Anal. Chem. **2009,** *81,* 3017–3021

Systematic Investigation of the Sorption Properties of Tenax TA, Chromosorb 106, Porapak N, and Carbopak F

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Publication Date (Web): March 24, 2009 | doi: 10.1021/ac802686p

A variety of sorbents is available for the sampling of airborne organic pollutants. However, choosing the right sorbent for a certain analytical target is still a challenge. Here we present a systematic sorption study for a diverse set of up to 200 compounds at temperatures between 40 and 250 °C for four frequently used sorbents: Tenax TA, Chromosorb 106, Porapak N, and Carbopack F. The experimental data are used to calibrate a polyparameter linear free energy relationship (pp-LFER) for each sorbent which allows one to predict the safe sample volume and the complete sample elution volume of chemicals not tested here at any desirable temperature.

A variety of sorbents are available for air sampling and subsequent thermal desorption. Often choosing the right sorbent can be difficult, because different aspects need to be considered. The goal in selecting the proper sorbent is to choose one that can retain a specific or a group of analytes for a defined sample volume. However, the adsorbent must also be able to release the analyte(s) quantitatively into a specified volume of carrier gas during the desorption process.

Figure 1a shows a typical breakthrough curve of an analyte in a sampling situation with a sorbent cartridge. At the beginning of the sampling, the analyte sorbs completely to the resin and the concentration in the outflow equals zero. After awhile, the sorption capacity for the compound is reached and the concentration of the compound rises in the outflow and eventually reaches the concentration in the inflow. The shape of the breakthrough curve is influenced by diffusion and dispersion processes and can vary, depending on the sampling conditions. The 50% breakthrough volume $BTV_{50\%}$ (in $mL/g_{sorbens}$), though will always be characteristic for a given compound and a specific sorbent at a given temperature.

On the basis of the $BTV_{50\%}$, two parameters can be calculated that are important for practical purposes: the safe sample volume V_s and the complete sample elution volume V_e.

The safe sample volume equals the gas volume per gram of sorbent at which the analyte starts to elute from the sorbent cartridge (Figure 1a). If the breakthrough curve shows a Gaussian shape, it can be estimated as follows:[1]

$$V_s = BTV_{50\%} \times 0.5 \qquad (1)$$

This volume (in milliliter/grams of sorbent) should not be exceeded during the sample process to make sure the analyte is trapped quantitatively on the resin. Very short columns with coarse sorbents may have a small number of plates (<5), and then the shape of the breakthrough curve will differ from the Gaussian function.[2,3] In the current study, the columns showed plate numbers above 10 and the curves showed nearly a Gaussian form. The columns shape and material in the current study were similar to the ones that are normaly used for active sampling. Therefore eq 1 should be applicable to our data and most practical sampling situations. Every user has to make sure, though, that the used sampling column has a sufficient number of plates. If not, a correction according to Lövkvist and Jönsson should be applied.[2]

The complete sample elution volume V_e (in milliliter/grams of sorbent) defines the volume of gas per gram of sorbent that is needed to elute the analyte completely from the resin (Figure 1b). It can be estimated from[4]

$$V_e = BTV_{50\%} \times 3.0 \qquad (2)$$

This empirical formula already accounts for possible tailing in the desorption curve. For a typical thermodesorption procedure (in combination with GC analysis), the temperature should be selected such that the complete sample elution volume is smaller than 10 mL/g.[4] Note that it is preferred to use the lowest possible desorption temperature that elutes the analytes of interest off the adsorbent resin in order to avoid interferences, sample decomposition, and adsorbent resin decomposition. The above considerations show that the $BTV_{50\%}$ is the central parameter for selecting the optimal type and amount of sorbent as well as

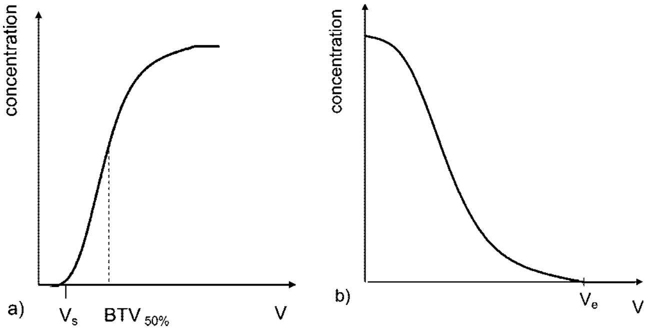

Figure 1. Breakthrough curve (a) of a compound through and its elution (b) from the sorption cartridge.

