A MICRO-PRECONCENTRATOR/FOCUSER FOR A MICRO-GAS CHROMATOGRAPH: DEVICE AND MATERIALS CHARACTERIZATION

R. A. Veeneman¹ and E. T. Zellers^{1,2*}

Center for Wireless Integrated Microsystems, Departments of ¹Chemistry and ²Environmental Health Sciences, University of Michigan, Ann Arbor, Michigan, USA

ABSTRACT

The modeling and characterization of a microfabricated adsorbent preconcentrator/focuser (μ PCF), designed for use in a micro-scale gas chromatograph (μ GC) for the analysis of mixtures of vapors at parts-per-billion concentrations, are described. Classical models of vapor adsorption capacity and breakthrough volume are used to relate material properties and operating parameters to device performance. Adsorption studies on graphitized carbon adsorbents revealed two distinct adsorption-energy regimes that dictate the capacity for vapor adsorption over the relevant concentration range. Breakthrough volumes measured for two test vapors with the μ PCF and a reference PCF of conventional design were in agreement and were used to define the upper limits on the allowable flow rate through the microfabricated device. The prediction of μ PCF breakthrough volumes appears feasible.

INTRODUCTION

It has been nearly 30 years since the first report of a microfabricated gas chromatograph (μ GC) [1]. Since then numerous efforts have been mounted to develop low-power μ GCs that are capable of capturing, separating, and detecting the components of mixtures of gases and vapors [2-6]. Most potential applications of such microsystems require detection of target compounds in the parts-per-billion or parts-per-trillion concentration range. Since most detector technologies are not sensitive enough to achieve limits of detection in this range, it is necessary to employ a preconcentration step prior to separation and detection.

The research described here is part of a larger effort within the Center for Wireless Integrated MicroSystems (WIMS) to develop a μ GC for comprehensive analysis of complex mixtures of volatile organic compounds (VOC) of arbitrary composition [5-6]. Applications in indoor air quality monitoring, human exposure assessment, homeland security, and biomedical diagnostics are envisioned.

Figure 1. Block diagram of the WIMS μ GC with arrows showing flow paths during sampling and analysis.

Figure 1 shows a block diagram of the WIMS μ GC. The multi-stage μ PCF is an integral component of the system, whose evolving design and associated fabrication techniques have been described elsewhere [7-9]. The μ PCF is packed with different adsorbent materials to achieve quantitative trapping and efficient thermal desorption of VOCs spanning a wide range of structures

and volatilities (Figure 2). Operated at ambient temperature during sample collection, it is resistively heated to desorb trapped vapors for subsequent separation and detection by downstream components.

Although a number of other miniaturized or microfabricated preconcentrator devices have been reported [10-15], few consider explicitly the fundamental thermodynamic or kinetic factors affecting device design and operation [7, 14-15]. This study explores the application of some classical models of adsorption and breakthrough volume to the design and operation of the WIMS μ PCF, and reveals some heretofore unrecognized factors affecting performance. Adsorption isotherms were collected for a series of vapors on two of the graphitized carbon adsorbents used in the μ PCF, and breakthrough tests were conducted with a single adsorbent loaded into the μ PCF as well as in a more conventional reference PCF. Results are considered in the context of the Dubinin-Radushkevich (D-R) and Wheeler Models for predicting the performance of the μ PCF.

Figure 2. The WIMS μ PCF filled with adsorbent (left) and a finished device in its testing package (right).

THEORY

Among the thermodynamic models used to describe the equilibrium adsorption of vapors on porous and non-porous solids, the D-R model is perhaps the most widely applicable [16-18]. It is presented in its so-called linearized form in Eq. 1:

$$\ln W_e = \ln V_o \rho_L - \left[\left(\frac{RT}{\beta E_o} \right) \ln \left(\frac{p_{sat}}{p} \right) \right]^2 \quad (1)$$

where W_e is the adsorption capacity (g/g), V_o is the micropore volume (cc/g), ρ_L is the analyte density (g/cc), R is the ideal gas constant, T is temperature (K), β is an affinity coefficient, E_o is the adsorption energy (kcal/mole) and p_{sat}/p is the inverse of the vapor concentration expressed as a fraction of its saturation vapor pressure, p_{sat} .

