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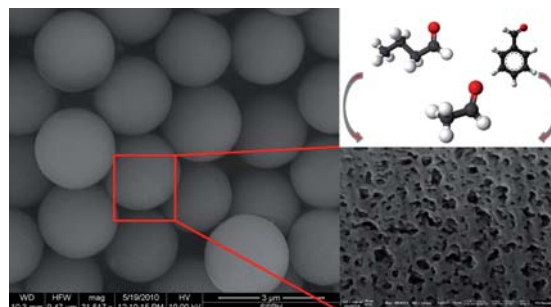
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Porous silica spheres as indoor air pollutant scavengers

Paul Delaney, Robert M. Healy, John P. Hanrahan, Lorraine T. Gibson, John C. Wenger, Michael A. Morris and Justin D. Holmes*

Porous silica spheres were investigated for their effectiveness in removing typical indoor air pollutants.



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■ Porous silica spheres as indoor air pollutant scavengers†

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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 a 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.¹ Aldehydes in particular have adverse health effects (eye and lung irritation), and formaldehyde and acrolein are suspected carcinogens.^{2,3} Changes in building design and improved energy efficiency, along with maximising insulation and minimising air exchange,⁴ have led to increasingly airtight buildings.⁵ 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 and 260 °C.⁶ The relatively low boiling point of VOCs means they can easily release vapours into indoor air.² 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.^{7–9}

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.¹⁰ The high specific surface area, controlled pore diameters and controlled morphology, for example spheres, rods and disks, of mesoporous silica make them ideal candidates for adsorption applications. Indeed much research has recently focused on using mesoporous materials for the adsorption of VOCs.^{11–13} 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.^{14–16}

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Environmental impact

In recent years indoor air pollution has received much attention due to its well demonstrated effect on human health. In particular carbonyl pollutants have been shown to be of significant importance due to their relative abundance in indoor air. Typical sources include off-gassing from building and furnishing materials and emissions from various consumer products such as, sealants, plastics and solvent-based coatings. Several carbonyl compounds have been associated with health effects such as airway irritation, asthma and cancer at concentrations typically found indoors. We have developed high surface area, highly porous silica spheres for the adsorption of indoor air pollutants. These spheres were investigated in both simulated and real indoor test environments and shown to outperform a commercially available polymer adsorbent.

1 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
5 passing of a gas through a suitable cartridge or container filled
with an adsorbent;^{17,18} 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;
10 devices are usually cartridge like in design and based on diffusion
through a well defined barrier,^{19–22} 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.^{23,24} A more
15 detailed description of denuder sampling devices is presented
below.

Denuders have been widely used as a means to minimise
sampling artefacts during partitioning studies,^{25,26} and provide
an ideal platform on which to coat high surface area sorbents for
gas flow testing. Designs include parallel plates, capillary tube
20 bundles, glass honeycomb configurations and cylindrical annular
denuders.^{24,27} 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
25 air streams. Annular denuders in particular have been used in
several partitioning studies, both in ambient air and simulation
chamber experiments.^{25–28} They are comprised of several coaxial
glass tubes, separated by an annular space of 1–2 mm through
which the air flows.²⁵ Under laminar flow conditions the annular
30 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
35 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
40 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
45 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.

50 Experimental

Sample preparation

Porous silica spheres were prepared based on the method
previously described by Keane *et al.*²⁹ and Shimura and Ogawa.³⁰
55 Tetraethyl orthosilicate (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

1 stirred for 2 h. Ammonium hydroxide (32 ml, 32.66% w/w NH₃
in H₂O) 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
5 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
10 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 N₂
15 adsorption/desorption isotherms.³¹ The average pore size distri-
bution of the calcined silicas was calculated using the Barrett–
Joyner–Halenda (BJH) model from a 60 point BET surface area
plot.³² Adsorption isotherms were used to calculate mean pore
diameters and distributions. Scanning electron microscopy
20 (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
(PaSDs) were measured using a Malvern particle sizer. D10 is
25 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. 30