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(1) Pankow, J. F. *Atmos. Environ.* **1989**, *23*, 1107–1111.

10.1021/ac802686p CCC: $40.75 © 2009 American Chemical Society
Published on Web 03/24/2009

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selecting the desorption temperature required for the thermodesorption of a specific analyte.

Data collections on breakthrough volumes of up to 198 compounds for different technical sorbents as a function of temperature already exist (http://www.sisweb.com). However, these data collections provide no means for extrapolations to other analytes. A reliable model that predicts $BTV_{50\%}$ data for all possible combinations of analyte, sorbents, and temperature based on a limited set of experimentally determined values does not yet exist.

The $BTV_{50\%}$ is identical to the equilibrium sorption constant, $K_{air/sorbent}$ of the analyte between the gas phase and the sorbent. Pankow et al.[1] and others have used correlations between log $K_{air/sorbent}$ and log p_l, the saturated liquid vapor pressure of the analytes to predict sorption constants that had not been measured experimentally. However, this approach only holds within a given compound class and not across compound classes.[5,6]

An accurate instrument for predicting sorption coefficients across all kinds of compound classes are polyparameter linear free energy relationships (pp-LFER) like the one in eq 3:

$$\log(BTV_{50\%}) = \log(K_{air/sorbent}) = l_{sorbent}L_{i16} + s_{sorbent}S_i + a_{sorbent}A_i + b_{sorbent}B_i + v_{sorbent}V_i + c_{sorbent} \quad (3)$$

The capital letters are compound descriptors for the various types of interactions a compound can undergo. L_{i16} is the logarithm of the hexadecane/air partition constant at 25 °C in units of ($m_{air}^3/m_{hexadecane}^3$), and V_i is the McGowan characteristic volume in units of (cm^3/mol)/100. These descriptors describe nonspecific interactions (van der Waals interactions and cavity formation) between the analyte and the sorbent. The remaining three descriptors stand for various specific intermolecular interactions: A_i characterizes the H-donor (or electron-acceptor) property of the compound, B_i stands for the H-acceptor (or electron-donor) property, and S_i is called the dipolarity/polarizability descriptor. The determination of these compound descriptors is described in detail by Abraham et al.[7] The small letters represent the complementary system descriptors, which here stand for the sorption properties of the studied sorbents. pp-LFERs such as the one in eq 3 have been shown to successfully describe the variance of sorption coefficients for very diverse compounds in all kinds of partition media (e.g., solvents,[8] polymers,[9] surfaces,[10] humic material[11]). The compound descriptors required in eq 3 are tabulated for a large number of compounds in the literature.[12−14] The system descriptors can be determined from regressing eq 3 to a diverse set of experimentally determined sorption coefficients on the sorbent of interest for compounds with known compound descriptors. Equation 3 is a modification of the well-known Abraham equation where an *E*-descriptor (for dispersive interactions) is used instead of the *V*-descriptor in eq 3. The *E*-descriptor is directly related to the refractive index of a compound and has the disadvantage that for solid compounds it has to be estimated which involves considerable uncertainty.[15,16] The *V*-descriptor that we use instead is calculated from molecular increments and does not involve any uncertainty. For further discussions of the different equation types see ref 17.

In order to integrate temperature dependence into this approach, one can establish pp-LFERs for different temperatures treating the sorbent descriptors as temperature dependent and the compound descriptors as temperature independent.[18] In practice, one typically finds that the sorbent descriptors exhibit a steady trend with temperature which facilitates safe inter- and extrapolation to other temperatures.[15] The disadvantage of this method is that it requires a complete calibration data set for every temperature.

