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Use of thermally modified carbon black and carbon molecular sieve adsorbents in sampling air contaminants

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Abstract

Effective adsorption of airborne contaminants is a function of interactions that occur at the adsorbate/adsorbent surfaces. Adsorbates typically have different molecular sizes and shapes, as well as different functional groups; hence it becomes difficult to choose an adsorbent with the appropriate surface characteristics for each sampling situation. Use of Type I, non-specific adsorbents eliminates the concern over matching adsorbent and adsorbate characteristics and allows analysts to use a single material to adsorb many adsorbates. Furthermore, use of several Type I adsorbents, possessing different characteristics, in one adsorbent tube allows for effective adsorption and subsequent desorption of adsorbates possessing a wide range of molecular sizes, as well as different functional groups.

Graphitized carbon blacks are classified as Type I, non-specific adsorbents. Adsorbent characteristics were evaluated to determine the interactions between several key adsorbates and several graphitized carbon black and carbon molecular sieve adsorbents. Adsorbates were selected to represent a range of both molecular sizes and functional groups. Adsorbent applications for the thermally modified materials have evolved from these studies.

INTRODUCTION

Evaluations of ambient air and indoor air atmospheres typically entail qualitative and quantitative analyses of a wide range of organic contaminants. This wide range of organic contaminants typically exist at sub-parts per million levels; hence concentrating techniques are required. Utilization of multi-bed adsorbent tubes, which function to adsorb and subsequently thermally desorb (release) the contaminants (adsorbates) to a gas chromatographic system, allows for effective evaluations of the atmospheres of interest. Utilization of Type I, non-specific adsorbents in these adsorbent tubes eliminates the concern over which functional group(s) an adsorbate possesses, and allows for the analyses of these complex, airborne samples.

A Type I adsorbent is defined as an adsorbent possessing a surface without ions or active groups, and only a Type I adsorbent interacts non-specifically with the four groups of adsorbates. Construction of an adsorbent tube containing several Type I adsorbents functioning to adsorb different molecular size fractions of the adsorbates allows for a single analysis of the volatile, semi-volatile, and non-volatile fractions. This tube, which differentiates between the molecular size fractions, functions as a small gas chromatographic packed column, where the adsorbate migration rate is inversely proportional to its molecular size. Adsorbent characterization evaluations were performed to effectively evaluate the adsorbate/ adsorbent relationships occurring between several Type I adsorbents (three graphitized carbon blacks) and a weak, Type III adsorbent (carbon molecular sieve) and Group A, Group B, and Group D adsorbates.

The adsorbent characterizations were performed to establish the specific retention volumes, and for the chosen adsorbates and adsorbents. The data obtained from these evaluations were utilized to develop a predictive model to predict the sampling volumes (or specific retention volumes) for adsorbates not evaluated. This predictive model assigns a numerical value to an adsorbate molecule which is used as the input value in the established straight line equation for each adsorbent.

DISCUSSION

The determination of the adsorbent surface characteristics was performed using a U-tube configuration designed to interface with a gas chromatogram. Two L-shaped, silanized glass tubes (1/4" OD x 4 mm ID) were utilized to connect an adsorbent tube (1/4" OD x 4 mm ID x 10 cm length) to the injector and detector ports of a Varian 3700 gas chromatograph. Nitrogen was chosen as the carrier gas, with a flow rate of 30 milliliters/minutes (previous in-house work indicates that flow rates $\geq$ 500 milliliters/minute provide similar data). Adsorbent bed weights = 0.2500 $\pm$ 0.0002 grams were chosen to parallel bed weights typically utilized in air sampling tube.

The adsorbents investigated were three graphitized carbon blacks and one carbon molecular sieve. The physical properties of these four adsorbents are described in Table I.

The adsorbents were characterized by determining adsorbate/adsorbent interactions using experimentally determined specific volumes.

The specific retention volume data are obtained by experimentally determining the specific retention volumes at 4 elevated gas chromatograph oven temperatures, and extrapolating, via linear regression analytes, to obtain the desired data at 20°C (Equation 1). The heats of adsorption data for each chosen adsorbate were obtained by calculation of the slopes of the lines fitted for the plots of specific retention volume versus the inverse of the temperature (Equation 2).