Trapping efficiency experiments

The design and operating principles of the atmospheric simula-
35 tion chamber are similar to those described in detail elsewhere.^{33–35}
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
40 were monitored by a dewpoint meter (Vaisala DM70). Experi-
ments were typically performed at 295 ± 2 K and at a dewpoint
temperature of 223 ± 5 K. Between experiments the chamber was
cleaned by flushing with purified air at a flow rate of 150 l min⁻¹
for a minimum of 6 h. The carbonyls, aromatic aldehydes and
45 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
50 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.²⁵ The annular denuder (University Research Glass-
ware, Chapel Hill, NC) consisted of five concentric glass tubes,
242 mm in length, separated by a space of 1 mm. The trapping
55 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

1 aromatic aldehydes this measurement involved the use of two
2 impingers, connected in series, containing 10 ml of a 0.25 g l⁻¹
3 solution of *O*-2,3,4,5-pentafluorobenzyl hydroxylamine
4 (PFBHA) in deionised water to derivatise the carbonyls *in situ*.³⁶
5 Yu *et al.*³⁷ found that reacting carbonyls with this reagent
6 coupled with gas chromatography mass spectrometry (GC-MS)
7 provided a much better alternative to other methods available for
8 the measurement of carbonyl-containing VOCs. Sampling using
9 this technique proceeded for 50 min at a flow rate of 10 l min⁻¹
10 from the pump through the tube and an additional flow of 1 l
11 min⁻¹ from the tube exit through the impinger system. The
12 impinger solutions were replaced every 10 min to monitor the
13 change in trapping efficiency with time. These solutions were
14 then left to react for 24 h before extraction into *n*-hexane (2 ml)
15 and dried using sodium sulfate in preparation for GC-MS
16 analysis. The analytical method has been described in detail in
17 previous publications.^{34,35} The aromatic hydrocarbons, benzene,
18 toluene, *p*-xylene and 1,3,5-trimethylbenzene, were monitored
19 using a gas chromatograph (Varian 3800) with flame ionisation
20 detection (GC-FID) connected directly to the denuder tube inlet
21 and outlet *via* a 6 port gas sampling valve (Valco). Sampling was
22 carried out over a 120 min period, with a sample being injected
23 every 8 min.

25 Indoor air sampling

26 The indoor air sampling was carried out in a typical wet chem-
27 istry laboratory to ensure maximum exposure to a variety of
28 VOCs. Two identical denuders were coated, as described above,
29 with SSPH or XAD-4 resin. Sampling was carried out at 10 l
30 min⁻¹ for a period of 24 h. The adsorbed material was then
31 extracted in 10 ml of methanol and reacted with PFBHA (0.0025
32 g). These solutions were then left for 24 h before they were
33 reduced to almost complete dryness and reconstituted in 2 ml of
34 hexane and dried using sodium sulfate in preparation for GC-MS
35 analysis.

36 GC-MS analysis

37 A Varian GC-MS system (Saturn 2000) equipped with a split/
38 split-less injector (Varian 1079) was used for chemical analysis.
39 The chromatographic column used was a Chrompack CP-Sil-
40 8CB (5% phenyl and 95% dimethylpolysiloxane), 30 m in length,
41 with an internal diameter of 0.25 mm. The derivatives were
42 analysed using the following column oven temperature program:
43 60 °C held for 1 min and then ramped from 60 to 100 °C at 5 °C
44 min⁻¹, from 100 to 280 °C at 10 °C min⁻¹ and from 280 to 310 °C
45 at 30 °C min⁻¹. The temperature was then held at 310 °C for 5
46 min. The injector temperature was held at 280 °C for 1 min and
47 then ramped to 310 °C at 50 °C min⁻¹. EI mass spectra were
48 acquired over a mass range *m/z* 60–650 amu. When analysing the
49 PFBHA derivatives, reconstructed ion chromatograms were
50 used. The *m/z* 181 ion EI fragment was used in most cases for
51 quantification of the derivatised carbonyls.^{37,36} Three groups of
52 carbonyls were investigated: small carbonyls (acetaldehyde,
53 acetone, butanal, valeraldehyde and hexanal), dicarbonyls
54 (glyoxal and methylglyoxal) and aromatic aldehydes (benzal-
55 dehyde and *p*-tolualdehyde), these compounds were studied as they
are known to be common indoor air pollutants.³⁸ 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 quantifica-
tion by GC-MS are given in Table 1.