The D-R isotherm equation relates the adsorbed mass of vapor per unit mass of adsorbent to essential properties of the vapor and the adsorbent. A plot of uptake mass versus $(\ln p_{sat}/p)^2$ yields E_o and V_o from the slope and y-intercept, respectively. Interestingly, most reports on the application of the D-R model to VOC adsorption have been restricted to vapor concentrations ranging from high-parts-per-million to saturation [16-18].

The Wheeler model has been used to describe the breakthrough of VOCs in packed adsorbent beds as a function of several key design and operating variables [19-20]. The most

common form of the equation is given in Eq. 2:

$$V_b = \frac{W_e W_B}{C_0} \left[1 - \frac{1}{k_v \tau} \ln \left(\frac{C_0}{C_x} \right) \right] \quad (2)$$

where V_b is the breakthrough volume (L) evaluated at some predetermined fraction of the challenge concentration, W_e the equilibrium adsorption capacity (g/g), W_B is bed mass (g), C_0 is the challenge concentration (g/L), C_x is the concentration downstream from the bed (g/L), k_v is the kinetic rate coefficient (min^{-1}), and τ is the bed residence time (min), which is proportional to the volumetric flow rate, Q (L/min). The so-called 'critical bed residence time' is reached when the flow rate is such that $V_b = 0$.

Most applications of the Wheeler model have been related to predicting the performance of respirator cartridges [20], which contain very large beds and are challenged with high VOC concentrations. Its application to characterizing micro-scale preconcentrators is less common [7, 14-15].

EXPERIMENTAL

Devices and Materials

The μ PCF consists of a series of three 450- μm -deep Si cavities fabricated using DRIE and sealed using wafer-level Au-Au thermo-compression bonding. Backside Pt RTDs are integrated to monitor heating rates. Etched holes in the sealing plate accept deactivated fused-silica capillaries for connecting to upstream and downstream components. The volumes of the cavities are, in order, 4.41, 2.54, and 1.63 μL , and were varied to accept different masses of three different adsorbent materials estimated to provide sufficient capacity for generalized use with the WIMS μGC . Overall device dimensions are 11mm $\times$ 4mm $\times$ 1mm.

A reference preconcentrator (PCF_{ref}) of conventional design was constructed by packing a 2.5-mm section of stainless steel tubing (1.35 mm i.d.) with a quantity of adsorbent material similar to that contained in the μ PCF and held in place by plugs of stainless steel mesh and silanized glass wool.

The two adsorbent materials studied here are the graphitized carbons Carbpac B (C-B, specific surface area = 100 m^2/g) and Carbpac X (C-X, specific surface area = 250 m^2/g) (Supleco, Eight-Four, PA) which were sieved to a size range of 112-140 μm .

Adsorption isotherms were collected for 17 vapors. Eleven of these were tested on C-X and 12 were tested on C-B (five were tested on both adsorbents). The test compounds spanned a range of vapor pressures from 1.4 to 151 mm Hg and contained vapors with various functionalities (i.e., alkanes, aromatics, ketones, chlorinated hydrocarbons, alcohols, aldehydes, and esters).

