

EVALUATION OF CARBON NANOTUBE BUCKYPAPER AS SORBENT FOR PASSIVE SAMPLING OF TOLUENE

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ABSTRACT

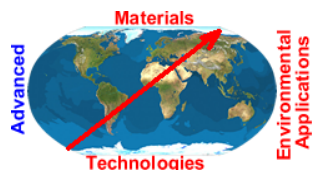
Passive air sampling is a preferred method of air sampling for many applications. Traditionally, this method uses activated carbon as the sorbent and samples are analyzed by chemical or thermal desorption. This research explores the use of carbon nanotubes in the form of a buckypaper as a sorbent for passive sampling by comparing the mass uptake and percent yield to that of the 3M™ Organic Vapor Monitor 3500 over four time trials (30, 60, 120 and 240min) using toluene as the sorbate. A total of 48 samples were taken and results were analyzed using a gas chromatograph. The desorption efficiency and mass uptake rate of the carbon nanotube sorbents were similar to the 3M™ Organic Vapor Monitor 3500. Desorption efficiencies were 85.5 – 100.3% for 3M samplers and 89.5 – 95.5% for carbon nanotube sorbents. The mass of toluene collected at 30-minute and 120-minute time trials showed no significant differences ($p = 0.37$, 0.1 , respectively) while 60min and 240min time trials were significantly different with fabricated sorbents collecting closer to the expected mass ($p = 0.02$, 0.04 respectively). Overall sampling capacity is lower in the 20mg carbon nanotube buckypapers compared to the 200mg activated carbon pad of the 3M™ OVM 3500 due to somewhat lower adsorption capacity and much lower sorbent mass. While the objective of this study was to explore the suitability of buckypaper sorbents for sampling exposures at low concentration for short durations, a larger mass buckypaper sorbent should provide a similar sampling capacity to standard passive samplers.

Keywords: passive sampling, carbon nanotubes, buckypaper, diffusive badges, photothermal desorption

INTRODUCTION

Diffusive sampling is utilized in many areas of industry and for various environmental and occupational applications as it provides an efficient, non-obtrusive method for air sampling. It is approved in methods for various substances of interest by NIOSH, OSHA, and the EPA. Granular activated carbon (GAC) is widely used in air sampling devices to trap volatile organic compounds (VOC) for quite some time [1,2]. However, the emergence of new materials with high

specific surface area and microporosity such as carbon nanotubes (CNT) could bring new opportunities in the air sampling and analysis field. CNT have been demonstrated to be efficient gas and vapor sorbents in many studies, but their use in air sampling devices has been limited. Preliminary work by Floyd *et al.* has successfully demonstrated the use of visible light as a means to desorb analytes from CNT sorbents [3]. This could serve as a versatile method to desorb a portion of the collected analyte for immediate exposure feedback



while preserving the remaining sample for further analysis. A key concern with using CNT as a sorbent is the potential toxicity of the small fibers and bundles [4-7]. For this reason, CNT powder was processed into a buckypaper (BP), a thin paper-like pad, to minimize the potential for aerosolization and facilitate sorbent handling.

A diffusive sampler consists of a permeable membrane, a diffusive path length and a sorbent with high affinity for the analyte of interest. The mass uptake rate of the sampler is governed by the concentration gradient across the diffusive path length and the geometric characteristics of the sampler (diffusive path length and sampler surface area) [2,8]. Mass uptake can be calculated using Equation 1.

$$m = D \left(\frac{A}{L} \right) (C)(t) \quad (1)$$

where

m = total mass uptake (g)

D = diffusion coefficient (cm^2/min)

A = cross sectional area of diffusion path (cm^2)

L = length of diffusion path (cm)

C = ambient concentration being sampled (g/cm^3)

t = sampling time (min)

In this study, a well characterized diffusive sampler (3M™ OVM 3500) was used to evaluate the sampling performance of laboratory fabricated BP sorbent substrates. The 3M sampler body was equipped with BP sorbents (BP-OVM) that were fabricated to fit the body of the 3M sampler, allowing direct comparison between the BP-OVM and the un-modified 3M sampler (3M-OVM). Sampler bodies, sorbent assignment, and location was randomized for all trials and performed in triplicate.