56 GC-FID analysis

57 The concentrations of the aromatic hydrocarbons, benzene,
58 toluene, *p*-xylene and 1,3,5-trimethylbenzene, were monitored
59 using a gas chromatograph (Varian 3800) with flame ionisation
60 detection (GC-FID) connected directly to the chamber *via* a 6
61 port gas sampling valve (Valco). The valve is fitted with a 1 cm³
62 sampling loop and is equipped with a pneumatically controlled
63 actuator to enable automated injection of reaction mixtures onto
64 the column. Samples (1 cm³) were injected and then separated
65 using a Chrompack CP-Sil-8CB (5% phenyl, 95% dimethylpo-
66 lysiloxane), 30 m in length, with an internal diameter of 0.25 mm
67 and helium as the carrier gas (1.5 ml min⁻¹). The oven temper-
68 ature program used was as follows: 60 °C held for 0.3 min,
69 ramped to 110 °C at 80 °C min⁻¹, then ramped to 160 °C at 40 °C
70 min⁻¹ and to 250 °C at 70 °C min⁻¹. The injector temperature was
71 held at 250 °C for the duration of the 3.46 min run.

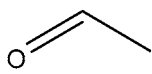
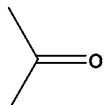
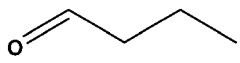
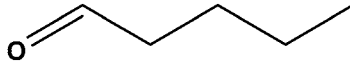
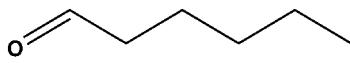
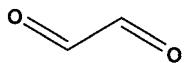
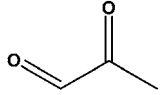
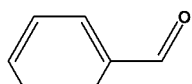
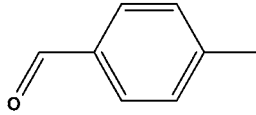
72 Results and discussion

73 Characterisation of adsorbents

74 Nitrogen adsorption/desorption isotherms for the SSPH and
75 XAD-4 materials are shown in Fig. 1(a) and (b). The XAD-4
76 resin displays a type IV isotherm,³⁹ indicating that it has a meso-
77 porous structure. The isotherm for the SSPH displays a sharper
78 curve and is typical of a type I isotherm, indicating that the
79 material is microporous.³⁹ The pore size distribution curve for
80 both materials is given in Fig. 1(c) and (d) and Table 2 details the
81 physiochemical properties of the two materials. The XAD-4
82 adsorbent exhibits a significantly higher mean surface area
83 compared to SSPH, *i.e.* 1038 m² g⁻¹ compared to 804 m² g⁻¹, and
84 a larger mean pore diameter, *i.e.* 124 Å for XAD-4 compared to
85 19 Å for SSPH, due to the mesoporous nature of the XAD-4
86 resin.

87 Gundel *et al.* investigated the coating of XAD-4 on the surface
88 of glass denuder tubes for the determination of phase distribu-
89 tions of semi-volatile aromatic hydrocarbons in indoor air.²⁶ As
90 shown in Fig. 2(a), XAD-4 has a random structure consistent
91 with its polymeric nature. The spherical morphology of the
92 SSPH adsorbent provides a distinct advantage over the XAD-4
93 resin as the SSPH can pack better onto the surface of the denuder
94 tube and suffers little or no aggregation. The average particle size
95 of the SSPH was 2.17 µm, Fig. S1†, and is in good agreement
with the particles measured from SEM. The D90/10 ratio, which
is a measure of the mono-dispersivity of the SSPH, was show to
be 1.35, Table S1†, indicating a high level of monodispersivity.

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

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

45 Trapping efficiency

45 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⁻¹. 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.³⁴ The precision of the analytical method has previously been calculated for carbonyls and aromatic hydrocarbons using the impinger system.^{36,40} 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

45 which are outlined in the ESI (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.

