup> sampling loop and is equipped with a pneumatically controlled actuator to enable automated injection of reaction mixtures onto the column. Samples (1 cm<sup>3</sup>) were injected and then separated using a Chrompack CP-Sil-8CB (5 % phenyl, 95 % dimethylpolysiloxane), 30 m in length, with an internal diameter of 0.25 mm and helium as the carrier gas (1.5 ml min<sup>-1</sup>). The oven temperature program used was as follows: 60 °C held for 0.3 min, ramped to 110 °C at 80 °C min<sup>-1</sup>, then ramped to 160 °C at 40 °C min<sup>-1</sup> and to 250 °C at 70 °C min<sup>-1</sup>. The injector temperature was held at 250 °C for the duration of the 3.46 min run.

## Results and discussion

### Characterisation of adsorbents

Nitrogen adsorption/desorption isotherms for the SSPH and XAD-4 materials are shown in figures 1(a) and (b). The XAD-4 resin displays a type IV isotherm<sup>39</sup>, indicating that it has a mesoporous structure. The isotherm for the SSPH displays a sharper curve and is typical of a type I isotherm, indicating that the material is microporous<sup>39</sup>. The pore size distribution curve for both materials is given in figures 1(c) and (d) and Table 2 details the physiochemical properties of the two materials. The XAD-4 adsorbent exhibits a significantly higher mean surface area compared SSPH, *i.e.* 1038 m<sup>2</sup> g<sup>-1</sup> compared to 804 m<sup>2</sup> g<sup>-1</sup>, and a larger mean pore diameter, *i.e.* 124 Å for XAD-4 compared to 19 Å for SSPH, due to the mesoporous nature of the XAD-4 resin.

**Figure 1** Nitrogen adsorption/desorption isotherms for (a) SSPH and (b) XAD-4 resin. Pore size distributions for (c) XAD-4 and (d) SSPH based on the adsorption profiles.

**Table 2** Physiochemical properties of XAD-4 and SSPH as determined by nitrogen adsorption/desorption measurements.

Gundel *et al.* investigated the coating of XAD-4 on the surface of glass denuder tubes for the determination of phase distributions of semi-volatile aromatic hydrocarbons in indoor air<sup>26</sup>. As shown in figure 2(a), XAD-4 has a random structure consistent with its polymeric nature. The spherical morphology of the SSPH adsorbent provides a distinct advantage over the XAD-4 resin as the SSPH can pack better onto the surface of the denuder tube and suffers little or no aggregation. The average particle size of the SSPH was 2.17  $\mu\text{m}$ , figure S1, and is in good agreement with particles measured from SEM. The D90/10 ratio, which is a measure of the mono-dispersivity of the SSPH, was shown to be 1.35, table S1, indicating a high level of monodispersivity.

**Figure 2** SEM images showing the structural morphologies of (a) XAD-4 and (b) SSPH.

### Trapping efficiency

The performance of the SSPH and XAD-4 coated denuder tubes for trapping indoor VOCs was investigated through a series of trapping efficiency tests on four groups of compounds; small carbonyls, dicarbonyls, aromatic aldehydes and aromatic hydrocarbons. Sampling for the

carbonyls and aldehydes was performed at 10 min intervals using a flow rate of 10 L min<sup>-1</sup>. The trapping efficiency (%) of the coated denuder tube for each compound was calculated as  $(1 - C_{out}/C_{in})$ , where  $C_{in}$  and  $C_{out}$  are the concentrations of the compound at the entrance and at the exit of the tubes, respectively<sup>34</sup>. The precision of the analytical method has previously been calculated for carbonyls and aromatic hydrocarbons using the impinger system<sup>36, 40</sup>. Standard deviation in the range of 3 % to 15 % was obtained for a range of carbonyl compounds similar to those used in this study, details of which is outlined in the Supporting Information (see table S2). An overall error of  $\pm 15$  % was subsequently estimated for all carbonyl compounds studied in this work. The error in the trapping efficiency of the aromatic hydrocarbons is given in table S3. Standard deviation for these compounds ranged from 1.1 % to 27.71 % and an overall error of 27 % was estimated for these experiments.

