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Measuring Concentrations of Volatile Organic Compounds in Vinyl Flooring

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ABSTRACT

The initial solid-phase concentration of volatile organic compounds (VOCs) is a key parameter influencing the emission characteristics of many indoor materials. Solid-phase measurements are typically made using solvent extraction or thermal headspace analysis. The high temperatures and chemical solvents associated with these methods can modify the physical structure of polymeric materials and consequently affect mass transfer characteristics. To measure solid-phase concentrations under conditions resembling those in which the material would be installed in an indoor environment, a new technique for measuring VOC concentrations in vinyl flooring (VF) and similar materials was developed. A 0.09 m^2 section of new VF was punched randomly to produce approximately 200 0.78-cm^2 disks. The disks were milled to a powder at -140^{o} C to simultaneously homogenize the material and reduce the diffusion path length without loss of VOCs. VOCs were extracted from the VF particles at room temperature by fluidized bed desorption (FBD) and by direct thermal desorption (DTD) at elevated temperatures. The VOCs in the extraction gas from FBD and DTD were collected on sorbent tubes and analyzed by gas chromatography/mass spectrometry. Seven VOCs emitted by VF were quantified. Concentration measurements by FBD ranged from 5.1 $\mu g\ g^{-1}$ VF for n-hexadecane to 130 $\mu g\ g^{-1}$ VF for phenol. Concentrations measured by DTD were higher than concentrations measured by FBD. Differences between FBD and DTD results may be explained using free-volume/dual-mobility sorption theory, but further research is necessary to more completely characterize the complex nature of a diffusant in a polymer matrix.

IMPLICATIONS

Knowledge of the initial concentrations of volatile organic compounds (VOCs) in a solid material such as vinyl flooring (VF) is crucial for assessing the emission characteristics of the material and its potential to contaminate indoor air. Solid-phase concentration measurement methods such as thermal headspace analysis and solvent extraction may affect the physical structure and consequently the emissions characteristics of polymeric materials. The fluidized bed desorption technique developed in this study does not employ solvents or high temperature for VOC extraction and improves the representative sampling of larger pieces of materials. With this technique, VOC content can be determined under conditions similar to those to which the material would be exposed when installed in an indoor environment. This concentration can be used as a parameter in mechanistic models to estimate VOC emission rates. The direct thermal desorption technique may prove useful as a simple procedure for directly comparing the overall potential of similar materials to contaminate indoor air over long periods of time.

INTRODUCTION

Vinyl flooring (VF) is manufactured in a variety of styles and compositions and is widely installed in residential and commercial buildings in either sheet or tile form. VF is primarily composed of a mixture of polyvinyl chloride (PVC), inert filler (usually calcium carbonate, $CaCO_3$), and organic plasticizers such as dioctylphthalate (DOP). Other additives such as stabilizers, lubricants, antioxidants, and colorants are used to aid in processing and improve product functionality and appearance. VF may also be manufactured as a multi-layer system with a bottom backing (usually glass fiber) and a top coating of transparent PVC or polyurethane.[1] In the United States during 1998, 214 million kilograms of PVC were used in the production of VF.[2]

VF has been shown to emit a number of volatile organic compounds (VOCs).[3, 4] VOCs can migrate from the interior to exposed surfaces by diffusion and then partition into the surrounding air. Most of the VOCs that are emitted by VF are probably present as contaminants in the various raw materials or as residues from the manufacturing process.

Characterizing VF as a source of indoor VOCs requires assessing both the rate at which VOCs are emitted and the total amount of VOCs that can potentially be emitted. Initial concentration (C_0) is a parameter of a model to predict emission rates of VOCs from diffusion controlled materials.[5, 6, 7, 8] Traditional methods for measuring concentrations of VOCs in solid materials have used solvents or heat to extract target compounds. However, free-volume theory has been used to describe how the structure of a polymer can be affected by temperature and the presence of chemical solvents. As summarized by Sperling[9], free-volume refers to the voids in polymeric materials that must be present in order for diffusion to occur. Amorphous polymeric materials such as the PVC in VF consist of high weight molecular chains (30,000 to 1,000,000 g mol^{-1}) held together by entanglement and van der Waals' forces. Free-volume is the sum of the void spaces that exist between the imperfectly arranged polymer chains. The amount of void space depends on the conformational arrangement of the polymer chains. At lower temperatures chain motion is primarily vibrational and conformational arrangement of the polymer chains, and consequently free volume, is largely independent of temperature. However, at temperatures above the glass transition temperature (Tg), polymer molecules possess sufficient energy so that coordinated chain movement becomes possible, resulting in a relatively large net increase in free-volume. Tg can be characterized as the temperature at which an inflection point in the free-volume-temperature curve occurs. Polymers at temperatures below Tg are referred to as "glassy" and at temperatures above Tg as "rubbery". Due to the additional free-volume, the rate of diffusion through the polymer is higher when the material is above Tg than when below Tg. Small non-polymeric molecules present in a polymer can reduce Tg. These small molecules can separate polymer chains making chain movement easier. This effect is termed plasticization. The Tg of un-plasticized PVC is ~80^{o} C; when plasticized, the Tg of PVC is ~20^{o} C and can be lower.[9]

Although several models have been proposed to describe sorption in polymers, the dual-mode theory is frequently cited. This conceptual model describes solution and diffusion of small, non-polymeric molecules in amorphous polymers. According to Vieth,[10] if a polymer is cooled from the rubbery state to the glassy state, a distribution of microvoids is frozen into the structure. Because free segmental chain movement is restricted in the glassy state, the microvoids in a glassy polymer immobilize a portion of diffusant molecules by entrapment. The resulting system consists of polymer chains, small mobile molecules, and small molecules immobilized by the polymer chains.[10]

Paul and Koros extended earlier research to construct a dual-mobility model of mass transport in glassy polymers.[11] Here, the diffusants trapped in frozen microvoids are not completely immobilized, but have partial mobility. The overall diffusional flux is the sum of the flux of the diffusants partially immobilized in the polymer microvoids and the flux of the mobile diffusants. The flux rate is determined by the concentration gradient and the diffusion coefficient of each of the two diffusant populations in the glassy polymer system.[12] The ratio of the diffusion coefficients ($D_{\text{mobile}}/D_{\text{partially immobilized}}$) is inversely proportional to the diameter of the diffusing molecule. For a relatively small diffusant such as methane, this ratio has been measured to be 8.7 for a polycarbonate system.[13]

The preceding analysis describes how the physical structure and consequently the mass transport properties of polymeric materials such as VF can be affected by heat and the presence of solutes. For this reason new techniques to measure VOC concentrations in VF and similar materials were developed.