50 Fig. 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 min. However, the trapping efficiency for both sorbents decreased gradually with time due to the progressive saturation of the sorption surface with trapped species, resulting in a breakthrough of the carbonyls at the denuder outlet; as is

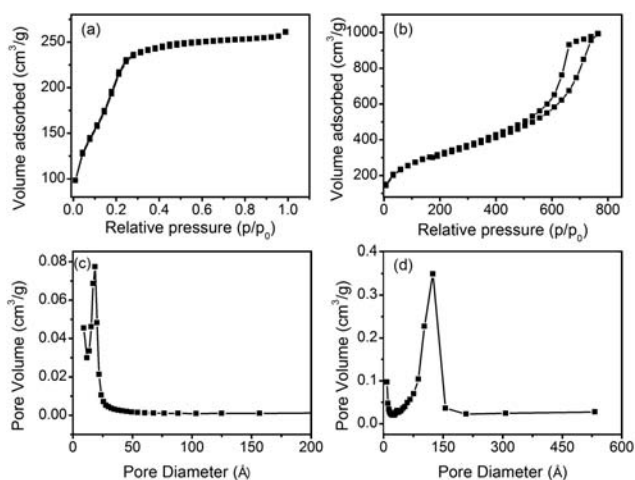


Fig. 1 Nitrogen adsorption/desorption isotherms for (a) SSPH and (b) XAD-4 resin. Pore size distributions for (c) XAD-4 and (d) SSPH based on the adsorption profiles.

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

Sample	Mean surface area/m ² g ⁻¹	Mean pore volume/cm ³ g ⁻¹	Mean pore diameter/Å
Silica spheres (SSPH)	804	0.40	19
XAD-4	1038	1.56	124

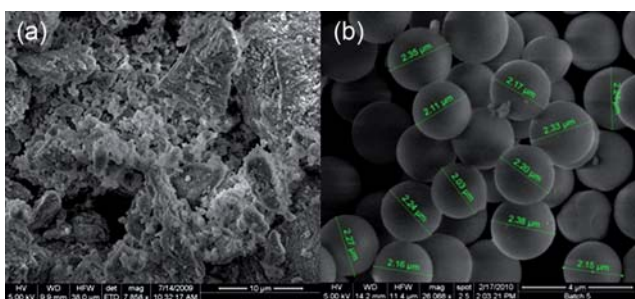


Fig. 2 SEM images showing the structural morphologies of (a) XAD-4 and (b) SSPH.

clearly shown in Fig. 3(a) where acetone saturates both adsorbents after a 50 min sampling period. Fig. 3(b) shows a similar trapping efficiency by XAD-4 and SSPH for butanal. Overall the data demonstrate, with the exception of hexanal which is trapped with 100% efficiency by both adsorbents (Fig. 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.

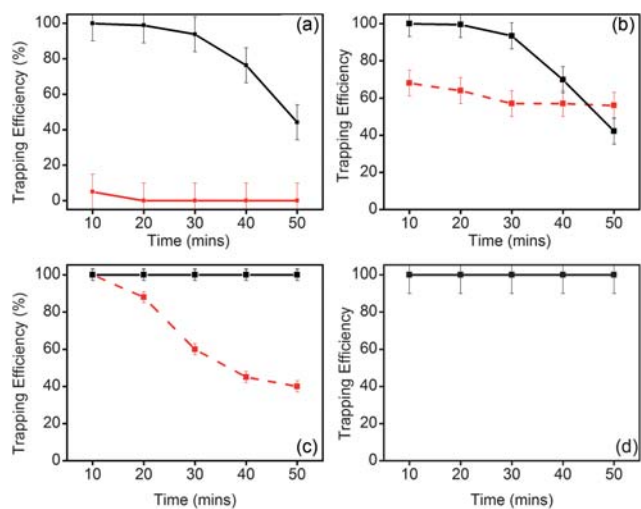


Fig. 3 Data showing the trapping efficiency of XAD-4 (dashed line) and SSPH (solid line) for (a) acetone ($\pm 9.9\%$ error), (b) butanal ($\pm 7\%$ error), (c) pentanal ($\pm 3\%$ error) and (d) hexanal (10% error).

Fig. 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 in Fig. 4(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% after 50 min. However, the SSPH adsorbent remained constant at a 100% trapping efficiency over 50 min. 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 min, SSPH is clearly a more efficient adsorbent for this compound.