METHODS AND MATERIALS

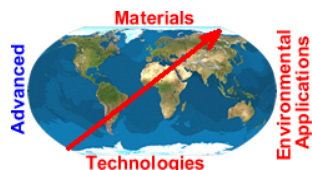
Toluene was selected as the analyte of interest in these experiments. In order to best compare the sorbents, toluene uptake was measured in 3M-OVM and BP-OVM samplers at 10 ppm for four exposure

lengths. All BPs were fabricated using the same technique, as described below, and both types of samplers were simultaneously exposed in randomized triplicates.

Buckypaper Fabrication Procedure

Buckypapers were fabricated using a fluid filtration technique outlined by Zheng et al. and customized for the application discussed [9]. Approximately 20 mg (± 1 mg) of single-walled carbon nanotubes (MK Nano: +90% pure, OD: 1-2 nm, length: 5-30 μm) were suspended in 500 mL toluene for 30 minutes via ultrasonic bath (Branson Ultrasonics, Danbury, CT, USA). Suspended CNT solution was deposited on nylon filters (47 mm diameter, 5 μm pore size) using vacuum filtration. Nylon filters were oven dried and pre-weighed before placing in the vacuum apparatus. Larger agglomerates that would not disperse were left in the sonication vessel after decanting the suspended CNT for filtration. Toluene filtrate was captured, used to rinse the sonication vessel and the remaining agglomerates were re-sonicated for an additional 30 minutes. A 50 Watt halogen lamp was placed above the vacuum apparatus to aid in drying the first layer while the remaining CNT solution was sonicating. This secondary suspension was added over the primary filtration after the first layer had set-up. Once the second layer dried, the deposited CNT and filter membrane were placed in an oven at 200°C for approximately five minutes to remove any remaining liquid. Using a hollow punch, a 31 mm BP disk was cut out of the nearly dry filter cake to fit the 3M sampler bodies.

Completely drying the BP before cutting caused the BP to flake along the cut edges and delaminate from the nylon membrane, thus leading to inconsistent sorbent surface area. Cut BP sorbents were placed in the oven at 200°C overnight to fully dry and cure. After curing, BP sorbents were removed from the oven and weighed to determine the dry mass of CNT. For sampling, BP sorbents were desorbed at 200°C overnight prior to being



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inserted into the sampler body and covered with the draft shield and capped. New activated carbon pads were used for each trial while the BP sorbents were reused several times. New and used bodies were randomized across sorbents. Sampler bodies were retired after three uses.

To prevent exposure when handling CNT powder, handling, transferring and weighing was conducted in a fume hood. Additionally, PPE was used including half-mask respirator with P-100 aerosol filters, gloves and other appropriate lab attire. Used BP sorbents were recycled where possible or disposed through the university hazardous waste disposal program.

Desorption Efficiencies

Desorption efficiencies (DE) were performed following 3M™ Technical Data Bulletin 1028 and NIOSH Method 4000 protocols [10,11]. The internal standard used was 4-chlorobenzotrifluoride. DE were performed using the expected mass at each time trial. Five 3M-OVM samplers and five BP-OVM samplers were spiked with 36, 71, 141 and 303 µg of toluene to bracket the anticipated range of collected toluene during the timed exposures.

Adsorption Capacity

Due to its applications and wide spread use, it was known that the 3M™ activated carbon pad would not saturate at such a low loading. 3M Technical Data Bulletin 1028 states the capacity for toluene to be > 25 mg [10,11]. However, the BP sorbents were previously uncharacterized and it was necessary to determine the toluene adsorption capacity prior to experimentation to ensure suitable sampling capacity at the expected loading (up to 303 µg).

Adsorption isotherms were collected for several of the BP sorbents and 3M™ activated carbon pads to estimate their toluene adsorption capacity. An adsorption isotherm represents the equilibrium between the gas phase (un-adsorbed) and liquid

phase (adsorbed) of the adsorbate at a given temperature. In this case, adsorption isotherms were determined by injecting known masses of toluene into a small chamber (120 mL) containing the sorbent and allowing the concentration to achieve a steady state. The steady state concentration (C_{ss}) was measured using a photoionization detector (PID) (Baseline Inc., Lyons, Colorado, USA) embedded in the chamber. Steady state concentration was defined as less than one ppm change across 10 minutes. Injections continued until C_{ss} was greater than 150 ppm. Adsorption capacity was estimated from the mass of toluene adsorbed by the sorbent when the steady state concentration was 10 ppm.