Sprunger et al.[19] suggested a method for combining experimental partitioning coefficients from different temperatures into a single pp-LFER regression that contains temperature as a separate parameter. This method is based on the finding that both the Gibbs free energy and the enthalpy of a partition process can be predicted by linear free energy relationships using the same compound descriptors. The approach of Sprunger et al. in combination with the modified Abraham equation from Goss results in

$$\log[K/(\mathrm{L/g})] = c_s - \frac{c_h}{T} + \left(v_s - \frac{v_h}{T}\right)V_x + \left(s_s - \frac{s_h}{T}\right)S + \left(a_s - \frac{a_h}{T}\right)A + \left(b_s - \frac{b_h}{T}\right)B + \left(l_s - \frac{l_h}{T}\right)L \quad (4)$$

The model described by eq 4 has the advantage that it requires a smaller set of experimental calibration compounds than would be needed for calibrating eq 3 for different temperatures. To calibrate pp-LFER models for various sorbents we have carried out sorption experiments at different temperatures for a wide variety of polar and nonpolar organic compounds.

EXPERIMENTAL SECTION

Method. The $K_{air/sorbent}$ (= $BTV_{50\%}$) is commonly estimated using the elution technique. This can easily be done if the sorbent serves as the stationary phase of a packed column in a GC system. The analyte is entered as a small pulse into the column, while a substance-free gas flow is passed through the column. The elution of the analyte from the column is recorded

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(2) Lovkvist, P.; Jonsson, J. A. *Anal. Chem.* **1987**, *59*, 818–821.
(3) Poole, C. F.; Gunatilleka, A. D.; Sethuraman, R. *J. Chromatogr., A* **2000**, *885*, 17–39.
(4) Manura, J. J. Scientific Instrument Services, 1999; Vol. 2008.
(5) Kamprad, I.; Goss, K.-U. *Anal. Chem.* **2007**, *79*, 4222–4227.
(6) Goss, K.-U.; Schwarzenbach, R. P. *Environ. Sci. Technol.* **2001**, *35*, 1–9.
(7) Abraham, M. H.; Ibrahim, A.; Zissimos, A. M. *J. Chromatogr., A* **2004**, *1037*, 29–47.
(8) Acree, W. E.; Abraham, M. H. *Fluid Phase Equilib.* **2002**, *201*, 245–258.
(9) Braun, J.-M.; Guillet, J. E. *Adv. Polym. Sci.* **1976**, *21*, 107–145.
(10) Goss, K.-U. *Crit. Rev. Environ. Sci. Technol.* **2004**, *34*, 339–389.
(11) Niederer, C.; Goss, K.-U.; Schwarzenbach, R. P. *Environ. Sci. Technol.* **2006**, *40*, 5374–5379.
(12) Abraham, M. H.; Andonian-Haftvan, J.; Whiting, G. S.; Leo, A.; Taft, R. S. *J. Chem. Soc., Perkin Trans.* **1994**, *2*, 1777–1791.
(13) Abraham, M. H.; Chadha, H. S.; Whiting, G. S.; Mitchell, R. C. *J. Pharm. Sci.* **1994**, *83*, 1085–1100.
(14) Abraham, M. H. *J. Chromatogr.* **1993**, *644*, 95–139.
(15) Atapattu, S. N.; Poole, C. F. *J. Chromatogr., A* **2008**, *1195*, 136–145.
(16) Tülp, H. C.; Goss, K.-U.; Schwarzenbach, R. P.; Fenner, K. *Environ. Sci. Technol.* **2008**, *42*, 2034–2040.
(17) Goss, K.-U. *Fluid Phase Equilib.* **2005**, *233*, 19–22.
(18) Abraham, M. H.; Poole, C. F.; Poole, S. K. *J. Chromatogr., A* **1999**, *842*, 79–114.
(19) Sprunger, L.; Acree, W. E.; Abraham, M. H. *Anal. Chem.* **2007**, *79*, 6891–6893.