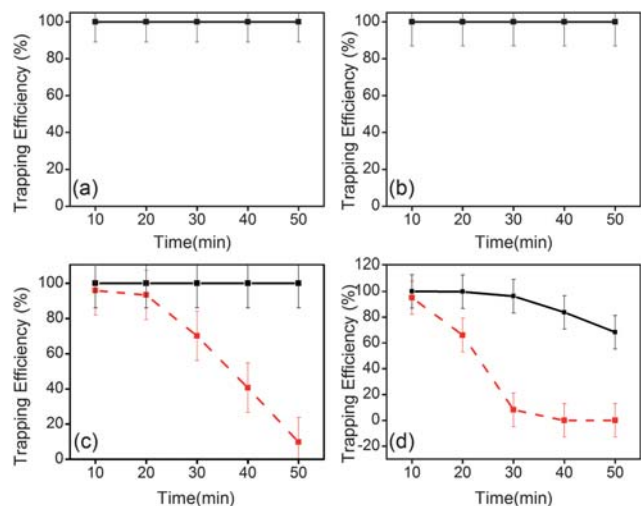


Fig. 4 Data showing the trapping efficiency of XAD-4 (dashed line) and SSPH (solid line) for (a) benzaldehyde ($\pm 11\%$ error), (b) *p*-tolualdehyde ($\pm 13\%$ error), (c) glyoxal ($\pm 14\%$ error) and (d) methylglyoxal ($\pm 13\%$ error).

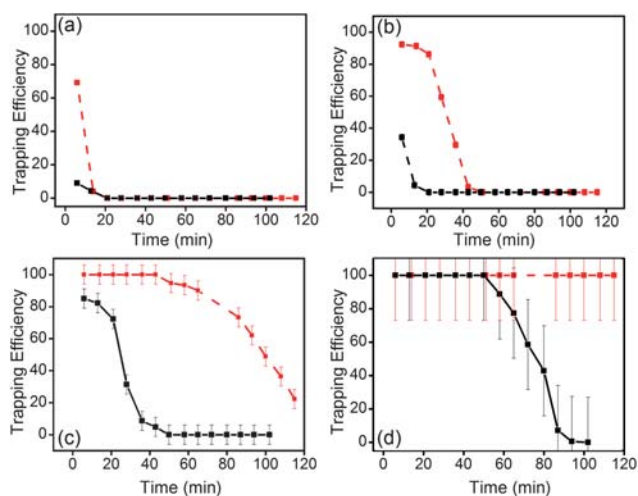


Fig. 5 Data showing the trapping efficiency of XAD-4 (dashed line) and SSPH (solid line) for (a) benzene ($\pm 1\%$ error), (b) toluene (2% error), (c) *p*-xylene ($\pm 6\%$ error) and (d) 1,3,5-trimethylbenzene ($\pm 27\%$ error).

Fig. 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 Fig. 5(a). The data suggest 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 Fig. 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 decreased 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.⁴⁰

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^{-1} for a period of 24 hours. The adsorbents were then extracted into methanol (20 ml) and derivatised with PFBHA (0.0025 g). Fig. 6 displays the reconstructed ion chromatogram for the SSPH and XAD-4 extracts from the indoor experiment. The C_5 and C_6 unsaturated dicarbonyl compounds are tentatively identified based on their