Sampling

Sampling was conducted in a 17.35 L stainless steel dynamic exposure chamber with a mixing fan and diffuser. Toluene concentration was established at 10 ppm by a streamline injection injecting liquid toluene at a known rate (15.5 µL per hour) into a constant air flow. The chamber concentration for each time trial was calculated from concentration measurements logged by a PID inside the chamber.

Sampling was conducted in two sessions. Each session consisted of triplicate sampling with 3M-OVM and BP-OVM samplers at each of four time trials (30, 60, 120, and 240 minutes). The experimental set-up is shown in Figure 1. Sample placement and direction of sampler face were randomized to avoid bias. A total of 48 samples were collected. Samples were removed and desorbed the same day as sampling.

Analysis and Statistics

Desorption efficiencies and sampling results were determined via chemical desorption and gas chromatography. The gas chromatograph (Agilent Technologies 6850 GC, Santa Clara, CA, USA) was calibrated using a 6 point curve: 10.3, 41.9, 172, 686, 2,750, and 8,580 µg/mL with $R^2 = 0.9942$.

A two-tailed t-test was conducted to compare the mass uptake for the 3M-OVM and BP-OVM samplers at each period. Since the toluene concentration was slightly different between session

1 and session 2, recovery rate (or percent yield) was used to standardize between sessions. All statistical tests were conducted with an alpha level of 0.05.

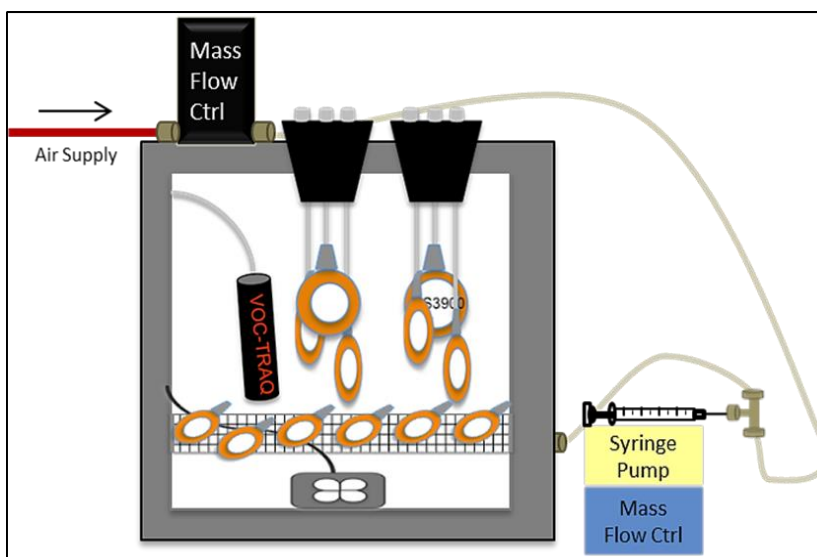


Figure 1. Sampling Experimental Setup

RESULTS

Desorption Efficiency

Desorption efficiency results for the BP sorbents ranged from 89.5 - 95.5%, while DE for the 3M™ ranged from 85.6 - 100.3% (Table 1). Buckypapers showed a greater percent yield at the 35.5µg mass DE than the 3M™ activated carbon pads. Both BP and 3M™s had greater than 95% yield at the 142.0µg DE. The 3M™ activated carbon pads produced a greater percent yield at both the 71.0µg and 281.6µg ranges. However, an outlier of 126% is included in the average at the 71.0µg DE and three measurements are greater than 100% at the 281.6µg DE. The ideal yield of 100% is included in the 95% confidence interval of each time trial.

Adsorption Capacity

Toluene adsorption isotherms were performed on two BP sorbents and one 3M™ activated carbon adsorbent pad. The adsorption capacity at 100 ppm

equilibrium concentration was determined from the fitting of the isotherm curves with polynomial equations. The adsorption capacity of BP and 3M sorbents were 153µg/mg and 183µg/mg, respectively (Figure 2 and Table 2).