**Figure 3** Data showing the trapping efficiency of XAD-4 (dashed line) and SSPH (solid line) for (a) acetone ( $\pm 9.9$  % error), (b) butanal ( $\pm 7$  % error), (c) pentanal ( $\pm 3$  % error) and (d) hexanal (10 % error).

Figure 3 shows a trapping efficiency plot for a selection of small carbonyls; acetone, butanal, pentanal and hexanal. The trapping efficiency of the SSPH for each of these compounds was close to 100 % after the first 10 min. The XAD-4 resin showed varying trapping efficiency values ranging from 100 to 8 % after the first 10 mins. However, the trapping efficiency for both sorbents decreased gradually with time due the progressive saturation of the sorption surface with trapped species, resulting in a breakthrough of the carbonyls at the denuder outlet; as is clearly shown in figure 3(a) where acetone saturates both adsorbents after a 50 min sampling period. Figure 3(b) shows a similar trapping efficiency by XAD-4 and SSPH for butanal. Overall the

data demonstrates, with the exception of hexanal which is trapped with 100 % efficiency by both adsorbents (figure 3(d)) that the SSPH adsorbent is more efficient at trapping the carbonyl compounds compared to the XAD-4 resin. The higher trapping efficiency observed with the SSPH is probably due to the hydrophilic nature of the surface of the particles as a result of the silanol groups present, suggesting that SSPH is an ideal adsorbent of gaseous polar VOCs through hydrogen bonding. XAD-4, on the other hand, has a non-polar polymeric hydrocarbon surface and thus exhibits hydrophobicity.

**Figure 4** Data showing the trapping efficiency of XAD-4 (dashed line) and SSPH (solid line) for (a) benzaldehyde ( $\pm 11$  % error), (b) *p*-tolualdehyde ( $\pm 13$  % error), (c) glyoxal ( $\pm 14$  % error) and (d) methylglyoxal ( $\pm 13$  % error).

Figure 4 shows the trapping efficiency of the XAD-4 and SSPH adsorbents for dicarbonyls and aldehydes. The XAD-4 and the SSPH adsorbents both showed a 100 % trapping efficiency for benzaldehyde and *p*-tolualdehyde over the sampling period of 50 minutes, as shown figures 3(a) and (b). Both the SSPH and the XAD-4 displayed 100 % trapping efficiency for glyoxal after the first 10 minutes of sampling. The XAD-4 resin reached saturation after 20 minutes, with the efficiency gradually decreasing to almost 0 % efficiency after 50 min. However the SSPH adsorbent remained constant at a 100 % trapping efficiency over 50 mins. Although both the XAD-4 and the SSPH displayed an initial trapping efficiency for methylglyoxal of 100 %, which gradually decreased with saturation of the sorbents over the 50 mins, SSPH is clearly a more efficient adsorbent for this compound.

**Figure 5** Data showing the trapping efficiency of XAD-4 (dashed line) and SSPH (solid line) for (a) benzene ( $\pm 1$  % error), (b), toluene (2 % error), (c) *p*-xylene ( $\pm 6$  % error) and (d) 1,3,5-trimethylbenzene ( $\pm 27$  % error).

Figure 5 shows the trapping efficiency of the XAD-4 and SSPH adsorbents for aromatic hydrocarbons. The XAD-4 displays a much greater affinity for all of the aromatic hydrocarbons under investigation. The trapping efficiency for benzene can be seen in figure 5(a). The data suggests that both the adsorbents are completely saturated in the first 15 minutes of sampling due to the volatile nature of benzene. As the volatility of the aromatic hydrocarbons decreases the trapping efficiency of both adsorbents is seen to increase; this trend can be clearly seen for toluene, *p*-xylene and 1,3,5-trimethylbenzene as shown in figures 5(b)-(d). The least volatile compound present was 1,3,5-trimethylbenzene which both the SSPH and the XAD-4 adsorbents were able to trap with 100 % efficiency for the first 60 minutes of sampling. After 60 minutes the SSPH efficiency rapidly decreasing to almost 0 %, however the XAD-4 remained constant at 100 % over a duration of 120 minutes. The large experimental error associated with 1,3,5-trimethylbenzene can be attributed to a poor chromatography leading to broad peak shape and large experimental error. The poor trapping efficiency of SSPH for aromatic hydrocarbons can be attributed to the high concentration of polar silanol groups on the surface of the material. The polymeric non-polar surface of the XAD-4 makes it an ideal candidate for the adsorption of non-polar aromatic hydrocarbons through similar hydrophobic interactions<sup>40</sup>