EQUATION 1. Specific retention volume

$$V_g^t = \frac{\text{Milliliters of Gas}}{\text{grams of adsorbent}}$$

$$= (j)\,(F_c)\,\frac{(t_r - t_a)}{W_a}$$

where:
- j = Pressure correction factor
- F_c = Corrected flow rate
- t_r = Adsorbate peak retention time at apex
- t_a = Dead volume retention time
- W_a = Adsorbent bed weight
- P_i = Inlet pressure
- P_o = Outlet pressure

EQUATION 2. Heat of adsorption (WH_A)

$$WH_A = (2.303)\,(R)\,\frac{d\log (V_g^t/T)}{d(1/T)}$$

where:
- R = universal gas constant = 1.987×10^{-3} kcal/°k-mole
- V_g^t = specific retention volume = milliliters/gram
- T = temperature (°k)

Adsorption coefficient and equilibrium sorption capacity data have been extracted from the plots of log V_g^t vs. 1/T°k, but will not be cited here. Heats of adsorption data have been cited for explanatory purposes for the adsorbate/adsorbent relationships established with the Carboxen-569 sieve only.

The data obtained from the adsorbent characterization evaluations are tabulated in Table 2.

TABLE 1. Physical properties of adsorbents

	Particle (mesh) Size	Density (g/ml)	Surface Area (m^2/gram)	Description
Carbotrap B	20/40	0.38	98.3	Type I, gcb**
Carbotrap C	20/40	0.72	10.0	Type I, gcb
Carbopack F	60/80	0.60	5.1	Type I, gcb
Carboxen-569	20/45	0.58	490.0	*Weak Type III cms***

* Approaches Type I adsorbent behavior (e.g., hydrophobic surface,) due to large C:H ratio and absence of functional groups). Carboxen-569 chosen due to maximum retention of chosen adsorbates and minimum retention of water.
** (gcb) graphitized carbon black
*** (cms) carbon molecular sieve

TABLE 2. Specific retention volume data

Adsorbate Description	Specific Retention Volume (V_g^0) Carbotrap B	Carbotrap C	Carbopack F	Carboxen-569
Methane				8.50×10^{1}
Ethane				9.73×10^{2}
Propane				4.49×10^{3}
n-Butane	2.22×10^{2}	3.81×10^{1}	3.02×10^{1}	3.02×10^{4}
n-Pentane	8.25×10^{2}	8.35×10^{1}	6.66×10^{1}	4.86×10^{6}
n-Hexane	3.01×10^{3}	3.22×10^{2}	1.21×10^{2}	
n-Octane	5.64×10^{4}	1.37×10^{3}	9.03×10^{2}	
n-Decane	2.90×10^{7}	1.30×10^{4}	1.40×10^{4}	
n-Dodecane	4.93×10^{12}	3.30×10^{6}	5.69×10^{4}	
n-Tetradecane	--		2.10×10^{7}	1.39×10^{6}
Benzene	2.59×10^{3}	1.99×10^{2}	1.06×10^{2}	
Toluene	3.35×10^{4}	7.77×10^{2}	3.93×10^{2}	
Ethylbenzene	7.49×10^{4}	1.64×10^{3}	6.87×10^{2}	
Diphenyl	1.19×10^{11}	1.13×10^{5}	8.43×10^{4}	
Ethanol	1.31×10^{2}	1.22×10^{2}	8.72×10^{1}	3.01×10^{3}
n-Butanol	1.30×10^{3}	5.40×10^{2}	2.26×10^{2}	
n-Hexanol	1.40×10^{4}	2.14×10^{3}	2.83×10^{2}	
n-Octanol	2.52×10^{5}	3.85×10^{3}	1.52×10^{3}	
n-Decanol	--		2.58×10^{4}	8.82×10^{3}
Acetone	6.84×10^{2}	5.40×10^{2}	1.30×10^{2}	
2-Butanone	1.30×10^{3}	6.30×10^{2}	1.60×10^{2}	
Dichloromethane				1.73×10^{5}
Carbon Tetrachloride	9.40×10^{2}	7.19×10^{1}	6.00×10^{1}	
Chlorobenzene	1.27×10^{4}	5.39×10^{2}	3.51×10^{2}	
Benzylamine	2.00×10^{5}	1.60×10^{4}	2.12×10^{3}	

The specific retention volume data obtained for the 3 graphitized carbon blacks was utilized to construct predictive modes for the determination of specific retention volumes for other odsorbates. Physical descriptors, polarizability (α) and molecular connectivity (χ) were chosen as the input (X) variables for the construction of straight-line plots of the physical descriptors versus the experimentally derived specific retention volumes. The resultant straight line equation was consequently utilized to determine the predicted specific retention volumes from untested adsorbates.