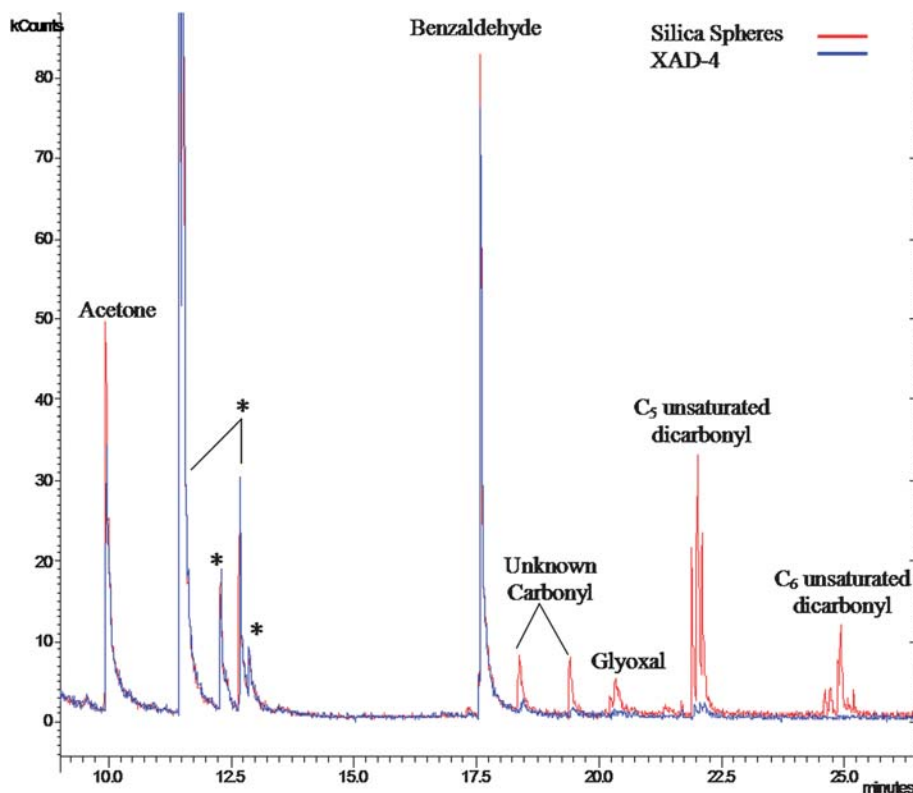


Fig. 6 Reconstructed ion chromatogram (m/z 181) of SSPH and XAD-4 indoor air extracts. * indicates unreacted PFBHA/oximes also present in the blank extracts.

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

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

retention times and the mass spectra of their oxime derivatives.^{35,36} 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, Fig. 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.

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⁻¹). 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, C₅ and C₆ 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,³³ these compounds pose a significant health risk. As SSPH was 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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Agency and does not necessarily reflect the views of the agency and no official approval should be assumed.

References

- N. E. Klepeis, W. C. Nelson, W. R. Ott, J. P. Robinson, A. M. Tsang and P. Switzer, *J. Exposure Anal. Environ. Epidemiol.*, 2001, **11**(3), 231–252.
- A. P. Jones, *Atmos. Environ.*, 1999, **33**, 4535–4564.
- G. Andraca-Ayala and L. G. Ruiz-Suarez, *Atmosfera*, 2005, **18**, 189–203.
- T. A. E. Platt-Mills and M. C. Carter, *N. Engl. J. Med.*, 1997, **336**, 1382–1384.
- C. A. Redlich, J. Sparer and M. R. Cullen, *Lancet*, 1997, **349**, 1013–1016.
- M. Maoni, B. Seifert and T. Lindvall, *Indoor Air Quality—a Comprehensive Reference Book*, Elsevier, Amsterdam, 1995.
- P. Wolkoff, C. K. Wilkins, P. A. Clausen and G. D. Nielsen, *Indoor Air*, 2006, **16**, 7–19.
- R. J. Delfino, *Environ. Health Perspect.*, 2002, **110**, 573–589.
- K. B. Rumchev, J. T. Spickett, M. K. Bulsara, M. R. Phillips and S. M. Stick, *Eur. Respir. J.*, 2002, **20**, 403–408.
- X. S. Zhao, Q. Ma and G. Q. Lu, *Energy Fuels*, 1998, **12**, 1051.
- R. Serna-Guerrero and A. Sayari, *Environ. Sci. Technol.*, 2007, **41**, 4761.
- X. S. Zhao, Q. Ma and G. Q. Lu, *Energy Fuels*, 1998, **12**, 1051.
- D. Serrano, G. Calleja, J. A. Boatas and F. J. Gutierrez, *Ind. Eng. Chem. Res.*, 2004, **43**, 7010.
- M. Popovaa, A. Szegedi, Z. Cherkezova-Zhelevac, I. Mitovc, N. Kostovac and T. Tsonchevaa, *J. Hazard. Mater.*, 2009, **168**, 226–232.
- J. Uchisawa, T. Nanba, S. Masukawa and A. Obuchi, *React. Kinet. Catal. Lett.*, 2008, **95**, 391–398.
- Q. Hu, J. Jun Li, Z. Ping Hao, L. D. Li and Z. S. Qiao, *Chem. Eng. J.*, 2009, **149**, 281–288.
- M. Harper, *J. Chromatogr., A*, 2000, **885**, 129–151.
- S. Shojania, R. D. Oleschuk, M. E. McComb, H. D. Gesser and A. Chow, *Talanta*, 1999, **50**, 193–205.
- A. Kot-Wasik, B. Zabiegała, M. Urbanowicz, E. Dominiak, A. Wasik and J. Namiesnik, *Anal. Chim. Acta*, 2007, **602**, 141–163.
- S. Batterman, T. Metts, P. Kalliokoski and E. Barnett, *J. Environ. Monit.*, 2002, **4**, 361–370.
- J. S. Hayward, T. Gouin and F. Wania, *Environ. Sci. Technol.*, 2010, **44**, 3410–3416.
- B. Zabiegała, A. Kot-Wasik, M. Urbanowicz and J. Namiesnik, *Anal. Bioanal. Chem.*, 2010, **396**, 273–296.
- M. Partyka, B. Zabiegała, J. Namiesnik and A. Przyjazny, *Crit. Rev. Anal. Chem.*, 2007, **37**, 51–78.
- A. Kloskowski, M. Pilarczyk and J. Namiesnik, *Crit. Rev. Anal. Chem.*, 2002, **32**, 301–335.
- B. Temime-Roussel, A. Monod, C. Massiani and H. Wortham, *Atmos. Environ.*, 2004, **38**, 1913–1924.
- L. A. Gundel, V. C. Lee, K. R. R. Mahanama, R. K. Stevens and J. M. Daisey, *Atmos. Environ.*, 1995, **29**, 1719–1733.