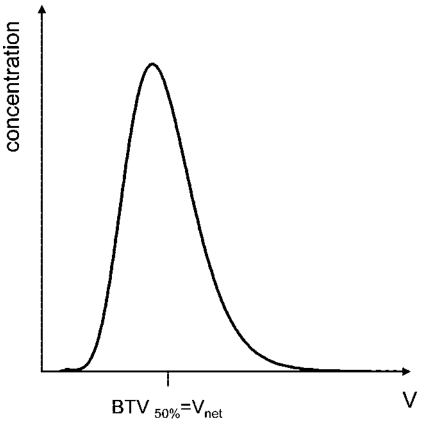

Figure 2. Elution method for the estimation of the breakthrough volume.

as a peak (see Figure 2). $K_{\mathrm{air/sorbent}}$ can be calculated from the retention volume V_i minus the elution volume of a nonretained tracer V_{tracer} and divided by the mass of sorbent M_{sorbent}:[20]

$$K_{\mathrm{air/sorbent}} = (V_i - V_{\mathrm{tracer}})/M_{\mathrm{sorbent}} \qquad (5)$$

The volumes V_i and V_{tracer} are determined from the volumetric flow rate of the mobile phase corrected for the pressure drop and the retention time of the respective peaks which are marked by their first statistical moment.[20] The experiments were conducted with stainless steel high-pressure liquid chromatography columns (1.0 and 5.0 cm length, 0.3 cm inner diameter) filled with the respective sorbent. The column was connected to the injector and flame ionization detector of a chromatograph (Carlo Erba 5300, Milan, Italy) with short stainless steel capillary tubings (0.5 mm id). Measurements without the sorbent revealed that sorption to the stainless steel system (capillaries, frits, and column walls) was negligible. In our experiments, the gas flow was set between 5 and 45 mL/min. This is equivalent to a linear flow velocity of 1.2−10.6 cm/s, which is in the range of what is used in typical sampling procedures. Nitrogen served as a carrier gas.

Chemicals and Materials. Sorption experiments were carried out with three polymer sorbents and one carbon sorbent (see Table 1). Sorption experiments were typically conducted with 40−50 different analytes representing the following compound classes: alkanes, alkenes, alkynes, halogenated alkanes, alkanols, phenols, ketones, ethers aldehydes, esters (including phthalates), alkylated and halogenated aromatic compounds, anilines, nitriles, nitro-compounds, carboxylic acids, and highly fluorinated and polyaromatic compounds.

RESULTS AND DISCUSSION

Tables with all calibration compounds, their interaction descriptors (for use in eqs 3 and 4) and all experimental sorption coefficients for various temperatures are given in the Supporting Information.

Model Calibration at Specific Temperatures. The fitted parameters for the pp-LFER equation (eq 3) of Tenax TA for three temperatures are summarized in Table 2. The H-bond descriptors *a* and *b* of the sorbent were excluded from the equation because statistically they were found not to be significantly different from zero.

Figure 3 exemplarily shows that eq 3 is well suited to fit all experimental data for a diverse set of chemicals at 100 °C. The sorbent descriptors for Tenax TA that result from the fitting of eq 3 (Table 3) indicate that only nonspecific interactions are relevant for this sorbent. The H-donor or H-acceptor properties are zero, and there is only a small polarity related to the *S*-value. Sorption on Tenax TA is therefore almost completely governed by the L_i and V_i-descriptors of the analytes that stand for nonspecific interactions. Abraham[21] and Hawkins[22] recommend a leave-one-out statistic including the PSD (predictive standard deviation) as a good test of the predictive ability of the model. Here we find the PSD-values to be only slightly larger than the standard error and thus show a good predictive capability of the model.

The other tested sorbents show a similar quality of fits. In general, at lower temperatures the fits showed more scatter than at higher temperatures. Chromosorb 106 and Porapak N gave better correlations than the other sorbents.

