Photothermal Desorption of Single-Walled Carbon Nanotubes and Coconut Shell-Activated Carbons Using a Continuous Light Source for Application in Air Sampling

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ABSTRACT

Many techniques exist to measure airborne volatile organic compounds (VOCs), each with differing advantages; sorbent sampling is compact, versatile, has good sample stability, and is the preferred technique for collecting VOCs for hygienists. Development of a desorption technique that allows multiple analyses per sample (similar to chemical desorption) with enhanced sensitivity (similar to thermal desorption) would be helpful to field hygienists. In this study, activated carbon (AC) and single-walled carbon nanotubes (SWNT) were preloaded with toluene vapor and partially desorbed with light using a common 12-V DC, 50-W incandescent/halogen lamp. A series of experimental chamber configurations were explored starting with a 500-ml chamber under static conditions, then with low ventilation and high ventilation, finally a 75-ml high ventilation chamber was evaluated. When preloaded with toluene and irradiated at the highest lamp setting for 4 min, AC desorbed 13.9, 18.5, 23.8, and 45.9% of the loaded VOC mass, in each chamber configuration, respectively; SWNT desorbed 25.2, 24.3, 37.4, and 70.5% of the loaded VOC mass, respectively. SWNT desorption was significantly greater than AC in all test conditions (P = 0.02–<0.0001) demonstrating a substantial difference in sorbent performance. When loaded with 0.435 mg toluene and desorbed at the highest lamp setting for 4 min in the final chamber design, the mean desorption for AC was 45.8% (39.7, 52.0) and SWNT was 72.6% (68.8, 76.4) (mean represented in terms of 95% confidence interval). All desorption measurements were obtained using a field grade photoionization detector; this demonstrates the potential of using this technique to perform infield prescreening of VOC samples for immediate exposure feedback and in the analytical lab to introduce sample to a gas chromatograph for detailed analysis of the sample.

KEYWORDS: air sampling; bucky paper; exposure assessment; industrial hygiene; photothermal desorption; single-walled carbon nanotubes; toluene; VOC

INTRODUCTION

Every year millions of tons of volatile organic compounds (VOCs) are released into the environment by anthropogenic sources globally and domestically (Middleton, 1995; Goldstein and Galbally, 2007; U.S. EPA, 2008), with a portion of these emissions resulting in occupational exposure of workers. Validated methods have been developed to measure these compounds to ensure compliance with the permissible exposure limits set forth by the U.S. Occupational Safety and Health Administration (OSHA) (U.S. EPA, 1999; NIOSH, 2003; OSHA, 2008, 2010).

For VOC monitoring, the most common and preferred sampling technique is sorbent-based pre-concentration in which the analyte is collected on a solid sorbent. Sorbent samples have good sample stability, are compact and convenient; in many cases, the preferred sorbent is high surface area granularized activated carbon (AC). Sorbent samples must be desorbed prior to analysis and desorption can be performed by solvent extraction or heat treatment. Solvent desorption is simple, provides high desorption efficiencies, and allows multiple analyses per sample. However, it requires significant lab preparation, uses toxic solvents, and has inherent sensitivity limitations due to the small fraction of sample injected into the gas chromatograph (GC), 1 µl out of 1000 µl such as in OSHA method 111 or NIOSH method 1500 (NIOSH, 2003; OSHA, 2008). Thermal desorption requires no lab preparation, is solvent free, and simple in principle: heat is applied to the sorbent under purge gas flow that releases the trapped analyte. The sensitivity of thermal desorption is excellent since the entire sample is delivered to the GC, but for many substances, more utility would be gained by delivering only a portion of the sample to the GC and reserving the rest of the sample for multiple analyses. Some drawbacks of this technique are the high cost associated with thermal desorption units and samplers, the added system complexity, and the added analysis time. Flow splitting thermal desorption units have been developed but are expensive and still require complete desorption of the original sample with the unanalyzed portion recollected on another sorbent tube (CDS Analytical, 2007).

In this study, we explore the use of high-intensity light irradiation to thermally desorb an analyte from a preloaded sorbent, single-walled carbon nanotubes (SWNT), and AC. Light energy is absorbed directly by the sorbent and converted to heat. SWNT can have high surface areas (Peigney *et al.*, 2001; Cinke *et al.*, 2002; Li *et al.*, 2004; Byl *et al.*, 2006) and are excellent light absorbers (Kataura *et al.*, 1999; Ajayan *et al.*, 2002; Bockrath *et al.*, 2002; Tseng *et al.*, 2007; Mizuno *et al.*, 2009; Tabakman *et al.*, 2010). SWNT are explored in parallel with AC due to their emerging potential as a sorbent for environmental samplers (Zheng *et al.*, 2006; Hussain *et al.*, 2008a; Takada et al., 2010a,b; Hussain and Mitra, 2011) and the ability to functionalize SWNT to alter chemical affinities (Georgakilas *et al.*, 2002; Hilding *et al.*, 2003; Tagmatarchis and Prato, 2004; Hussain *et al.*, 2009). While traditional thermal desorption heats the sorbent via conduction from a heating sleeve through the sampler body, using light reverses the heat flow. Heat is generated by the sorbent and conducted from the sorbent to the sampler body and the external environment. Reversing heat flow and isolating the sample could allow more precise control of heating than is possible with a simple resistive heater.

This work explores the use of high-intensity broad spectrum light to photothermally desorb a representative VOC from two sorbents, AC and SWNT. Differences in desorption between AC and SWNT substrates and the utilization of field grade PID to measure desorption are also examined.