As described, the total VOC concentration may be apportioned into mobile and partially immobilized fractions. The partially immobilized portion of the total VOC concentration is not readily emittable, but can be emitted over a long time period. For a single compound, C_0 is therefore defined as the readily emittable mass of the compound per unit mass of the material (*e.g.*, $\mu g\ g^{-1}$) subject to a particular set of environmental conditions.

During concentration measurement, it is desirable to minimize the time required to extract the target compounds from the solid-phase. Extraction time depends on the rate of mass transport from the solid-phase to the extraction fluid. For many materials the rate of mass transport is limited by the solid-phase diffusion rate. The time required for a VOC to diffuse through the solid-phase is proportional to the square of the diffusion path length and the reciprocal of the diffusion coefficient.[14] Therefore, extraction time can be reduced by decreasing the diffusion path length or by increasing the diffusion coefficient by heating the material.

In this study, a new sample preparation technique, cryogenic milling (CM) is applied to VF. A sample is obtained from a VF sheet by punching small disks from a large area of the material. The sample is then pulverized into small particles in a ball mill under a liquid nitrogen bath at temperatures of -140^o C. CM homogenizes the sample, decreases the diffusion path length, and increases the surface area of VF material. The low temperature significantly reduces VOC vapor pressure, minimizing VOC loss, and facilitates the milling process by making the VF more brittle.

Extraction of VOCs from the milled particles is accomplished at room temperature by fluidized bed desorption (FBD). For comparative purposes, direct thermal desorption (DTD) was also used to extract VOCs from the VF particles. In both extraction techniques, the VOCs are collected on a sorbent and then analyzed using a thermal desorption gas chromatography/mass spectrometry system.

MATERIALS AND METHODS

The VF material used in this study was a monolayer sheet vinyl (1.8-m wide) manufactured for the medical facilities market. In addition to PVC, the VF contained approximately 50% (by weight) $CaCO_3$ as well as plasticizers, pigments, and stabilizers.[15] The nominal thickness was 2 mm; the density was approximately 1.5 g cm^{-3}. The VF was manufactured four months prior to this investigation. A specimen of the material was tightly rolled into a 0.6-m long × 10-cm diameter cylinder, wrapped in Kraft paper, and shipped from the warehouse to our laboratory. Upon receipt, six 0.3-m × 0.3-m (0.09-m^2) squares were cut from the center of the specimen, stacked, wrapped in multiple layers of aluminum foil, and stored at -5^o C. Squares were removed as needed for experimental work. Experiments were completed within two months of receipt of the specimen.

The VF was pulverized using a cryogenic ball mill (Figure 1).[16] A 0.09-m^2 VF square was randomly sampled using a hollow arch punch to cut approximately 200 one-cm diameter disks (~50 g) from the square. The disks and two 20-mm diameter stainless steel balls were transferred to a stainless steel vial in the milling chamber of the ball mill. The milling chamber was flooded with liquid nitrogen for approximately five minutes before milling began. Upon commencement of milling, the surface temperature of the milling vial was -140^o C. The ball mill was operated at 480 revolutions per minute for 45 minutes while the milling chamber was continuously flooded with liquid nitrogen. After CM, the powdered VF material was transferred to 4.5-ml, zero-headspace glass vials and stored at -15^o C.

Scanning electron microscopy (SEM) was used to obtain images of the VF before and after CM. A cross-section sample of the original VF was prepared for SEM using a microtome. A sputter coater (Model S150B, Edwards) was used to apply a ~100 Å gold layer to the surface of both samples. Surface images were obtained using a scanning electron microscope (ISI, Model SX-40) operating at 20KV.

The size distribution of the cryogenically milled particles was determined using a laser diffraction particle-size distribution analyzer (Model LA-500, Horiba, Ltd.). Ethyl alcohol was used as the particle dispersant.

VOCs in VF particles were extracted at room temperature using a FBD apparatus shown in Figure 2. A known mass (~1 g) of VF particles was transferred to a FBD vessel (2.6-L) constructed of borosilicate glass. Clean air regulated by a mass-flow controller (MFC) at ~6 L min^{-1} was passed through the vessel to fluidize the VF particles. VOCs were collected by pumping a fraction (~15 mL min^{-1}) of the effluent fluidization air through a sorbent tube (described below). Four samples were successively collected over each seven-hour FBD test during periods from 0-60 (blank, no VF particles in the FBD apparatus), 60-120, 120-240, and 240-420 min. Duplicate tests were conducted.

VOCs were also extracted from VF particles at elevated temperature by a DTD apparatus shown in Figure 3. 17-18 mg of milled particles was weighed into a small aluminum foil boat. The boat was inserted into a 4-mm ID 20-cm long borosilicate glass tube. The glass tube was placed in a 150-W sleeve heater fitted with a thermocouple between the sleeve and the resistance winding. The inlet flow of humidified N_2 (~10% RH) to the tube was regulated by a mass flow controller (MFC) at 100 cm^3 min^{-1}. A fraction of the outlet gas stream (1/25) was drawn through a sorbent tube using a MFC and vacuum pump. The remainder of the flow was vented. At the start of desorption, the heater temperature was quickly ramped from ambient to 60^o C and held for 10 min. Next, the temperature was ramped over 20 min. to 150 $\pm$ 5^o C and then held constant. Gas samples were collected successively over 0-60, 60-120 and 120-180 min. after initiating a test. Blank tests and three replicate tests were conducted. A detailed DTD temperature study was subsequently conducted. Batches of 10-12 mg of milled particles were individually heated in the same apparatus from ambient temperature to final temperatures of 70, 90, 110, 130 and 150^o C at a rate of 10^o C min^{-1}. A PID (proportional/integral/derivative) controller regulated the ramp and soak temperatures. Samples for VOCs were collected from the outlet gas stream every 30 min. up to a total time of 150 min.