### **Indoor air sampling**

To evaluate the applicability of SSPH-coated denuders for field sampling, an indoor test was performed. Two denuder tubes were clamped in parallel, one coated with SSPH and one coated

with XAD-4 resin and left to sample indoor air in a synthetic chemistry laboratory at a flow rate of 10 L min<sup>-1</sup> for a period of 24 hours. The adsorbents were then extracted into methanol (20 ml) and derivatised with PFBHA (0.0025 g). Figure 6 displays the reconstructed ion chromatogram for the SSPH and XAD-4 extracts from the indoor experiment. The C<sub>5</sub> and C<sub>6</sub> unsaturated dicarbonyl compounds are tentatively identified based on their retention times and the mass spectra of their oxime derivatives<sup>35-36</sup>. The trapping ratios of SSPH against the XAD-4 resin are shown in table 3. The SSPH and XAD-4 resin were both efficient at trapping benzaldehyde, which corresponds to the trapping efficiency plot obtained from the simulation chamber, figure 4 (a). SSPH clearly outperformed XAD-4 in trapping the polar carbonyls, exhibiting an efficiency approximately 20 times greater than XAD-4 for unsaturated dicarbonyls. This result is also in agreement with the trapping efficiency curves generated from the simulation chamber experiments.

**Figure 6** Reconstructed ion chromatogram (m/z 181) of SSPH and XAD-4 indoor air extracts. \*Unreacted PFBHA/oximes also present in the blank extracts.

**Table 3** Details of the compounds used, retention times, oxime molecular masses, ions used for quantification and efficiency ratios of carbonyls using GC-MS during indoor sampling test.

## Conclusions

In this study we have demonstrated that porous silica spheres can be used to efficiently trap various indoor air pollutants, both in a simulated environment and in an indoor environment.

The adsorbent was tested at relatively high concentrations (500 ppb) and flow rates (10 L min<sup>-1</sup>). In our experiments SSPH was found to be more efficient than the commercially available Amberlite® XAD-4 resin at trapping non-polar VOCs and significantly more efficient at trapping polar VOCs present in ambient air, the XAD-4 resin demonstrated a higher trapping efficiency for aromatic hydrocarbons. The SSPH adsorbent was shown to trap 100 % of the gas phase carbonyl compounds present in a simulation chamber experiment in the first 10 minutes of sampling, while the XAD-4 resin was shown to have various levels of efficiency ranging from 100 to 8 % over the sampling period for the same group of carbonyl compounds. The indoor test demonstrated that the SSPH adsorbent is far more efficient at trapping polar carbonyls than XAD-4 resin in an indoor environment. Specifically, SSPH was shown to be significantly more efficient than the XAD-4 resin at trapping glyoxal, C<sub>5</sub> and C<sub>6</sub> unsaturated carbonyls. Given that aldehydes such as acetaldehyde and benzaldehyde are proven carcinogens and present in indoor air at concentrations 2 to 13 times higher than outdoor concentrations<sup>33</sup> these compounds pose a significant health risk. As SSPH were shown to trap a variety of aldehydes and carbonyls both in simulated and field campaign studies it has a distinct advantage over XAD-4 resin.

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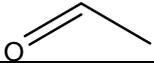
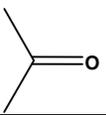
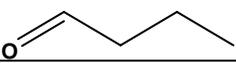
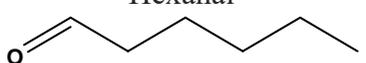
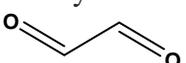
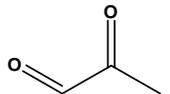
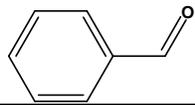
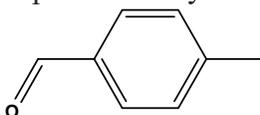
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## Tables

**Table 1** Structures, retention times, oxime molecular masses and ions used for quantification of carbonyls using GC-MS in trapping efficiency tests.