METHODS

Commercially available coconut shell AC and SWNT were loaded with a known mass of toluene vapor and irradiated with broad spectrum light at different light powers for several minutes. Desorbed toluene was quantified with a field grade PID and compared across lamp settings and materials. Three test chambers for photothermal desorption were evaluated for each sorbent: a static chamber (500 ml, Fig. 1a), a 'large' dynamic chamber (500 ml, Fig. 1b), and a 'small' dynamic chamber (75 ml, Fig. 1c). Toluene adsorption isotherms were obtained to compare sorbents and determine a maximum sample loading that does not saturate either sorbent. Samples were loaded with toluene vapor by injecting liquid toluene onto the interior sidewall of the chamber instead of directly on the sorbent and desorbed by irradiation with light for at least 4 min. Toluene was selected as a representative VOC because of its similarity to benzene and its use
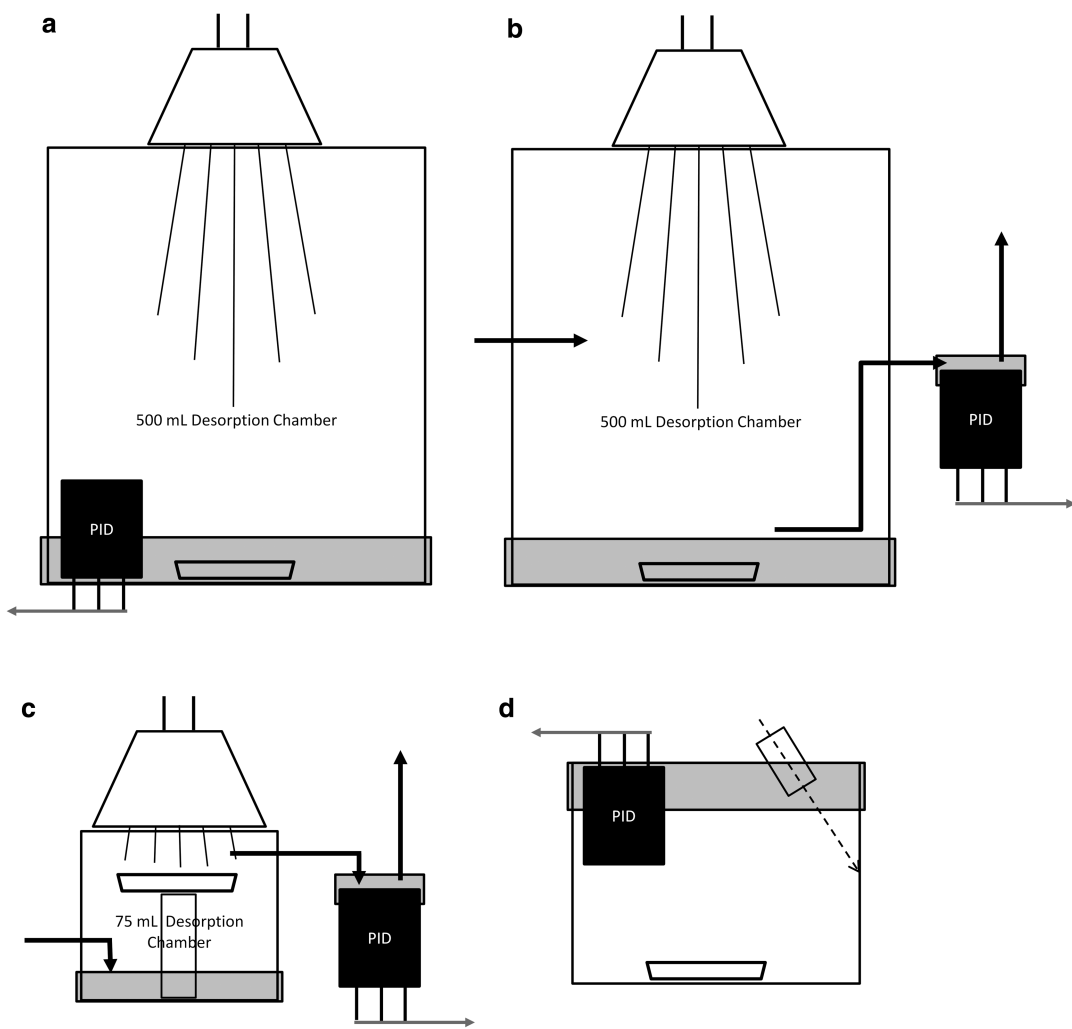
1   Schematic of test chambers used for adsorption and desorption experiments. (a) 500-ml static desorption chamber. (b) 500-ml flow desorption chamber. (c) 75-ml flow desorption chamber. (d) 120-ml adsorption chamber.

in similar studies (Zheng *et al.,* 2006; Hussain et al., 2008b, 2010; Balanay *et al.,* 2011).

Sample construction and material specifications
AC was purchased from SKC Inc. (Anasorb CSC, lot 2000, 20/40 mesh). SWNT was purchased as dry powder from M.K. Nano (90%+ SWNT, lot SCN0109) with the following specifications: tube diameter 1.4–2.1 nm, >90% SWNT, <3% metal catalyst, and <7% amorphous carbon or multiwalled carbon nanotubes. Due to potential negative health effects of SWNT, special care was taken when handling SWNT powder. All handling, transferring, and weighing were conducted in a fume hood while

wearing half-mask respirator with P-100 aerosol filters and other appropriate lab attire. Used materials were recycled where possible and disposed though the university hazardous waste disposal program otherwise. Specific surface area and pore size distribution were measured for each material using nitrogen porosymmetry at 77 K (Micromeritics ASAP2020). Sorbent grain size was estimated from the manufacturer's stated mesh size for AC and by SEM imaging of the SWNT powder. Fifty milligrams (±1 mg) of sorbent was weighed using a four-digit analytical balance and spread across a 26-mm diameter sample tray to an average depth of 0.25 mm for SWNT and a monolayer of granules of AC.