VOC concentrations in un-milled VF were also measured. A microtome was used to cut thin strips or slivers (~200-µm thick) sequentially from the top to the bottom of a VF specimen (~4-mm wide × 25-mm long). The slivers were weighed (15-30 mg) and individually transferred to 2-ml glass vials for storage at -15^o C. VOC concentrations in the VF slivers were determined by DTD at 150^o C following the same procedures described for the particles.

VOCs were collected on sorbent tubes containing Tenax-TA® (P/N 16251; Chrompack, Bergen op Zoom, The Netherlands). VOCs were quantitatively analyzed by gas chromatography/mass spectrometry (GC/MS) following U.S. Environmental Protection Agency (EPA) Method TO-1.[17] Sorbent tubes were thermally desorbed with a cryogenic inletting system (Model CP-4020 TCT; Chrompack).

RESULTS AND DISCUSSION

The scanning electron micrographs of the VF cross section shown in Figure 4 were taken at magnifications of 40× (left) and 300× (right). The number above the white rectangular bar at the bottom of each micrograph is the length of the bar in µm. The micrographs show that the VF is a monolayer (white lines at the upper and lower surfaces are artifacts) composite material. $CaCO_3$ particles imbedded in the PVC matrix can be seen in the image on the right. After CM, the median particle size was ~80 µm when calculated on the basis of the particle number distribution. As shown in Figure 5, the median particle size was ~160 µm when calculated on a weight distribution basis.

The concentrations of seven VOCs obtained by FBD and DTD are presented in Table 1. Results obtained by FBD were 30% to 70% lower than those obtained by DTD. This suggests the high temperatures associated with DTD (above the Tg for PVC) significantly affected the mass transport properties of the VF and that VOCs that were not extractable at room temperature during the 6-hour FBD extraction period could be extracted by DTD.

The cumulative mass extracted by FBD and DTD are compared in Figures 6, 7, and 8 for n-tetradecane, n-pentadecane, and phenol, respectively. To help interpret the results, a simple model describing diffusion in spheres[18]

$$\frac{M_t}{M_\infty} = 1 - \frac{6}{\pi^2}\sum_{n=1}^{\infty}\frac{1}{n^2}\cdot\exp\left\{\frac{-Dn^2\pi^2 t}{r^2}\right\} \tag{1}$$

is employed. In Equation 1, M_t is the mass of diffusant in the solid-phase at time t, M_∞ is the initial mass of diffusant in the solid-phase, D is the solid-phase diffusion coefficient (1.2, 0.67, and 1.2×10^{-13} m^2 s^{-1} respectively for n-tetradecane, n-pentadecane, and phenol in VF), and r is the particle radius. To apply this model to desorption of VOCs in the fluidized bed, build-up in the gas-phase concentration is assumed to be negligible. The diffusion coefficients for each of the three VOCs in VF were measured in earlier work,[19] and the median particle size (based on weight) was used to estimate particle radius.

For mobile VOCs, the model provides estimates of the mass fraction extracted after 6 hours (99% for phenol and n-tetradecane; 93% for n-pentadecane) and predicts the rate of mass transport from the VF particles during FBD, as shown in Figures 6, 7, and 8. The experimental FBD data suggest that desorption of the VOCs continues beyond the 6 hour period, albeit at a slow rate. In contrast, with the exception of phenol, the DTD data show that desorption is both rapid and complete. Taken together, these results appear to be consistent with the dual-mobility conceptual model described earlier. During DTD, the temperature of the polymer is raised above Tg causing expansion of the void spaces releasing the partially immobilized diffusant molecules and resulting in rapid desorption of all the VOC. It is worth noting that the diffusion coefficients used to make the model predictions were measured during rapid and completely reversible sorption/desorption experiments at room temperature.[19] Although these experiments confirmed Fickian diffusion of the specific VOCs in VF, it is possible that they only quantified diffusion through the readily accessible void volume within the polymer matrix.

The concentration estimates obtained by DTD of sliver samples are also shown in Table 1. The values are averages for eight successive slivers. Although the sliver data are for a single small piece of VF, they are in good agreement with results obtained by DTD of the particles representing a much larger piece of VF. This suggests that initial concentrations are relatively uniformly distributed and that target VOCs are not lost during the CM/FBD sample preparation process. The only significant difference occurred for phenol, for which DTD of the particles produced a higher concentration estimate.

In contrast to the alkanes, results suggest that phenol was not completely extracted by either technique. This difference cannot be attributed to diffusion coefficients or vapor pressures (0.19, 0.95, and 29 Pa at 20^{o} C respectively, for n-tetradecane, n-pentadecane, and phenol) of the molecules. Possible explanations are hydrogen bonding between the relatively polar phenol, PVC, calcium carbonate system or that phenol is a degradation product of some ingredient in the VF.

Measurement precisions are presented in Table 1 as standard deviations. With the exceptions of phenol and 2,2,4-trimethyl-1,3-pentanediol monoisobutyrate (TMPD-MIB), relative standard deviations for the FBD method were approximately ten percent or better. For DTD of particles, the relative standard deviations were approximately one to four percent, again with the exception of phenol. Standard deviations for di(propylene glycol) methyl ether (DPGME) and TMPD-MIB by DTD of the slivers were not calculated because the concentrations of these compounds varied strongly with depth.[21]

The results of the DTD temperature study are summarized in Table 2. A linear regression analysis of the data show that, within a 95% confidence interval, there is no significant relationship between the concentration estimates and extraction temperature for the seven VOCs over the desorption temperature range of 70-150° C. These results suggest that the extractable amounts are not substantially different within the range of temperatures studied.