Sampling

Actual chamber concentration was measured during all sampling events using a calibrated PID. Chamber concentration during the first sampling round ranged from 9.2 to 9.4ppm and from 10.0 to 10.2ppm in the second sampling round. Average concentrations during the first and second sampling rounds are shown in Table 3.

Table 4 shows results of all time trials for both rounds one and two, comparing the percent yield for each material. These results are significantly different at the 60 and 240min time trials ($p=0.02$, 0.04 , respectively) but not significantly different at the 30 and 120min time trials ($p=0.37$, 0.10 , respectively).

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Table 1. Desorption Efficiency by Expected Mass

Samples	Expected Mass (µg)	Average Yield (%)	Avg. Std. Dev.	P-value
3M	35.5	85.6	1.82	0.07
BP	35.5	89.7	3.92	
3M	71.0	100.3	14.69	0.45
BP	71.0	94.9	4.23	
3M	142.0	99.7	6.62	0.26
BP	142.0	95.5	3.78	
3M	281.6	97.0	7.03	0.09
BP	303.4	89.5	6.22	

Table 2. Adsorption Isotherms Data

Sorbent	Adsorbent Mass (mg)	Adsorption Capacity at 100 ppm (µg/mg)
BP sorbent	27	153
3M™ Charcoal Pad	200	183

Table 3. Expected mass for each time trial for sampling rounds one and two

Time Trial (min)	Sampling Round	Average Concentration (ppm)	Expected Mass (µg)
30	1	9.2	32.7
	2	10.1	35.9
60	1	9.3	65.9
	2	10.0	71.5
120	1	9.4	132.9
	2	10.0	142.1
240	1	9.3	264.0
	2	10.2	289.7

DISCUSSION

The DE (average percentage yield) of BP-OVMs and 3M-OVMs were quite similar although there was a significant difference for two out of the four

spiked conditions. For one of the conditions the average DE for the 3M-OVM was greater than 100%. A study from Voelte et al. [12] also shows evidence of the 3M™ activated carbon pads having a DE of greater than 100%. It is hypothesized in this

study and the Voelte et al. study that evaporation occurs due to the elution caps during chemical desorption. Some BP sorbents were used multiple

times for DE (with thermal regeneration between uses), which did not appear to affect the sampling capabilities of the BP sorbent.

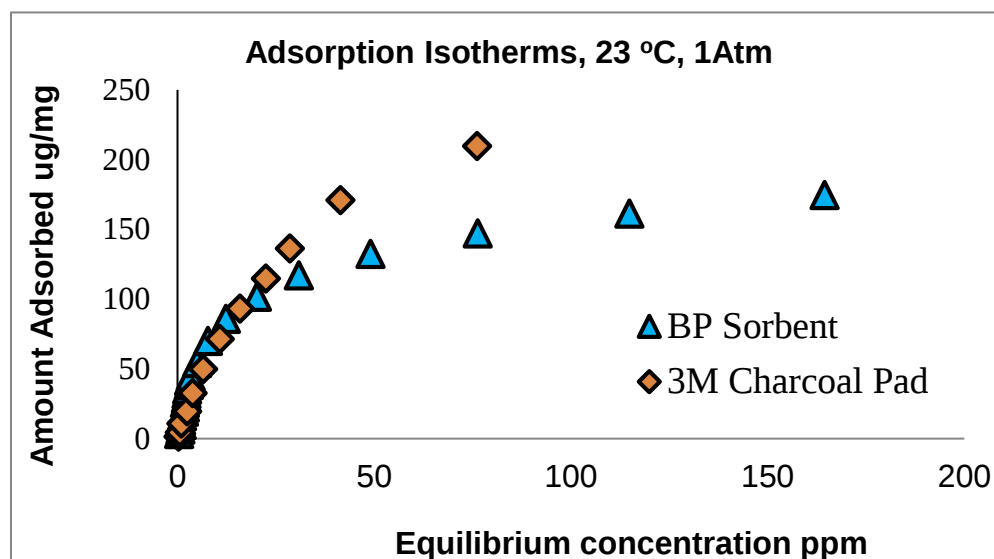


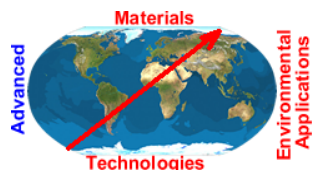
Figure 2. Adsorption Isotherm Plots for BP Sorbent and 3M Charcoal Pad