Sample loading procedure

To evenly dose each adsorbent sample with a discrete mass of toluene, samples were placed inside a 120-ml glass jar having a polytetrafluoroethylene (PTFE) lid and injection port (Fig. 1d). Analytical grade toluene was injected onto the side wall of the jar using a microliter syringe. As toluene evaporated, it was adsorbed from the vapor phase, ensuring the most homogeneous loading possible, which is not achieved with direct liquid dosing. This technique was validated for both materials by monitoring toluene concentration with an embedded photoionization detector inside the jar and by chemical desorption using a modified NIOSH 1501 method (NIOSH, 2003). The PID readings were used to determine the minimum time necessary to fully adsorb injected toluene. The solvent extraction was used to determine desorption efficiencies and verify actual adsorbed mass. Samples were loaded with toluene and allowed to stand at least 2 h before analysis.

Adsorption isotherm procedure

The same loading technique as above was utilized to obtain the adsorption isotherm of each sorbent at 23°C. A known mass of sorbent was placed into the 120-ml glass jar with PTFE lid and PID (Fig. 1d). Using the injection port, the sorbent was dosed with a small mass of toluene by injection of liquid toluene onto the chamber sidewall and allowed to reach steady state. Upon achieving steady state, the next dose was administered until a final steady state concentration of >150 p.p.m. was achieved. An isotherm plot of adsorbed mass per sorbent mass (mg g^{-1}) versus equilibrium concentration (p.p.m.) was constructed. Adsorbed mass was calculated from the difference between the injected mass and the airborne mass using measures of headspace concentration and headspace volume.

Desorption procedure

A common 12-V DC, 50-W halogen/incandescent spot lamp (FEIT, 12V50WEXN) was mounted to the bottom of an inverted glass jar with PTFE lid. The lid was mounted to a stand and equipped with a sample holder and PID socket similar to the adsorption chamber described above (Fig. 1a–c). DC voltage was supplied to the lamp at 8, 10, 12, and 15 V using a laboratory power supply. Light power was measured with an Ophir Nova II light power meter and 30A-BB-18 general purpose probe (Ophir, North Logan, UT, USA). Initially, the 500-ml static system was evaluated, followed by the 500-ml dynamic system at 0.3 and 3.2 air changes per minute and finally the 75-ml dynamic system at 12 air changes per minute. For the static system, 50 mg samples were loaded with 6.525 mg toluene and desorbed at each lamp voltage ($n = 1$) for 9 min as a screening process for lamp voltage and sorbent loading level. Then samples with 6.525, 4.350, and 2.175 mg of toluene were desorbed at 15 V for 4 min ($n = 6$–7). For the 500-ml dynamic system, the same screening process was performed with 50 mg samples loaded with 6.525 mg toluene and desorbed at each lamp voltage ($n = 1$) with 0.3 air changes per minute. Since this was a flow system, desorption occurred differently than in the static system, and irradiation was continued for 14 min to fully characterize desorption behavior. After screening at each lamp voltage, samples loaded with 6.525 mg of toluene were desorbed at 15 V for 4 min at 0.3 and 3.2 air changes per minute ($n = 3$). For the 75-ml dynamic system, 50 mg samples were loaded with 0.435 mg of toluene and desorbed at 15 V for 4 min ($n = 3, 4$).

As a control, preloaded samples were placed in the desorption chamber and loosely covered with a reflective foil cap. The sample was irradiated as above such that it was subjected to the same conductive and convective heating mechanisms but not direct radiative heating. Control and non-control samples were compared.

PID calibration

For these experiments, a field grade photoionization detector typical of that used in direct reading devices and 4-gas meters was adapted for laboratory use (Baseline-Mocon, 2012, 2013). This type of PID was selected for its compact size and to demonstrate the transferability of this desorption technique to hand-held direct reading devices commonly employed by hygienists. A two-point calibration (0.0 and 507.2 p.p.m.) was performed using manufacturer guidelines and supplied software. The sensor was exposed to a flow of filtered air for 10 min before setting the zero, then exposed to a flow of calibration gas (AirGas, Port Allen, LA, USA) at 507.2 p.p.m. toluene for 4 min before setting the span value. The manufacturer rates sensor accuracy at ±3% when calibrated

according to their guidelines (Baseline-Mocon, 2013); calibration checks by injection of a known mass of toluene into the empty Adsorption Chamber were within 1% of the expected value.

Statistics

A *t*-test was used to evaluate differences between AC and SWNT within each condition (i.e. 500-ml static, 15 V). Since incremental improvements in the chamber design eventually led to the 'small' dynamic chamber, results from the 'small' dynamic chamber were compared to the best results from the 'large' dynamic chambers to determine if the design 'improvements' were significant. This comparison was also made with a *t*-test. In all statistical tests, the 95% confidence was used as a minimum level of significance ($\alpha = 0.05$).

RESULTS

Light power and material characterization

Light power measurements for the 500-ml desorption chambers with 8, 10, 12, and 15 V applied to the lamp were 94, 149, 224, and 361 mW cm^{-2}, respectively. Light power for the 75-ml desorption chamber with 15 V applied to the lamp was 752 mW cm^{-2}.