CONCLUSIONS

This study has demonstrated that CM is a valuable technique for preparing VF for concentration measurement. The benefits of CM include reduced potential for VOC loss during sample preparation, reduced VOC extraction time due to shorter diffusion path lengths, and improved representative sampling of the material.

The benefit of FBD is extraction of target compounds under conditions similar to those in which the material would be installed in the indoor environment. This avoids the problems associated with C_0 measurement methods that potentially alter the mass transport properties of polymeric materials and minimizes the chance of thermal degradation of organic compounds and artifact formation.

The results of FBD and DTD concentration measurement are consistent with the dual-mobility conceptual model of diffusion in polymers. Below the glass transition temperature, one fraction of the diffusant population is considered mobile while the other is considered partially immobilized. In accordance with this theory, concentration determined by FBD approximates the mobile portion of VOCs, while concentration determined by DTD represents the total VOC initially present in the VF. Further research is clearly needed to more completely characterize the nature of these diffusant fractions.

The primary purpose of this study was to determine C_0 of a VOC in bulk VF for use in a mechanistic model for predicting the rate at which the compound is emitted from VF.[21] While somewhat speculative, it now appears that FBD provides a measure of the readily emittable fraction of the VOC while DTD quantifies the potential amount that can be emitted over a long period of time. Although additional work is needed, it appears that emission characterizations based on both of these solid-phase concentration measurements may prove more useful and possibly less costly than commonly employed chamber techniques.[22]

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REFERENCES

1. Coaker, A.W.; Wypart, R.W. Vinyl Chloride Resins: Suspension, Emulsion, Microsuspension, and Bulk (Mass), In Handbook of PVC Formulating; Wickson, E.J., Ed.; John Wiley & Sons: New York, 1993; 15-113.
2. Resins Report, Modern Plastics, 1999, 76, 43-80
3. Clausen, P.A.; Lauersen, B.; Wolkoff, P.; Rasmusen, E.; Nielsen, P.A. Emission of Volatile Organic Compounds from a Vinyl Floor Covering, In ASTM STP 1205; Nagda, N.L., Ed.; American Society for Testing and Materials: Philadelphia, 1993; 3-13.
4. Lundren, B.; Jonsson, B.; Ek-Olausson, B.A. Material Emissions of Chemicals – PVC Flooring Materials, Indoor Air, **1999**, 9; 202-208.
5. Zhao, D.Y., Cox, S.S., and Little, J.C. Source/Sink Characterization of Diffusion Controlled Building Materials, In Proceedings of The 8th International Conference on Indoor Air Quality and Climate - Indoor Air ‘99, Edinburgh, Scotland, 1999, 1; 408-413.
6. Little, J.C.; Hodgson, A.T. A Strategy for Characterizing Homogeneous, Diffusion Controlled Indoor Sources and Sinks, In ASTM STP 1287, Bruce A. Tichnenor Ed.; American Society for Testing and Materials: Philadelphia, 1996; 294-304.
7. Cox, S.S.; Little, J.C.; Hodgson, A.T. A New Method to Predict Emission Rates of Volatile Compounds from Vinyl Flooring, In Proceedings of Healthy Buildings 2000, Helsinki, Finland, 2000, 4; 169-174.
8. Little, J. C., Hodgson, A. T. and Gadgil, A. J. Modeling emissions of volatile organic compounds from new carpets, Atmospheric Environment, **1994**, 28; 227-234.
9. Sperling, L. Introduction to Physical Polymer Science, 2nd Edition; John Wiley & Sons: New York, 1992.
10. Vieth, W. Diffusion in and Through Polymers; Hanser Publishers: Munich, 1991; p. 29.
11. Vieth, W. Diffusion in and Through Polymers; Hanser Publishers: Munich, 1991; p. 38.
12. Paul D. and Koros W. Effect of partially immobilizing sorption on permeability and the diffusion time lag, Journal of Polymer Science, Polymer Physics Edition, **1976**, 14; 675-685.

13. Koros, W., Chan, A., and Paul, D. Sorption and transport of various gases in polycarbonate, Journal of Membrane Science, **1977**, 2; 165-190.
14. Schwarzenbach, R.; Gschwend, P.M.; Imboden, D.M. Environmental Organic Chemistry; John Wiley & Sons: New York, 1993; p. 200.
15. Tshudy, J.A. Personal communication, 1998.
16. Shultz, J.P.; Martin, J.P.; Kander, R.G.; Suchicital, C.T.A. Processing-Structure-Property Relationships of Polymer-Polymer Composites Formed by Cryogenic Mechanical Alloying for Selective Laser Sintering Applications, In *Proceedings of the Solid Freeform and Additive Fabrication-2000 MRS Symposium,* San Francisco, CA, 2000, 625; 75-80.
17. U.S. Environmental Protection Agency. Method TO-1, Revision 1.0: Method For The Determination Of Volatile Organic Compounds in Ambient Air Using Tenax® Adsorption and Gas Chromatography/Mass Spectrometry (GC/MS); Center for Environmental Research Information, Office of Research and Development, 1984.
18. Crank, J. The Mathematics of Diffusion; Oxford University Press: Oxford, England, 1975; p. 91.
19. Cox, S.S.; Zhao, D.Y.; Little, J.C. Measuring Partition and Diffusion Coefficients of Volatile Organic Compounds in Vinyl Flooring, Accepted for publication in *Atmospheric Environment*, 2001.
20. Cox, S.S., Hodgson, A.T. and Little, J.C. A New Method to Measure the Concentration of Volatile Organic Compounds in Vinyl Flooring, In Proceedings of the Engineering Solutions to Indoor Air Quality Problems Symposium, Raleigh, North Carolina, 2000; 65-75.
21. Cox, S.S., Little, J.C. and Hodgson, A.T. Predicting the Emission Rate of Volatile Organic Compounds from Vinyl Flooring, Submitted for publication in *Environmental Science and Technology*, 2001.
22. ASTM. D 5116-97, Standard Guide for Small-Scale Environmental Chamber Determinations of Organic Emissions From Indoor Materials/Products; American Society for Testing and Materials, West Conshohocken, PA, 1997.