- 1 27 B. T. Mader, R. C. Flagan and J. H. Seinfeld, *Environ. Sci. Technol.*, 2001, **35**, 4857–4867.
- 28 A. J. Peters, D. A. Lane, L. A. Gundel, G. L. Northcott and K. C. Jones, *Environ. Sci. Technol.*, 2000, **34**, 5001–5006.
- 5 6 29 D. A. Keane, J. P. Hanrahan, M. P. Copley, J. D. Holmes and M. A. Morris, *J. Porous Mater.*, 2009.
- 30 N. Shimura and M. Ogawa, *Bull. Chem. Soc. Jpn.*, 2005, **78**, 1154–1159.
- 31 S. Brunauer, P. H. Emmett and E. Teller, *J. Am. Chem. Soc.*, 1938, **60**, 309.
- 32 E. P. Barrett, L. G. Joyner and P. P. Halenda, *J. Am. Chem. Soc.*, 1950, **73**, 373.
- 10 33 L. P. Thuner, P. Bardini, G. J. Rea and J. C. Wenger, *J. Phys. Chem. A*, 2004, **108**, 11019.
- 34 B. Temime, R. M. Healy and J. C. Wenger, *Environ. Sci. Technol.*, 2007, **41**, 6514.
- 35 R. M. Healy, J. C. Wenger, A. Metzger, J. Duplissy, M. Kalberer and J. Dommen, *Atmos. Chem. Phys.*, 2008, **8**, 3215–3230.
- 36 B. Temime, R. M. Healy and J. C. Wenger, *Environ. Sci. Technol.*, 2007, **41**, 6514–6520. 7 5
- 37 J. Z. Yu, H. E. Jeffries and R. M. Lelacheur, *Environ. Sci. Technol.*, 1995, **29**, 1923–1932.
- 38 A. T. Hodgson and H. Levin, Lawrence Berkeley National Laboratory, 2003. 8
- 39 K. S. W. Sing, D. H. Everett, R. A. W. Haul, L. Moscou, R. A. Pierotti, J. Rouquerol and T. Siemieniewska, *Pure Appl. Chem.*, 1982, **54**, 2201.
- 40 B. Temime-Roussel, A. Monod, C. Massiani and H. Wortham, *Atmos. Environ.*, 2004, **38**, 1925–1932. 10

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