Compound	Retention time (mins)	Molecular mass of PFBHA oxime	<i>m/z</i> used for quantification
<b><i>Small Carbonyls</i></b>			
Acetaldehyde 	9.68, 9.75	239	181
Acetone 	11.05	253	181
Butanal 	13.06, 13.19	267	181
Valeraldehyde 	1.48, 14.55	281	181
Hexanal 	15.7, 15.75		181
<b><i>Dicarbonyls</i></b>			
Glyoxal 	Tri-derivative 21.18, 21.22, 21.27	448	181, 448
Methylglyoxal 	Tri-derivative 21.3, 21.41, 21.57	462	181, 265
<b><i>Aromatic carbonyls</i></b>			
Benzaldehyde 	18.6	301	181
p-Tolualdehyde 	19.74	315	181, 315

**Table 2** Physiochemical properties of XAD-4 and SSPH as determined by nitrogen adsorption/desorption measurements.

<b>Sample</b>	<b>Mean Surface area (m<sup>2</sup> g<sup>-1</sup>)</b>	<b>Mean Pore Volume (cm<sup>3</sup> g<sup>-1</sup>)</b>	<b>Mean Pore Diameter (Å)</b>
<b>Silica spheres (SSPH)</b>	804	0.40	19
<b>XAD-4</b>	1038	1.56	124

**Table 3** Details of the compounds used, retention times, oxime molecular masses, ions used for quantification and efficiency ratios of carbonyls using GC-MS during indoor sampling test.

<b>Compound</b>	<b>Retention Time (minutes)</b>	<b>Molecular Mass of Derivative</b>	<b>m/z (EI mode)</b>	<b>Efficiency Ratio SSPH:XAD-4</b>
<b>Acetone</b>	10.3	253	181	1.4
<b>Benzaldehyde</b>	17.8	301	181 301	1.13
<b>Unknown carbonyl</b>	18.5	unknown	181	Peak not observed for XAD-4
<b>Glyoxal</b>	Tri-derivative 20.25, 20.35, 20.41	448	181, 448 (M), 251 (M-197)	4.40
<b>C<sub>5</sub> unsaturated dicarbonyl</b>	Di-derivative 21.9, 22.02	490	181, 490 (M), 293 (M-197)	19.94
<b>C<sub>6</sub> unsaturated dicarbonyl</b>	24.62, 24.71, 24.9, 24.98, 25.2	502	181, 502 (M), 321 (M-181)	Peak not observed for XAD-4

## Figure Captions

- Figure 1** Nitrogen adsorption/desorption isotherms for (a) SSPH and (b) XAD-4 resin. Pore size distributions for (c) XAD-4 and (d) SSPH based on the adsorption profiles.
- Figure 2** SEM images showing the structural morphologies of (a) XAD-4 and (b) SSPH.
- Figure 3** Data showing the trapping efficiency of XAD-4 (dashed line) and SSPH (solid line) for (a) acetone ( $\pm 9.9$  % error), (b) butanal ( $\pm 7$  % error), (c) pentanal ( $\pm 3$  % error) and (d) hexanal (10 % error).
- Figure 4** Data showing the trapping efficiency of XAD-4 (dashed line) and SSPH (solid line) for (a) benzaldehyde ( $\pm 11$  % error), (b) *p*-tolualdehyde ( $\pm 13$  % error), (c) glyoxal ( $\pm 14$  % error) and (b) methylglyoxal ( $\pm 13$  % error).
- Figure 5** Data showing the trapping efficiency of XAD-4 (dashed line) and SSPH (solid line) for (a) benzene ( $\pm 1$  % error), (b), toluene (2 % error), (c) *p*-xylene ( $\pm 6$  % error) and (d) 1,3,5-trimethylbenzene ( $\pm 27$  % error).
- Figure 6** Reconstructed ion chromatogram ( $m/z$  181) of SSPH and XAD-4 indoor air extracts. \*Unreacted PFBHA/oximes also present in the blank extracts.