Adsorption Isotherms and Breakthrough Volumes

For the applications of interest, vapor concentrations are expected to be quite low, so tests focused on concentrations in the range of 10 to 2,000 parts-per-billion (ppb). Test atmospheres were generated by passing clean, dry air through a fritted bubbler containing the liquid analyte and diluting the saturated vapor stream with clean, dry air via calibrated mass flow controllers. Vapor concentrations were periodically verified by GC-FID (HP-6890, Agilent, Palo Alto, CA) via a gas sampling valve/loop. Vapor adsorption was measured with a thermogravimetric analyzer (TGA, Pyris 1, Perkin Elmer, Waltham, MA) loaded with 1-3 mg of adsorbent material and connected to the vapor stream with stainless steel tubing. Exposures were preceded and followed by purging with N_2 for ~ 60 min. Mass uptake by the empty sample pan was subtracted from all measurements. The minimum mass

change detectable by the instrument is $\sim 1\mu\text{g}$. The materials were preconditioned by heating under N_2 to 270-300°C for 4.5 hr. The TGA was held isothermal at 26.6°C during vapor exposure. After each exposure series the adsorbent sample was heated to 300°C under N_2 for 30 min to remove adsorbed vapors.

Breakthrough volumes were determined by drawing a known concentration of vapor through the preconcentrator. The outlet stream was periodically injected into a GC-FID via a six-port sampling valve. Breakthrough curves were constructed by plotting C_x/C_0 versus the volume of air passed through the adsorbent at the specified flow rate. By convention, V_b was defined as the volume required for C_x/C_0 to reach 0.1 (10% breakthrough). For the tests reported here, only the first cavity of the μ PCF was used, and it was filled with 1.33 mg of C-X. The device was regenerated by heating under a flow of N_2 at 200-300°C for 30 min.

Figure 3. Representative linearized D-R plot for *m*-xylene on C-B showing two distinct regions, reflecting two different adsorption energies at different degrees of surface coverage.

RESULTS AND DISCUSSION

Adsorption Capacities

Of the 23 isotherms generated in this study, all but two gave D-R plots (cf. Eq. 1) similar to that shown in Figure 3 (for *m*-xylene on C-B) for both C-X and C-B. Two linear segments are apparent in all of these plots, the slopes of which are inversely proportional to the energy of the vapor-adsorbent interaction, E_o (note: values of β are calculated on the basis of the polarizability of each vapor [21], which can be found in standard references). The right-hand segment is the data at lower concentrations, which are

Figure 4. Isotherm for *m*-xylene (squares) and predictions using a single energy (dashed line) and dual energy (solid line) D-R equation.

characterized by a higher adsorption energy (shallower slope) for non-polar vapors. This is consistent with higher energy sites being filled in preference to lower energy sites. The left-hand segment is the data collected at higher concentrations and reflects adsorption at sites of lower energy.

For the polar vapors the slopes of each segment are reversed, in accordance with the lower affinity of polar vapors for the non-polar carbon surface at lower concentrations. At higher concentrations, vapor-vapor interactions become important for the polar vapors and lead to a higher apparent E_o value. Most studies report only a single linear relationship in such plots, consistent with experiments being conducted at higher concentrations [16-18].

The revelation of two regimes is quite significant, as it indicates, for example, that at low concentrations the capacity of the adsorbent for non-polar vapors is much higher than it is at even modestly higher concentrations. The values of V_b calculated were nearly zero in all cases (not shown), which is expected for C-B and C-X because they are nominally non-porous materials.

For both adsorbents, the points of discontinuity in the linearized D-R plots correspond to about the same (condensed) volume of sorbed vapor per gram of adsorbent material for all vapors tested: $\sim 0.26 \mu\text{L/g}$ for C-B and $\sim 1.2 \mu\text{L/g}$ for C-X. The lower value for C-B is attributed to its lower specific surface area.

This finding of two energy regimes has direct implications for modeling adsorption with the D-R equation. As shown in Figure 4, using a single (average) value of E_o leads to significant errors in the modeled adsorption isotherm (dashed line). When account is taken of the two energies (solid line) the average absolute error of the model is $< 2\%$.

Breakthrough Volumes as a Function of Bed Residence Time

Using the μPCF with the first cavity filled with 1.33 mg of C-X, breakthrough tests were performed with toluene and benzene over a range of flow rates (τ values). A similar series of tests was performed with the reference PCF (PCF_{ref}), which was packed with 1.35 mg of C-X. Figure 5 shows a representative μPCF breakthrough curve for toluene ($C_o = 150$ ppb).