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Table 1. Concentrations of seven VOCs in vinyl flooring determined by FBD and DTD of particles, and DTD of sliver samples

Table 2. Concentrations of seven VOCs in vinyl flooring determined by DTD of particles at 70^o C – 150^o C

Figure 1. Diagram of cryogenic ball mill

Figure 2. Diagram of fluidized bed desorption (FBD) apparatus

Figure 3. Diagram of direct thermal desorption (DTD) apparatus

Figure 4. Scanning electron micrographs of vinyl flooring cross section taken at 40× (left) and 300× (right)

Figure 5. Particle size distribution of cryogenically milled vinyl flooring

Figure 6. Cumulative extraction of n-tetradecane from vinyl flooring particles by DTD and FBD

Figure 7. Cumulative extraction of n-pentadecane from vinyl flooring particles by DTD and FBD

Figure 8. Cumulative extraction of phenol from vinyl flooring particles by DTD and FBD

Table 1

Compound	Concentration (µg VOC g^{-1} VF)		
	FBD of Particles[a]	DTD of Particles[b]	DTD of Slivers[c]
DPGME[d]	26.5 ± 1.5	38.2 ± 0.7	34.1
Phenol	134 ± 29	321 ± 16	259 ± 6
TMPD-MIB[e]	28.4 ± 24.1	51.8 ± 2.0	55.4
n-Tridecane	22.7 ± 2.9	33.4 ± 0.5	29.3 ± 2.4
n-Tetradecane	29.5 ± 2.5	43.5 ± 0.6	39.2 ± 3.3
n-Pentadecane	28.5 ± 0.6	47.7 ± 0.6	45.0 ± 2.7
n-Hexadecane	5.1 ± 0.6	17.6 ± 0.1	16.1 ± 2.4

[a] Mean and standard deviation for two tests

[b] Mean and standard deviation for three tests

[c] Mean and standard deviation for eight successive slivers

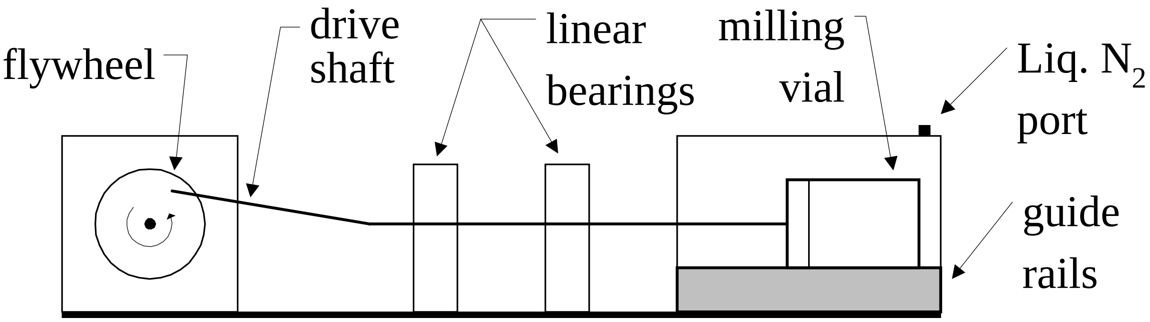
[d] Di(propylene glycol) methyl ether (three isomers)

[e] 2,2,4-Trimethyl-1,3-pentanediol monoisobutyrate (two isomers)

Table 2

Compound	Concentration (μg VOC g^{-1} VF)					
	70° C	90° C	110° C	130° C	150° C	Average
DPGME	35.7	40.2	33.6	38.6	37.7	37.1 ± 2.6
Phenol	307	302	311	304	315	308 ± 5
TMPD-MIB	31.7	29.2	46.0	41.1	46.4	38.9 ± 8.0
n-Tridecane	35.2	31.8	37.3	32.8	36.0	34.6 ± 2.3
n-Tetradecane	51.6	48.9	53.1	50.3	47.0	50.2 ± 2.3
n-Pentadecane	43.9	40.5	56.0	48.6	55.0	48.8 ± 6.7
n-Hexadecane	6.2	5.0	14.6	9.2	13.3	9.7 ± 4.2

Figure 1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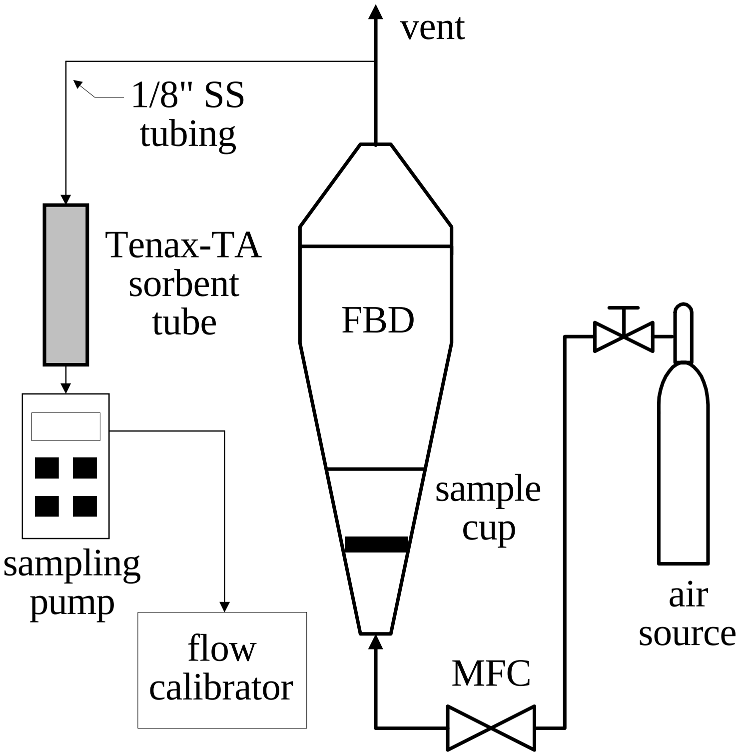
drive shaft
linear bearings
milling vial
Liq. N_2 port
guide rails