Specific surface area and pore size distribution are similar between AC and SWNT. AC has slightly larger surface area (S_{BET}, m^2 g^{-1}) and microporosity ($V_{\mu P}$, cm^3 g^{-1}, pore volume <20 Å) but notably lower total porosity (V_{TP}, cm^3 g^{-1}) (Table 1). From the plot of pore size distribution (Fig. 2), we can see that AC has a sharper peak with smaller pore diameter in the micropore range (<20 Å) than SWNT, while SWNT has greater total porosity than AC. Grain size of the AC was stated by the manufacturer as 20/40 mesh, and this translates to 400–800 μm; grain size of the SWNT was estimated to be 0.5–50 μm by SEM imaging (Fig. 3).

Table 1. BET surface area, micropore volume, and total pore volume for SWNT and AC samples

	S_{BET} (m^2 g^{-1})	$V_{\mu P}$ (cm^3 g^{-1})	V_{TP} (cm^3 g^{-1})
SWNT	980	0.39	0.59
AC	1030	0.41	0.45

BET, Brunauer, Emmett and Teller.

Toluene adsorption isotherms

The toluene adsorption isotherms at 23°C for both materials are shown in Fig. 4. The adsorption capacity of SWNT was lower than AC. Both adsorption isotherms (AC and SWNT) are quite similar up to 139 mg g^{-1} (red horizontal line in Fig. 4); therefore, the maximum loading of both sorbents was set below this level. High mass loading was used for initial characterization experiments and later reduced to realistic levels as the system performance became known.

Sample loading

Samples of AC and SWNT (50 mg) were loaded by indirect injection of pure toluene (6.525 mg), as described above. Loading samples at this level approach the upper range of linear adsorption for SWNT as shown in Fig. 3. The chamber containing the samples of AC or SWNT was monitored with the PID during loading to determine the time necessary to achieve complete adsorption. In both materials, 99% adsorption was observed by 30 min, and >99.4% adsorption by 60 min, as determined by dividing the mass of toluene in the chamber headspace (from p.p.m. measurements with PID) by the known injected amount.

Table 2 shows fraction of adsorption at 15-min intervals during the first hour of loading. Figure 5 is a representative sample loading (50 mg SWNT, 6.525 mg toluene). Adsorption using this technique was also confirmed by chemical extraction. Recoveries for AC loaded with 6.525 and 0.435 mg toluene were 98.8% (±1.8) and 99.0 (±1.3), respectively ($n = 5$); recoveries for SWNT loaded with 6.525 and 0.435 mg toluene were 100.5% (±2.1) and 99.0 (±1.9), respectively ($n = 5$).

Desorption

Desorption of AC and SWNT samples by irradiation at varied lamp voltages (8, 10, 12, and 15 V) using the 500-ml static chamber are shown in Fig. 6. The desorbed percentage of the loaded toluene mass calculated from the headspace concentration within the chamber is shown in the plot. As expected, desorption increases with input energy, with the highest lamp voltage (15 V) yielding the greatest desorption. Desorption was greater in SWNT than in AC at each lamp voltage but seems to differ even more so at 15 V. This experiment was used as a screening process to characterize desorption at varied
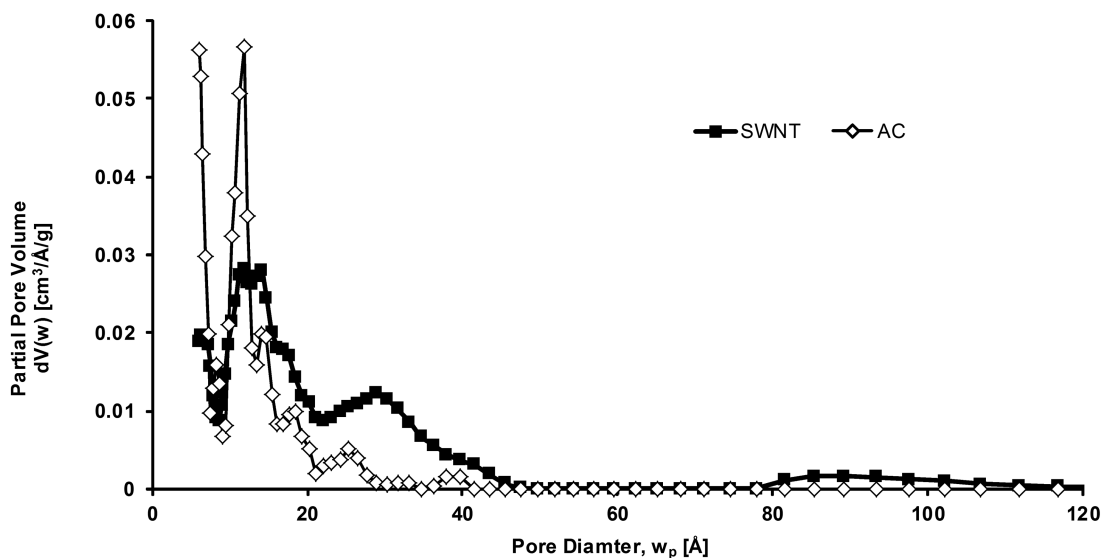
2   Pore size distribution of AC (hollow diamonds) and SWNT (solid squares).
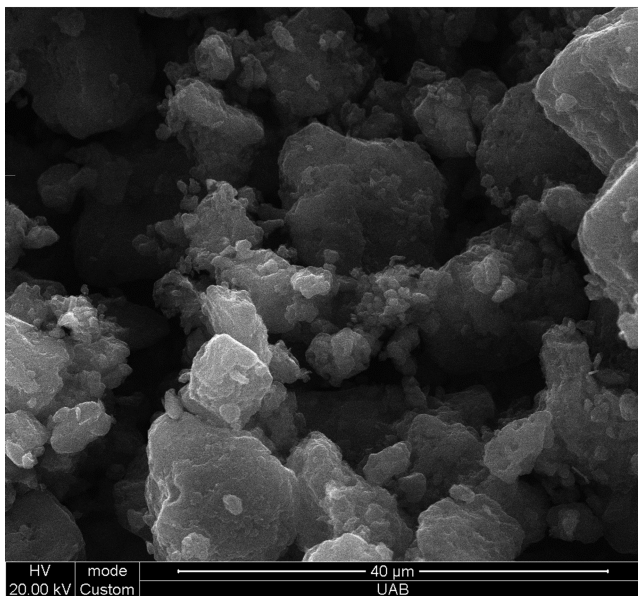
3   SEM image of SWNT powder shows a majority of particles between 0.5 and 4 μm with larger particles reaching 20–50 μm.