Comparison to Literature Data. Scientific Instruments Services (SIS) provides a big data set of BTV$_{50\%}$ for 198 compounds on Tenax TA at different temperatures under http://www.sisweb.com/index/referenc/resins.htm. For applying the pp-LFER model to these data, we first had to remove several outliers in the SIS data set. The sorbent descriptors that we derived for the revised SIS data set are significantly different from the ones we have presented here. These differences may be due to differences in the manufacturing of the Tenax TA. The SIS data have presumably been measured before 1997. The Tenax TA used here (lot batch 122) had been ordered by the end of year 2007. In order to get a better idea of the reproducibility of various charges of Tenax TA, we repeated our sorption experiments with an older Tenax sample (lot batch 85) without detecting significant differences between the two materials.

A sorption study for Tenax GC carried out by Poole et al. using data from 1988 agrees with our results[23] but provides data only for 20 °C. For Carbotrap, Abraham and co-workers have published data[24] that are consistent with the Carbopack data presented here.

Model Calibration Including Temperature Dependence. For the use in eq 4, all measured BTV$_{50\%}$ values at different temperatures were integrated into one data set. For Tenax TA, experimental data from 40 to 250 °C of Tenax TA were used. Note that in this case, our data sets for 200 and 250 °C had not been diverse and numerous enough for a fitting of the temperature specific pp-LFER (eq 3).

Sprunger's method assumes the enthalpy of sorption to be independent of temperature within the covered temperature range. To check this prerequisite, log $K_{\mathrm{air/sorbent}}$ was plotted against $1/T$ (Van't Hoff plot Figure 4) for selected compounds and found to be linear. The system's parameters for Tenax TA as they result from an evaluation with eq 4 are summarized in Table 3. A comparison of the fitted vs experimental values is shown in Figure 5. There, standard deviation amounts to 0.23 log units and the PSD shows a similar value.

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(20) Conder, J. R.; Young, C. L. *Physicochemical Measurement by Gas Chromatography*; Wiley: New York, 1979.

(21) Abraham, M. H.; Acree, W. E.; Leo, A. J.; Hoekman, D. *New J. Chem.* **2009**, DOI: 10.1039/b813581a.

(22) Hawkins, D. M. *J. Chem. Inf. Comput. Sci.* **2003**, *44*, 1–12.

(23) Poole, S. K.; Poole, C. F. *Anal. Comm.* **1996**, *33*, 353–356.

(24) Abraham, M. H.; Walsh, D. P. *J. Chromatogr.* **1992**, *627*, 294–299.

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Table 1. Summary of the Sorbents and Their Properties As Reported by the Manufacturer

name	type	specific surface area [m^2/g]	T_{max} [°C]	bulk density [kg/m^3]	size [mesh]
Tenax TA	polydiphenylene oxide	35	350	0.25	60/80
Chromosorb 106	polystyrene	750	250	0.28	60/80
Porapak N	polyethenylpyrrolidon	350	190	0.38	50/80
Carbopack F	carbon	5	na[a]	0.64	60/80

[a] na, Not available.

Table 2. Sorbent Descriptors (±Standard Deviations) for the Polymer Sorbent Tenax TA at Various Temperatures As Determined from a Fit of Equation 3 to the Experimental Logarithmic Sorption Constants, log[*K* (L/g)][a]

T [°C]	*l*	*v*	*s*	*c*	r^2	se	PSD	*n*
40	0.91 (0.07)	0.45 (0.16)	1.39 (0.23)	−2.70 (0.26)	0.83	0.34	0.38	49
100	0.74 (0.02)	0.09 (0.05)	0.54 (0.07)	−2.98 (0.09)	0.97	0.13	0.14	59
150	0.47 (0.03)	−0.20 (0.13)	0.53 (0.07)	−2.51 (0.12)	0.97	0.14	0.15	50

[a] The descriptors *b* and *a* were not significantly different from zero. r^2 = correlation coefficient, se = standard error in the estimation, *n* = number of compounds, PSD = predictive standard deviation.