Figure 2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1/8" SS tubing
Tenax-TA sorbent tube
FBD
sample cup
air source
sampling pump
MFC
flow calibrator

Figure 3

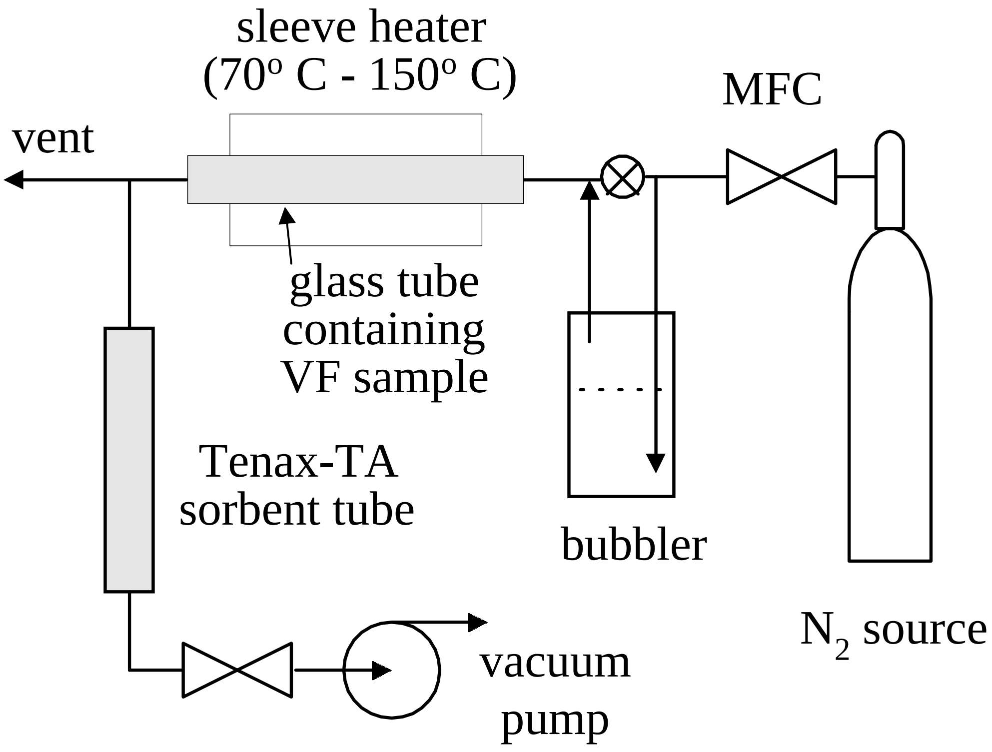

sleeve heater
(70° C - 150° C)
MFC
vent
glass tube
containing
VF sample
Tenax-TA
sorbent tube
bubbler
N_2 source
vacuum
pump