lamp settings; the 15-V lamp setting is explored in more detail later. Since this is a closed system, the desorbed mass accumulated in the headspace of the chamber and established a right-shifted dynamic equilibrium but could not achieve complete desorption with the applied light power. During experimental trials, when irradiated at 15 V, desorption concentration peaked after 5–6 min and then declined. It was determined that the declining concentration was due to the PID getting hot during sample irradiation since it was inside the chamber with the sample. To correct for this effect, the PID was shielded with reflective foil and a correction curve was developed for sensitivity loss during irradiation, which was applied to later trials.
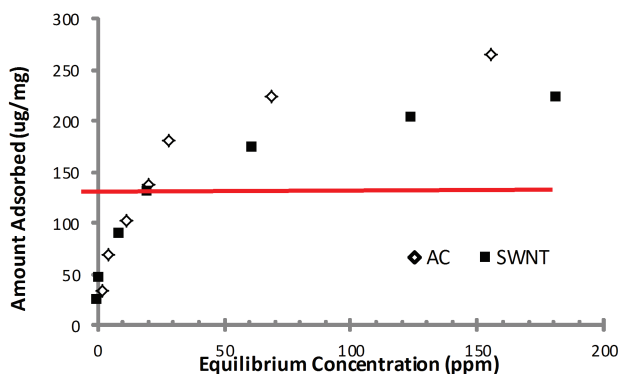
4   Adsorption isotherm (23°C, 1 atm) for AC (hollow
diamonds) and SWNT (solid squares) samples. The horizontal
line represents the upper range of linear adsorption for SWNT.
This was the maximum loading level used for both materials.

Table 2. Degree of adsorption for 50 mg AC and SWNT samples at 15, 30, 45, and 60 min post-injection of 6.525 mg toluene, $n = 3$

Sorbent		Adsorbed fraction at			
		15 min	30 min	45 min	60 min
SWNT, $n = 3$	Average (SD)	0.964 (0.009)	0.991 (0.002)	0.993 (0.001)	0.994 (0.001)
AC, $n = 3$	Average (SD)	0.957 (0.001)	0.992 (<0.001)	0.995 (0.001)	0.996 (0.001)

The same screening process as above was performed using the 500-ml 'large' flow chamber (Fig. 7). Air flow rate was maintained at 0.14 l min^{-1} (0.3 air changes per minute) and lamp voltages of 8, 10, 12, and 15 V were applied. A peak in concentration emerges around 5 min as lamp power increases, suggesting that a greater degree of desorption occurs faster with more light power. Figure 8 summarizes both screening experiments (static and dynamic flow) in units of total mass desorbed and percent desorbed.

Figure 9 shows percent desorption of 50 mg samples of AC and SWNT loaded with 6.525, 4.350, and 2.175 mg toluene and irradiated at 15 V in the static chamber for 4 min; output is corrected for PID sensitivity loss ($n = 6–7$). After 4 min of irradiation, the concentration inside the static chamber plateaus and minimal desorption is achieved beyond this point (Fig. 6). The effect of loading level on percent desorption after 4 min of irradiation was assessed by one-way analysis of variance (ANOVA) and found

to be significant for both AC and SWNT (<0.0001). The ANOVA was followed by Tukey's post hoc test to determine which loading levels were significantly different. In AC, the lowest loading level (2.175 mg) was significantly different (lower) than the higher levels (4.350 and 6.525 mg), but there was not a significant difference between the higher loading levels. In the SWNT, each loading level is significantly different from the others ($\alpha = 0.05$) with an increasing trend as loading level increases. These statistical observations are evident in Fig. 9.