Figure 5. Example of a breakthrough curve of toluene on the C-X bed of the μPCF ($Q = 4.1 \text{ mL/min}$; $\tau = 11.8 \text{ msec}$).

Among other things, the Wheeler model (Eq. 2) predicts that V_b will decrease with decreasing τ (increasing flow rate). Figure 6 shows the strong dependence of V_b on τ for the μPCF (filled symbols), particularly at τ values below 10 msec, which correspond to flow rates $> 5 \text{ mL/min}$. At lower flow rates, there is markedly less dependence. The critical bed residence time corresponds to a flow rate of 16 mL/min for toluene -- operation at

such high flow rates results in immediate breakthrough. Nearly identical results were obtained using the reference PCF (Figure 6, open symbols) indicating that bed geometry is not important and that data obtained with capillary-type devices are applicable to devices with rectangular cross sections, as long as the bed volumes are properly taken into account. Data collected for benzene thus far (not yet complete) are qualitatively consistent with that for toluene.

Figure 6. Dependence of V_b on bed residence time for toluene with the μPCF (filled symbols, solid curve) and the reference PCF (open symbols, dashed line).

Kinetic Rate Constants

Using values of W_e obtained from the TGA experiments and the values of V_b from the breakthrough experiments for the both the μPCF and reference PCF in the Wheeler model (Eq. 2), it was possible to calculate corresponding values of k_v for benzene and toluene over a range of linear velocities. Empirical models of k_v as a function of linear velocity, u , and particle diameter, d_p have been reported and are of the general form $k_v = m(d_p^{-1.5})(u)^n$ where m and n are empirically determined coefficients [22].

Plots of k_v versus u are shown in Figure 7 for both vapors and both devices. Given the range of d_p ($112\text{--}140 \mu\text{m}$) it was not possible to specify a value. Least-squares regression gave the following equations: $k_v = 102 u^{0.6}$ for the μPCF and $k_v = 73.8 u^{0.6}$ for the PCF_{ref} with r^2 values > 0.95 in both cases. Note that both vapors are described by the same relationship for a given device, consistent with the similarity in their diffusion coefficients. The difference in the coefficients is apparently due to small differences in average particle diameters loaded into the two devices. This suggests that k_v for a given bed may be effectively independent of vapor properties and dependent solely linear velocity.

Wheeler Model

Using the empirical equations derived for k_v and the D-R models for W_e it was possible to calculate modeled values of V_b for toluene from the Wheeler equation (Eq. 2) for the data shown in Figure 6. The curves shown in Figure 6 represent the modeled relationship for the μPCF (solid) and PCF_{ref} (dashed). As shown, the agreement between experimental and modeled V_b values is reasonably good.

CONCLUSIONS

This study has demonstrated the value of applying classical thermodynamic and kinetic models of adsorption to the design and operation of micro-scale preconcentrators for capturing vapors at trace-level concentrations. The finding of two adsorption energies among nearly all vapors on both adsorbents over the concentration

Figure 7. Kinetic rate coefficient (k_v) vs. linear velocity for both benzene and toluene on Carbopack X for the μ PCF (circles) and the reference PCF (squares).

range of interest is noteworthy. The corresponding improvement in the accuracy of modeled adsorption capacities leads to more accurate estimates of required adsorbent masses in such devices.

The relationships shown here between breakthrough volumes and flow rates are also of value in defining limits on the sampling rates. Our data suggest that operation at bed residence times < 5 msec may lead to rapid breakthrough of target vapors which, in turn, reduces the preconcentration factor and the accuracy of quantitation when using such devices in microanalytical systems.

Empirical models of the kinetic rate coefficient and theoretical models of adsorption capacity were applied to the prediction of breakthrough volumes as a function of flow rate (bed residence time) with sufficient accuracy to guide design efforts and define operating limits on μ PCF devices employing packed beds of adsorbents.

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