Figure 4

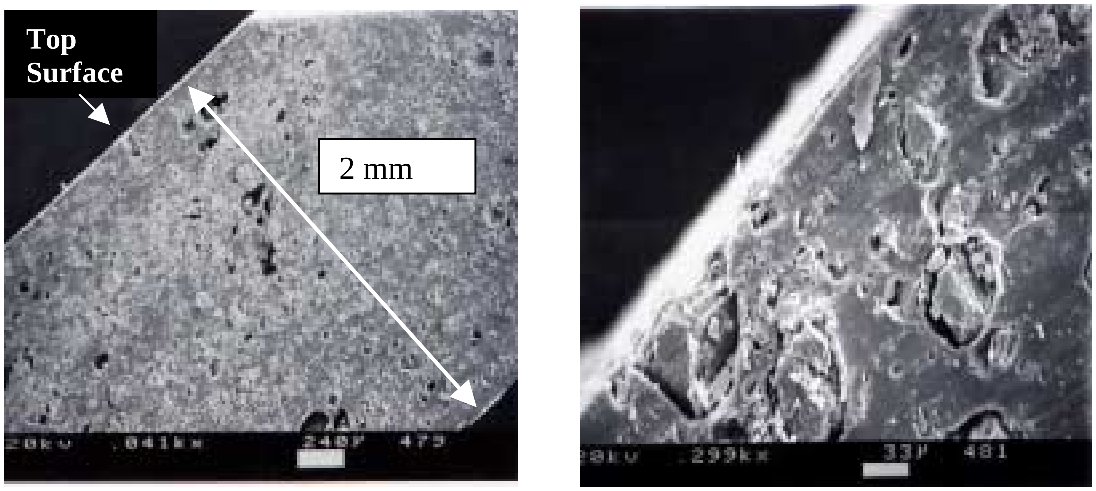


Figure 5

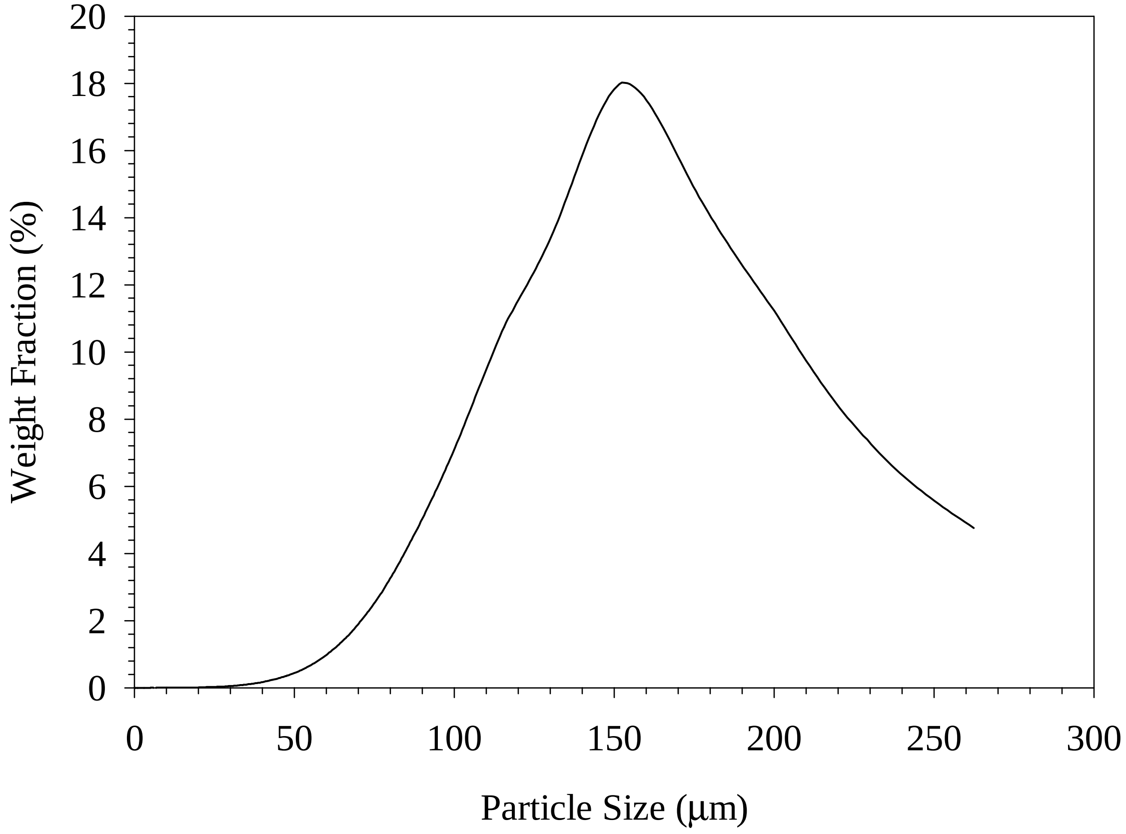

20
18
16
14
12
10
8
6
4
2
0
Weight Fraction (%)
0
50
100
150
200
250
300
Particle Size (μm)

Figure 6

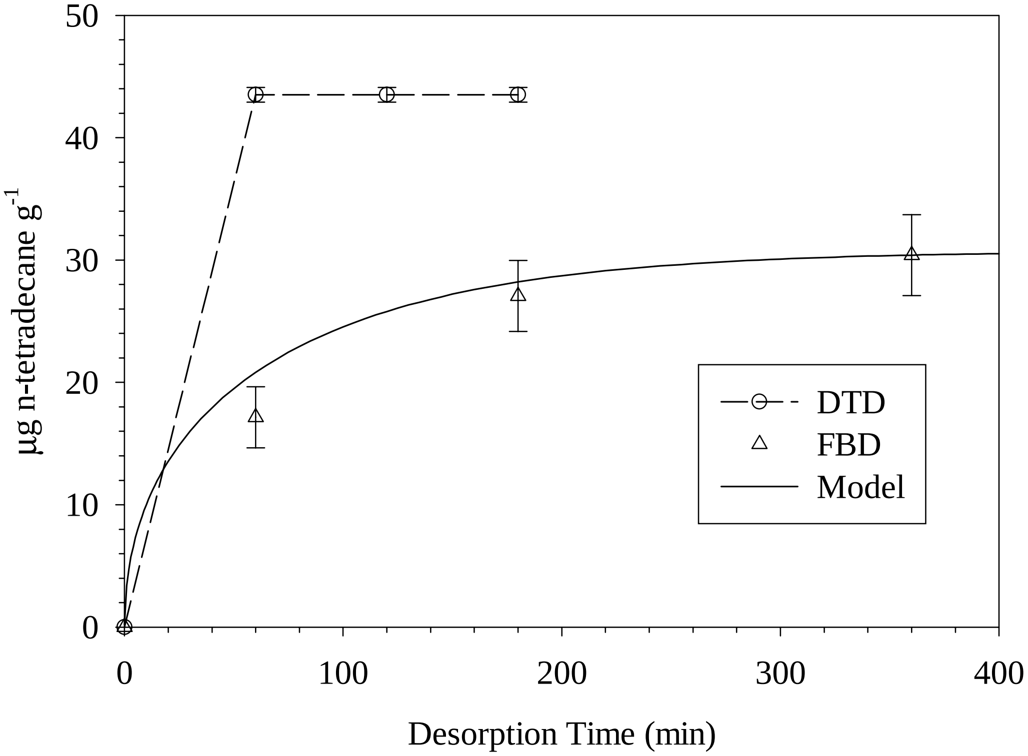

50
40
30
20
10
0
μg n-tetradecane g^{-1}
0
100
200
300
400
Desorption Time (min)
DTD
FBD
Model