The mass of toluene collected by a 3M diffusive sampler at 10 p.p.m. for 8 h would be approximately 0.6 mg. A similar mass (0.435 mg) was loaded for trials with the 75-ml dynamic desorption chamber ($n = 3$). In the 75-ml flow chamber, the air change rate was much higher due to the smaller volume and light power was much greater than in the 500-ml chamber because the sample was closer to the light source (Fig. 1c). On average, 0.199 mg (±0.014) and 0.316 mg (±0.009) of
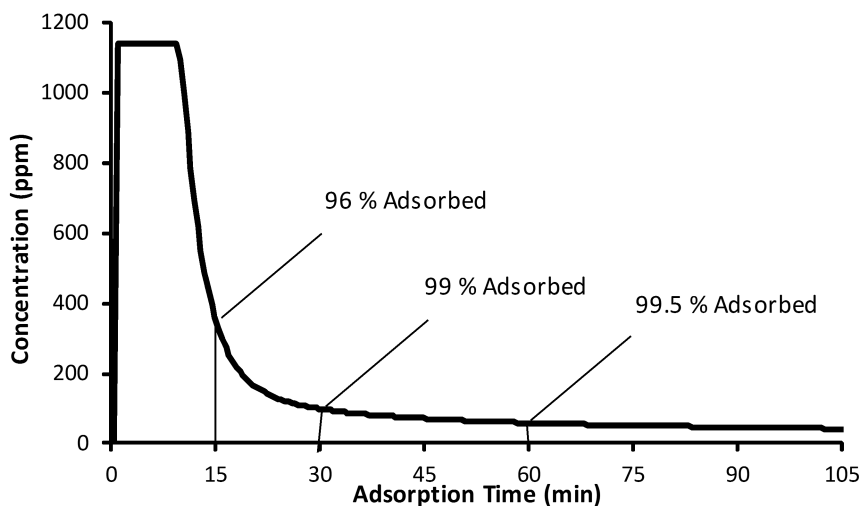
5 Representative sample loading, 50 mg SWNT loaded with 6.525 mg toluene.
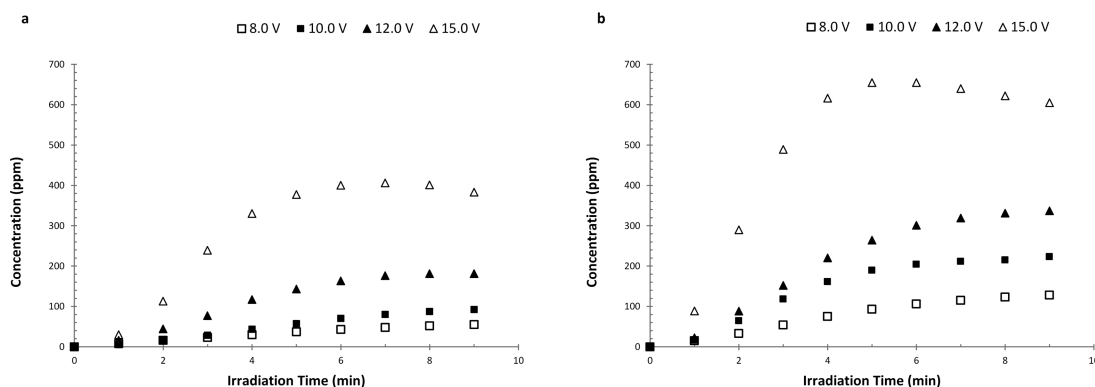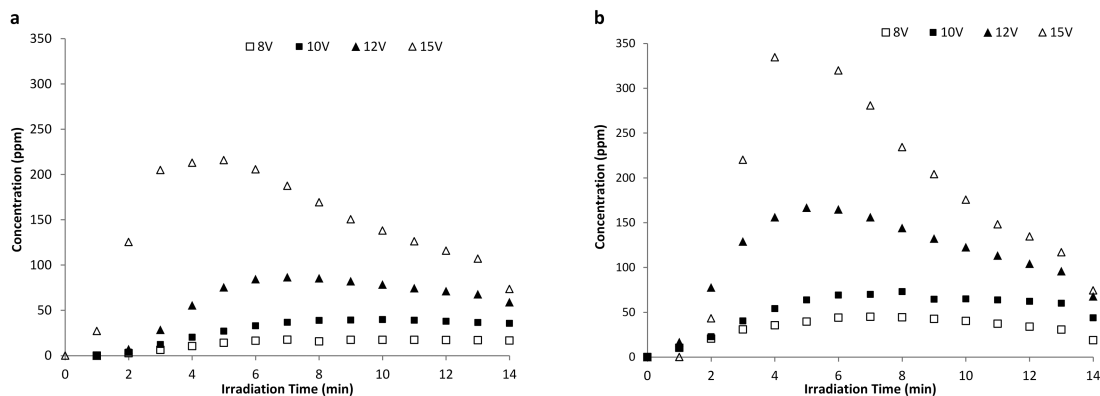

6 Screening of 50 mg AC (a) and SWNT (b) samples loaded with 6.525 mg toluene and desorbed by irradiation at varied lamp voltages (8, 10, 12, and 15 V) inside the 500-ml static chamber.

the loaded toluene was desorbed from AC and SWNT samples, respectively, when irradiated 4 min at the 15-V lamp setting. Figure 10 summarizes results from all trials with repeated measures at the 15-V lamp setting. Percent desorption in all configurations was significantly greater than controls and SWNT desorption was significantly greater than AC in all configurations. In the large chamber, when airflow was increased (1.6 l min⁻¹, 3.2 air changes per minute), desorption was greater than at 0.14 l min⁻¹ (AC, 0.06; SWNT, <0.001) and static test conditions (AC, 0.005; SWNT, <0.001).

DISCUSSION

Of the two sorbents evaluated, the materials are quite comparable, with AC having greater adsorption capacity and SWNT being more sensitive to photothermal desorption at all levels. The greater abundance of micropores in the AC accounts for the greater toluene adsorption capacity; however, the greater total porosity of SWNT suggests potential for greater adsorption capacity of larger molecules such as semivolatile organic compounds. Some observed differences could be due to differences in material grain size. Though SWNT were heavily agglomerated, particle diameters were still quite small (5–40 μm as determined by SEM imaging), whereas particle diameters for the AC were quite large (400–800 μm). The finer particle size of the SWNT was easier to spread evenly across the sample tray possibly resulting in greater light absorption; however, heat transfer through multiple layers of small