The predictive model was ineffective for the carbon molecular sieve. Plots of specific retention volumes vs. adsorbate physical descriptors do not provide a linear relationship with which to predict sampling volumes via these variables. This nonlinear relationship is due to the presence of

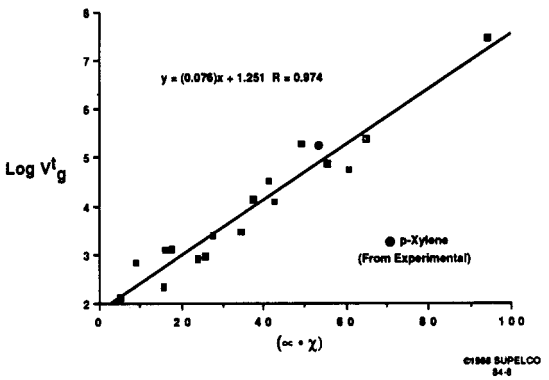

Figure 1 **Predictive Model Plot for Carbotrap™ B**
Log V^t_g vs. (∝ • χ)

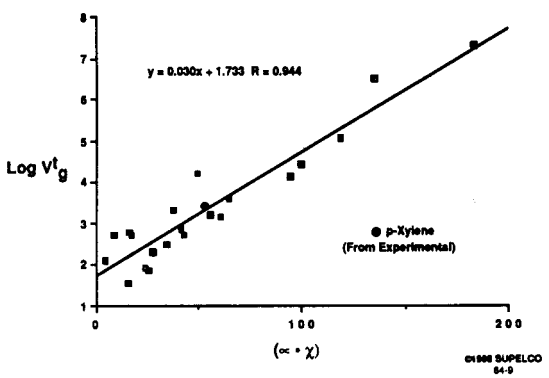

Figure 2 **Predictive Model Plot for Carbotrap™ C**
Log V^t_g vs. (∝ • χ)

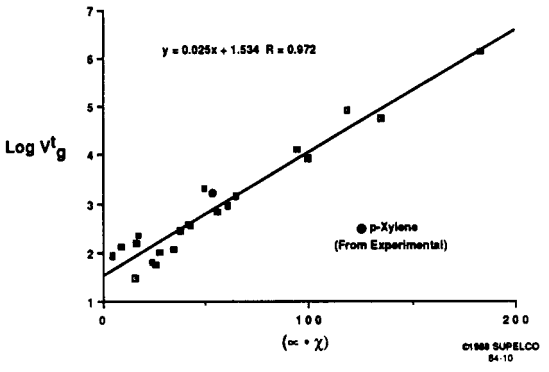

Figure 3 **Predictive Model Plot for Carbopack™ F**
Log V^t_g vs.(∝ • χ)

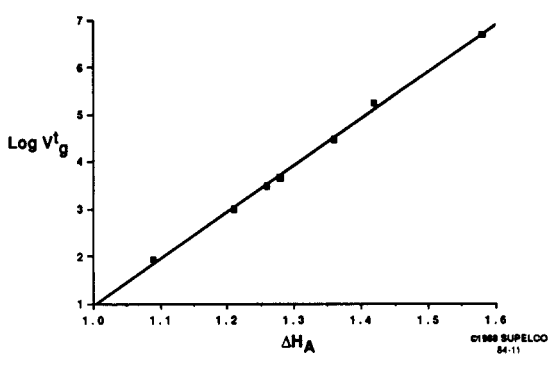

Figure 4 **Relationship Between Specific Retention Volume (V^t_g) and Heat of Adsorption (ΔH_A) for Carboxen™-569**

transition pores and micropores in the sieve particles which lead to unequal use of the internal surface throughout a range of adsorbates possessing varying molecular sizes. A plot of the log V^t_g vs. WH_A (heat of adsorption), however, provides insight into this unequal adsorbate/adsorbent relationships as illustrated in Figure 4.

The straight-line plots for the three graphitized carbon blacks are illustrated in Figure 1, 2, and 3.

CONCLUSION

Adsorbent characterization evaluations have been performed to effectively establish adsorbate/adsorbent relationships between four adsorbents and several chosen adsorbates. Three Type I adsorbents (i.e., graphitized carbon blacks) and one weak Type III adsorbent which approaches Type I performance (Carboxen-569) have been utilized to generate straight line plots to predict sampling volumes for untested adsorbates. The construction of a four bed adsorbent tube, which functions to adsorb and subsequently thermally desorb a wide range of airborne contaminants, has resulted from these characterization evaluations.

REFERENCES

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