Figure 7

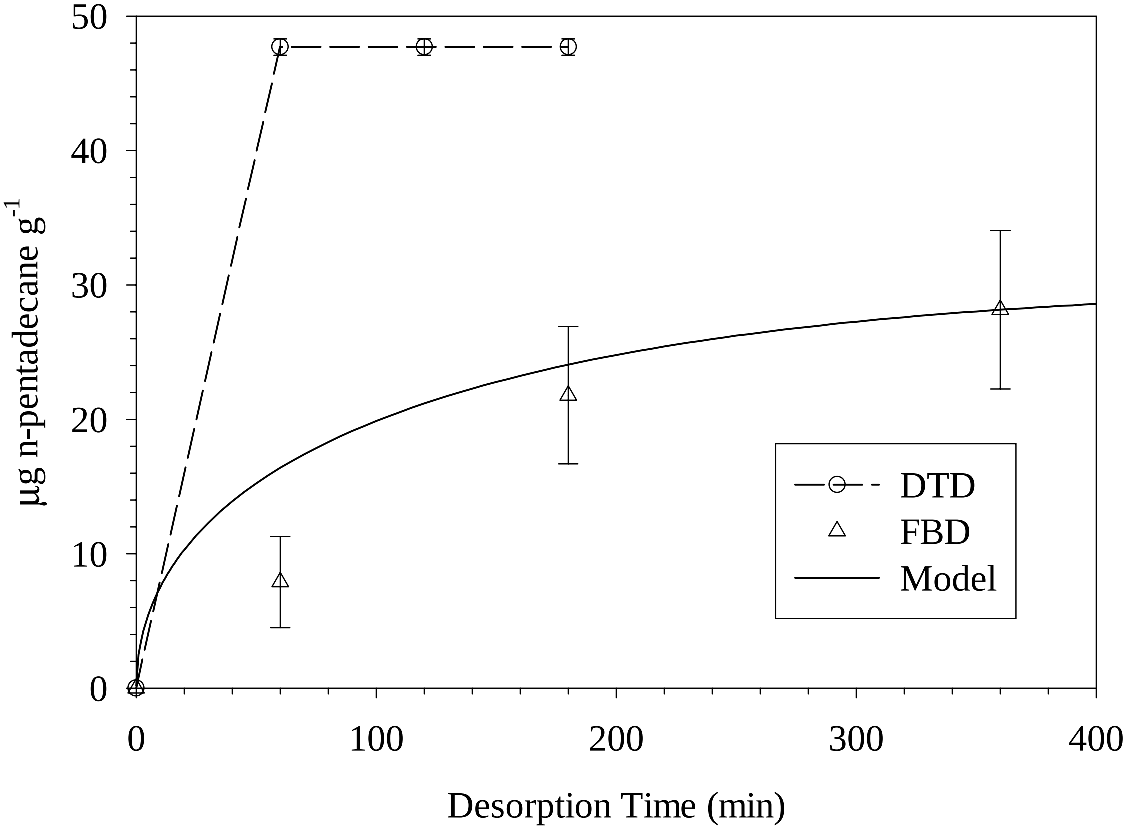
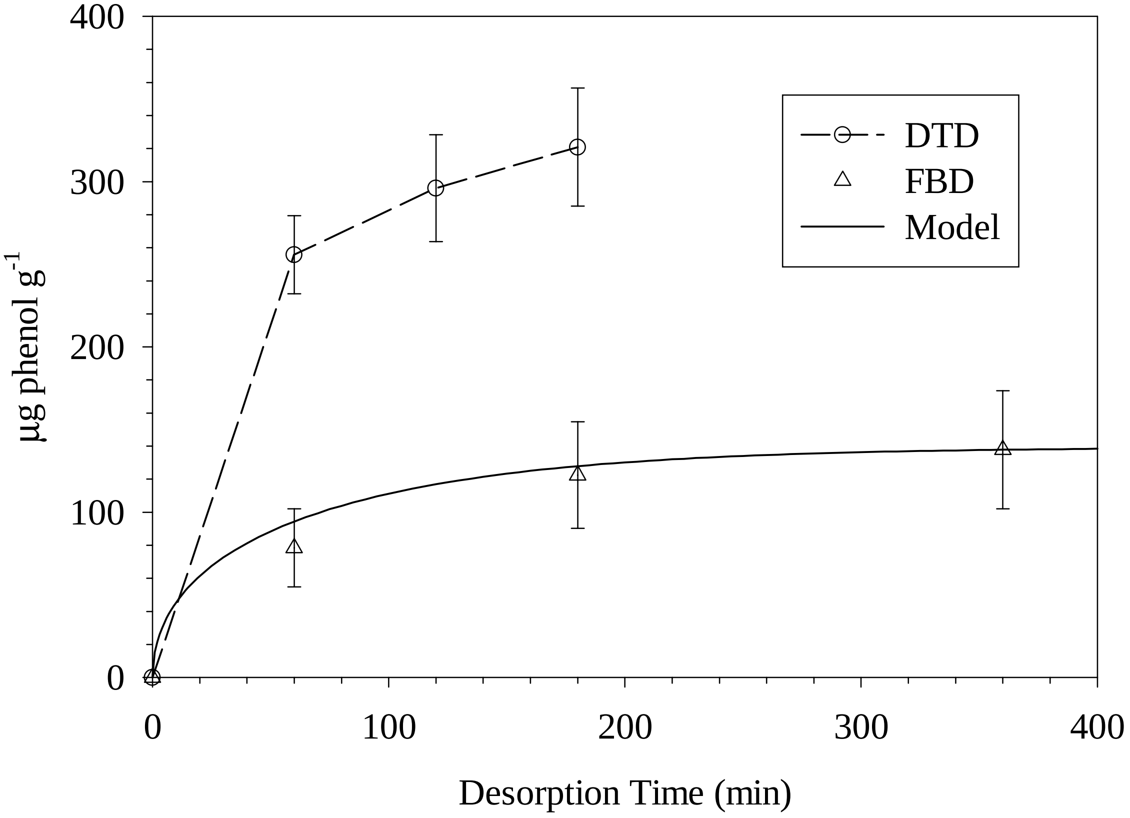

μg n-pentadecane g^{-1}
Desorption Time (min)
0
10
20
30
40
50
0
100
200
300
400
DTD
FBD
Model

Figure 8



400
300
200
100
0
µg phenol g^{-1}
0
100
200
300
400
Desorption Time (min)
DTD
FBD
Model