Table 4. Comparing average percent yield from sampling in both rounds

Sampling time (min)	Samples	Average Yield (%)	Average Standard Deviation	P-value
30	3M	105.6	8.72	0.37
	BP	99.7	11.55	
60	3M	78.4	3.9	0.02
	BP	95.9	14.52	
120	3M	80.7	2.39	0.10
	BP	84.1	3.93	
240	3M	86.4	1.42	0.04
	BP	97.0	10.65	

Comparison of average percent yield for both sampling rounds shows no statistical difference between the 30-minute and 120-minutes data sets ($p = 0.37$, 0.10 , respectively) but a significant difference between 60-minute and 240-minute trials

($p = 0.02$, 0.04 , respectively) with BP collecting greater mass, closer to the expected amount. When performing DE studies, the variation in the 3M sorbents (average standard deviation ranging from 1.82 to 14.69) were greater than the BP sorbents



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(average standard deviation ranging from 3.78 to 6.22) (Table 1). Additionally, when significant differences were observed between the 3M-OVM and BP-OVM samplers, the BP-OVM samplers were actually closer to the anticipated value.

Results indicate that the low mass BP sorbents possessed sufficient adsorption capacity to sample toluene for 240 minutes at 10 ppm and performed as well as the commercial product.

Limitations

At low mass uptake, equivalent sorbent performance is expected, at high mass uptake the BP sorbents are expected to approach saturation capacity and exhibit back diffusion due to their low mass compared to the standard activated carbon pad. At a concentration of ~10 ppm, the adsorption capacity of BP sorbent is 81.0 $\mu\text{g}/\text{mg}$ while the adsorption capacity of the 3M sorbent is 94.9 $\mu\text{g}/\text{mg}$. A 20 mg BP sorbent should therefore have a capacity of 1,897 μg at 10 ppm. Exposure to 10 ppm for 240 minutes was expected to result in 290 μg toluene adsorbed which is nearly 20% of capacity. At this level of loading some back diffusion would occur if the ambient concentration dropped to near zero. For this reason, these low mass CNT samplers are targeted toward low concentration, short duration monitoring. Results indicate that some of the BP yielded greater than 100 percent of the mass they were expected to collect. Loss of extraction solvent was likely the cause but should have been randomized across both sorbent types.

The overall variability of the BP sorbents was greater than that of the 3M sorbent, this is likely due to greater variability from one BP to the next due to the small scale fabrication technique used. Cutting the nylon supporting membrane filter was quite difficult and may have led to greater variability in CNT mass. The use of self-supporting BP would likely produce BP with less variability.

The original BP sorbent fabrication procedure outlined by Zheng et al. was reported to produce

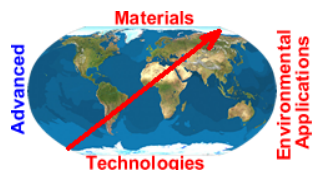
self-supporting BP; however, the CNT used in this project were synthesized by chemical vapor deposition rather than high pressure carbon monoxide reduction [9]. We suspect this is the cause of the difference in BP quality. Continued efforts have shown that the type of CNT (i.e. synthesis technique) does have a major effect on BP formation. Using this basic process, self-supporting BP have been produced using arc discharge and high pressure carbon monoxide SWNT."

CONCLUSION

The sampling rate of these two sorbents is similar as evidenced by the similar mass uptake and percent yields at each time trial. Buckypaper sorbent fabrication is scalable, and higher mass BP sorbents should have similar sampling capacity as commercially available passive samplers. Variation in BP sorbents may be due to the fabrication process. Although the results from the overall 30min percent yield are not significantly different between the BP-OVM and 3M-OVM, the BP-OVMs had a 97.7% yield while the 3M-OVM had a 105.6% yield. Regardless of the significant differences that exist, the sampling rate between samplers remains very similar. Buckypaper sorbents have great potential for use in conjunction with emerging desorption techniques, such as photothermal desorption. Future applications of this work include passive sampling with self-supporting BP sorbents using diffusive a sampler specifically designed to withstand high-energy light flash. It is likely that the low-cost CVD CNTs used in this project are not suitable for formation of self-supporting BP sorbents, but other types of CNT have since been tested and were easily formed into self-supporting BPs.

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