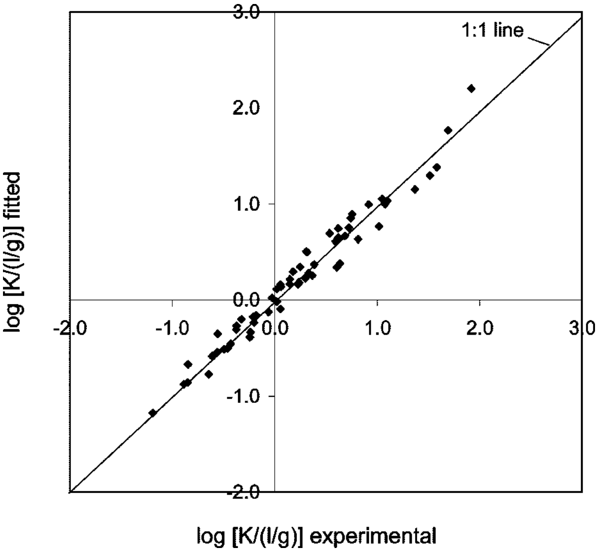

Figure 3. Experimental vs fitted (with eq 3) sorption constants of 59 organic compounds on the polymer sorbent Tenax TA at 100 °C.

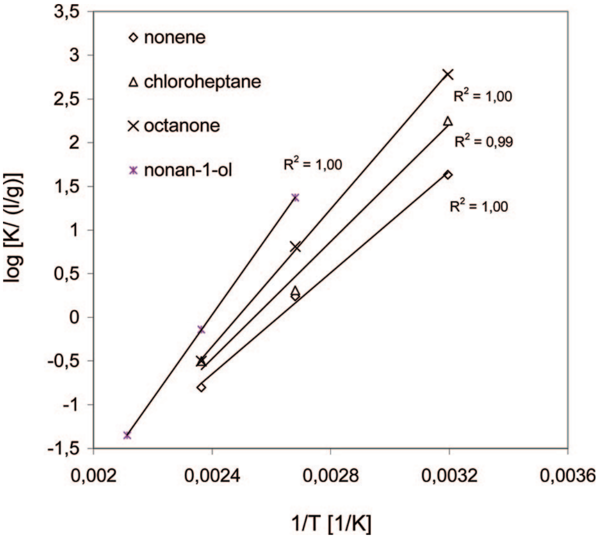

Figure 4. Van't Hoff plot of several compounds on the polymer sorbent Tenax TA.

Table 3. Temperature Independent Equation Coefficients and Standard Deviations (SD) for the Polymer Sorbent Tenax TA as Determined from a Fit of Equation 4 to the Experimental Logarithmic Sorption Constants, log[*K* (L/g)] at Temperatures between 40 and 250 °C

descriptor	numerical value	SD	descriptor	numerical value	SD
l_s	−0.42	0.14	l_h	−400	50
v_s	−1.29	0.49	v_h	−512	174
s_s	−0.44	0.43	s_h	−431	166
c_s	−5.23	0.43	c_h	−925	154

[a] r^2 = 0.92, se = 0.23, *n* = 187, PSD = 0.24.

For the other sorbents we also found the enthalpy of sorption Δ*H* to be constant over the whole temperature range (see Supporting Information). The parameters that resulted from applying eq 4 to the other sorbents (standard deviation between 0.08 and 0.26 log units) are presented in the Supporting Information together with the fits for the original equation used by Sprunger et al.[19]

With the temperature independent evaluation, it is possible to extrapolate the system's parameter to 20 °C to calculate the breakthrough volume of a target compound at room temperature. A big advantage of eq 4 is that data from different temperatures can be used even if they are not sufficiently diverse for a temperature specific evaluation.[19] Overall, eq 4 gives results nearly as accurate as the temperature specific interpretation with eq 3.