a

b

7 Screening of 50 mg samples loaded with 6.525 mg toluene and desorbed by irradiation at varied lamp voltages (8, 10, 12, and 15 V) inside the 500-ml flow chamber, $Q = 0.140\,l\,min^{-1}$. (a) AC and (b) SWNT.
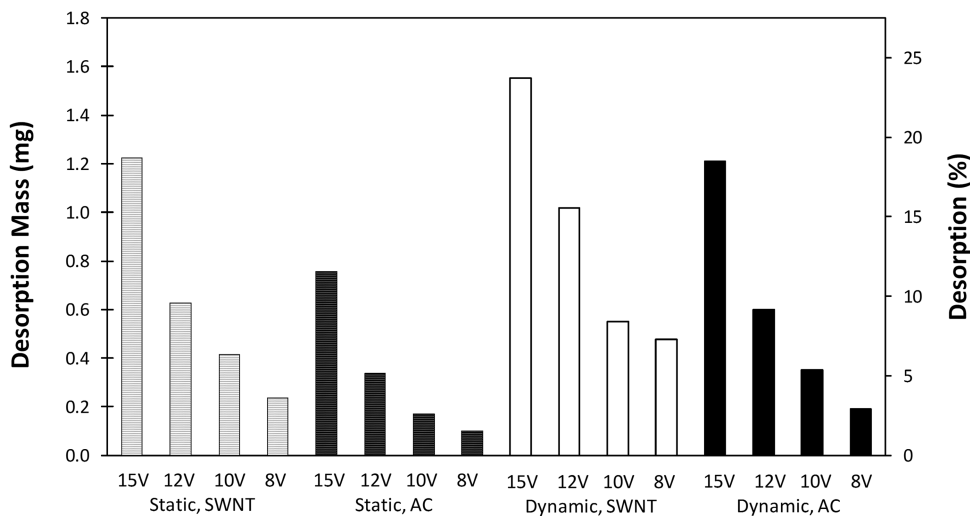

8 Screening of 50 mg samples (SWNT and AC) using the 500-ml flow chamber and irradiation at varied lamp voltages. Flow through chamber = $0.14\,l\,min^{-1}$, each sample loaded with 6.525 mg toluene and irradiated at 8, 10, 12, or 15 V.

particles is less efficient than through a monolithic large granule, so the effects may be offsetting.

Attempts were made to measure the temperature of the sample during irradiation using an infrared thermocouple but were non-quantitative; however, in the 75-ml chamber, the sample tray was held in place with a neodymium magnet on the sample pedestal (Fig. 1c). This magnet lost its magnetism with both sorbents after only a few trials. The Curie temperature (temperature at which magnetism is lost) of neodymium is 320°C; therefore, both AC and SWNT samples must have reached this temperature, suggesting differences due to grain size were minimal.

While both materials are amenable to photothermal desorption, it is clear that SWNT is more sensitive to this technique having significantly greater desorption in all test conditions and as much as 80% greater when highly loaded. With SWNT, each loading level played a significant role in percent yield, whereas with AC, significant differences in loading were observed between 2.175 and 4.350 mg loadings but not above this level (Fig. 9). These differences may diminish when sampling at low loadings typical of environmental and occupational sampling.

Using the 75-ml chamber, 70.5% of the initial mass was desorbed with 4 min of irradiation at the 15-V lamp
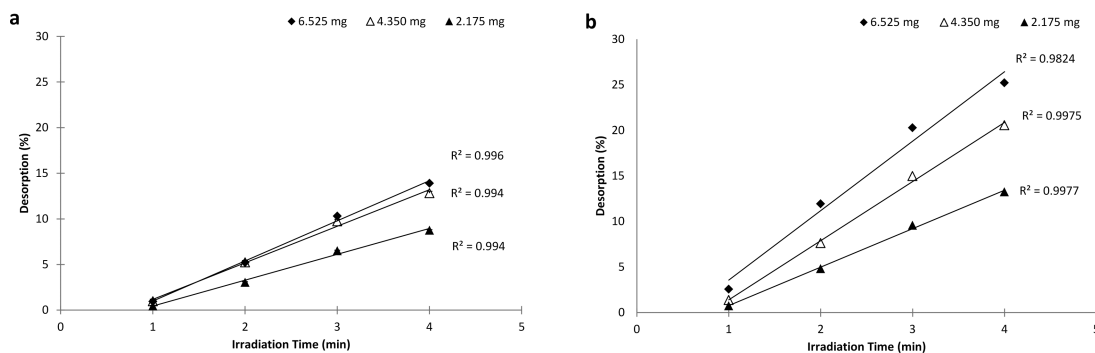
9 Percent desorption of 50 mg samples loaded with 6.525, 4.350, or 2.175 mg toluene and irradiated for 4 min at 15-V lamp setting in 500-ml static chamber ($n = 6–7$); results are corrected for PID sensitivity loss. (a) AC, percent desorption is significantly different at only the lowest loading level. (b) SWNT, percent desorption is significantly different at all loading levels.