CONCLUSIONS

The model, eq 4, in combination with the sorbent descriptors (Table 3) presented here allows the prediction of the safe sample volume and the safe elution volume for all kinds of analytes on four frequently used sorbents at a wide range of temperatures. For ease of use, a calculator is available on our Web site that provides $BTV_{50\%}$ values and other information for all four sorbents to the user when temperature and the CAS number of the analyte are entered. With this tool, the selection of an

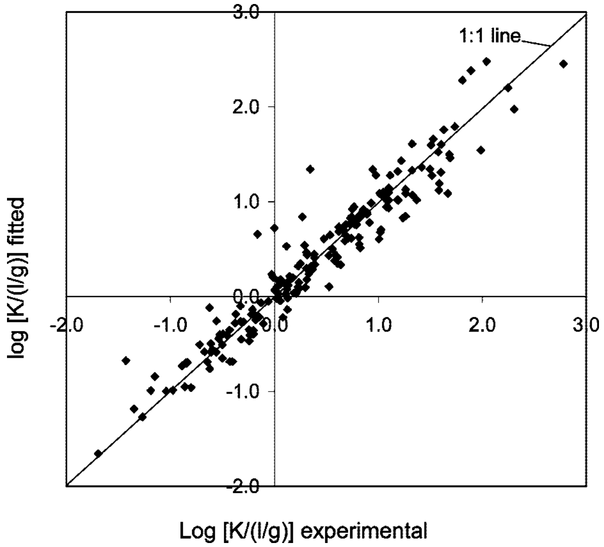

Figure 5. Experimental vs fitted (with eq 4) sorption constants of 187 organic compounds on the polymer sorbent Tenax TA at temperatures between between 40 and 250 °C.

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appropriate sorbent type and amount as well as desorption temperature becomes a simple task. It is available free of charge at http://www.ufz.de/index.php?en=16627.

However, it still remains interesting to also use the data presented here for a more general comparison of the sorption properties of the tested sorbents. The sorption capacity of a sorbent depends on the strength of interactions between the sorbate and the sorbent and the number of sorption sites. The latter is related to the specific surface area (SSA) of the sorbents and enters into eq 3 by the *c*-descriptor. The strength of interactions is represented by the other descriptors in eq 3. On the basis of the SSA (and the *c*-value) in Table 4, Chromosorb 106 and Porapak N can be expected to exhibit rather high sorption capacities for all compounds. In addition, these sorbents provide the strongest polar interactions (see the *a* and *s* values in Table 4), which renders them especially effective for sorbing polar compounds. Tenax TA has smaller polar and van der Waals interaction properties as well as a smaller SSA than the other two. This rather weak sorption capacity in combination with the highest temperature stability (desorption temperatures up to 350 °C are possible) makes it very suitable for less volatile compounds for which a quantitative desorption is the critical issue. Carbopack F is the least polar of all tested sorbents but exhibits the strongest van der Waals interactions. It is still a weak sorbent for all compounds because of its very low surface area. However, Carbopack sorbents also come with SSA up to 240 m^2/g (Carbopack X). These sorbents will have an extremely high sorption capacity for polar and nonpolar analytes alike. The high surface-area Carbopack sorbents will be the sorbents of choice when it comes to very small, volatile compounds where a safe sample volume is an issue.

Table 4. System Descriptors for All Sorbents at 20 and 190°C Calculated from the Temperature Specific Evaluation

sorbents	T [°C]	l	v	a	s	c	SSA (m^2/g)
Tenax TA	20	0.95	0.46	0.00	1.03	−2.07	35
Chromosorb		0.77	2.19	1.38	0.87	−1.88	750
Porapak N		0.58	3.22	2.05	1.80	−2.72	300
Carbopack F		0.80	3.14	0.00	0.33	−5.44	5
Tenax TA	190	0.44	−0.18	0.00	0.49	−3.23	35
Chromosorb		0.44	0.96	0.47	0.44	−3.51	750
Porapak N		0.38	0.97	0.89	0.69	−3.64	350
Carbopak F		0.49	1.53	0.00	0.53	−6.20	5

ACKNOWLEDGMENT

We thank Sigma-Aldrich, Germany, for providing the sorbent samples.

SUPPORTING INFORMATION AVAILABLE

Van't Hoff plots and the additional fitting equations for Chromosorb 106, Porapak N, and Carbopack F. This material is available free of charge via the Internet at http://pubs.acs.org.

Received for review December 18, 2008. Accepted March 4, 2009.

AC802686P