Percent Desorption at 15 V Irradiation, 4 minutes
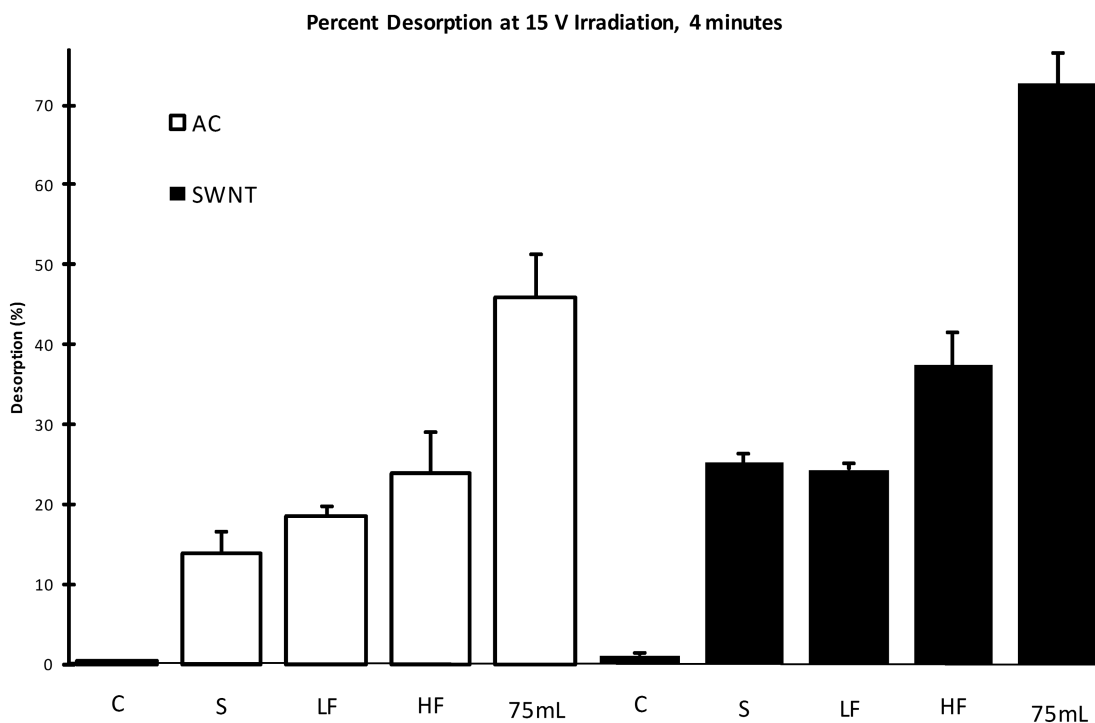
10 Desorption after 4 min of irradiation at 15 V, 50 mg samples, loaded with 6.525 mg toluene for 500-ml chamber and 435 mg toluene for 75-ml chamber. *t*-Test performed on each pair of AC/SWNT test conditions and SWNT was significantly greater in all pairs (S, $P < 0.0001$; LF, $P < 0.001$; HF, $P = 0.0219$; 75 ml, $P = 0.0006$). Additionally, all values were statistically different than controls. C = control, S = static chamber, LF = 'large' 500-ml chamber at low ventilation rate ($0.140 \, l \, min^{-1}$), HF = 'large' 500-ml chamber at high ventilation rate ($1.6 \, l \, min^{-1}$), and 75 ml = 'small' 75-ml chamber with high ventilation rate ($0.9 \, l \, min^{-1}$).

setting; after extinguishing the lamp, an additional 1% was desorbed over the following 10 min. This is due to the residual toluene in the dead volume of the chamber and latent heat of the system accumulated during irradiation. Desorbing to a partial end point introduces variability and some sample loss; likely, this is a reason why

traditional thermal desorption has not sought partial desorption end points previously. The real advantage of using a photothermal process is that heat is generated by the sorbent and not conducted to the sorbent. Reversing the direction of heat flow and heating without contact has the potential to allow precise control of desorption.

One intent of this study was to demonstrate the potential of using light as a thermal desorption technique that achieves partial desorption end points. We also investigated differences between sorbents (AC and SWNT) and the suitability of field grade monitoring equipment (PID) to measure desorption. We have clearly demonstrated the reliability of achieving partial desorption end points in both substrates since the relative standard errors of trials ranged between 3.3 and 12.4% for AC and 1.6 and 6.1% for SWNT. We also observe that SNWT desorbed a greater fraction with consistently lower variability than AC. Achieving partial desorption could be useful in occupational and environmental sampling by allowing field hygienists to prescreen samples using common equipment such as hand-held PIDs prior to submitting to an analytical lab. This would greatly accelerate the time to knowledge of integrated samples while still allowing full lab analysis of the remaining sample. The need for duplicate and triplicate field samples could be eliminated by only analyzing a portion of the original sample. Analytical labs could use this technique to improve sensitivity over analyses currently using chemical desorption. With current thermal desorption techniques, the sample must be completely desorbed; some systems allow the flow to be split with one portion recaptured and the other analyzed. These systems are quite expensive and can be subject to sample loss from leaks and sorbent collection efficiencies. Retaining the unanalyzed portion of the sample on the original sorbent seems a more reliable approach than completely desorbing the sample, passing it through various plumbing and valves and recollecting it on another sorbent sampler.

In this study, only one analyte was explored to eliminate the need for a chromatographic detection system. It is likely that the temperature ramp of the sorbent will not result in uniform desorption of all analytes in time. While specific desorption efficiencies could be determined for all potential analytes and mixtures thereof, a better approach would be to heat the sorbent above the desorption temperature of all analytes very rapidly. This could be accomplished by irradiating with very high energy density light over a short period of time, such as with a photo flash. This is currently being explored. A 20-J photo flash has the potential to pulse the temperature of 50 mg of SWNT by 340 °C within milliseconds (the duration of the photo flash) based on specific heat capacity measurements by Hepplestone *et al.* (2006) and light absorption properties of SWNT films and forests (Savage *et al.,* 2003; Zhang *et al.,* 2005; Mizuno *et al.,* 2009). Photothermal desorption with a photo flash would be easily field portable and could be used to release small quanta of adsorbed contaminants nearly instantaneously.

CONCLUSIONS

Photothermal desorption is a viable technique to be included in the analysis of occupational and environmental air samples. In this pilot study, we demonstrated the potential viability of photothermal desorption since it produced repeatable desorption that was significantly greater than controls. Desorption of toluene from SWNT was significantly greater than AC and a field grade PID has the sensitivity to detect contaminants from an integrated sampler loaded at occupationally relevant levels (0.435 mg toluene). Coupling this desorption technique to a sorbent sampler specifically designed for photothermal desorption (similar to a diffusive sampler) could facilitate infield estimations of total VOC using equipment routinely employed by hygienists while retaining enough sample for full laboratory confirmation using the same sample.

DISCLAIMER

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