PREDICTION OF BREAK-THROUGH PROFILES FOR ORGANIC VAPORS IN ACTIVATED CARBON AT DRY AND HUMID CONDITIONS. A MULTIVARIATE APPROACH.

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Introduction

Empirical models for service life (break-through time) are valuable tools in the selection and design of activated carbon filters for military as well as industrial applications. Such predictive models should ideally be based on easily obtainable physical properties of the adsorbent-adsorbate system.

In this paper, we present quantitative-structure-affinity models (QSAfR) for the break-through time of halogenated hydrocarbons, monofunctional amines, ketones and aldehydes in dry and humid carbon. The modeling strategy is based on statistical experimental design in the selection of the training-set followed by multivariate data analysis of a multitude of property descriptors to establish adsorbate properties that are influential during physisorption. The final QSAfR models were simplified to include only a few easily obtainable property descriptors.

Experimental

The predictive ability of a model is critically dependent on the composition of the training-set used to calibrate the model. Training-sets were therefore selected in such a way that they represent a balanced distribution of properties of importance for the break-through time in an activated carbon bed.

A brief summary of the strategy used for the selection of compounds to be included in the training-set is given below. For more details see Fängmark et al.[1]

1. Lists of 81 halogenated hydrocarbons, 54 amines and 51 aldehydes/ketones were compiled, based on high volume industrial chemicals.
2. The chemical structure of these compounds was parameterized with 13 – 18 property descriptors for volatility, size, polarity, electronic polarizability and hydrophilicity.
3. The dominant variation in the compiled descriptors was summarized in a few, orthogonal principal components (PCs).[2] In order to evaluate if class specific properties are important, separate training-sets were identified for each compound class.
4. The PCs were used as independent design variables in a two-level full factorial statistical design to select subsets of a minimum number of compounds to be experimentally evaluated. These compounds are shown in Table 1.

Break-through profiles for the training-sets, in three kinds of activated carbon beds, were experimentally evaluated. Tests were performed on carbon `as received ´ and carbon prewetted at 80 % relative humidity (RH) for 16 hours, using challenge vapors of the same RH. Challenge concentrations were 0.1 mol/m^3 at a flow rate of 1 l/min (5.6 cm/s) on 20 mm diameter packed beds with 23 mm depth.

Partial least squares analysis (PLS)[3] was used to relate the response, the break-through profiles (Y), to the systematic variation in the chemical descriptors (X), i e to develop the QSAfR models. Important descriptor variables were identified and included in the final simplified models.

Results and Discussion

Provided that service life is affected by physisorption only, it should be possible to include all three training-sets in the same model. In the modeling, completely water miscible compounds (numbers 1, 2 and 46, Table 1) and the two gaseous compounds (numbers 9 and 44, Table 1) form separate clusters. A possible explanation would be that a linear model could not cover the entire range of volatility and water solubility. The present study was therefore limited to cover the remaining 15 compounds.

PLS-models with predictive power above 0.8 and three significant PCs were developed for dry and prewetted carbon. These models demonstrate that the same properties influence the resulting three significant PCs of both the dry and humid QSAfR-models. However the order of importance varies between dry and prewetted carbon. Important properties for PC1 of the dry carbon model are the size/bulk of the molecule (molar volume, area etc.), for PC2: volatility (boiling point, vapor pressure), and for PC3: hydrophobicity (water solubility, octanol-water partition coefficient). For the prewetted carbon the order of importance is reversed between PC1 and PC2, i e volatility is important for PC1 and size/bulk important for PC2.

By removing variables that can be explained by other variables retained in the model, simplified QSAfR-models were developed. These models include the following property descriptors only; boiling point, volume, area and octanol-water partition coefficient. The predictive ability of these models is shown in Figure 1 for dry Norit carbon as calculated/predicted versus observed 1 % break-through time and in Figure 2 for prewetted carbon.

Conclusions

- The same properties are important for the QSAfR models in both dry and prewetted carbon, although the order of importance differ.
- OSAfR models with good predictive power can be established for halogenated hydrocarbons, monofunctional amines, ketones and aldehydes

References

1. Fängmark I, Hammarström L-G, Jönsson P-G, Norman PR, Ness AL, Baker SL, Osmond NM. Selection of Halogenated Hydrocarbons, Amines, Aldehydes and Ketones for Use in Structure-Affinity Modeling of Charcoal Filter Performance. Proceedings of the Scientific Conference on Chemical and Biological Defence Research, Aberdeen Proving Ground, MD, USA 1997.
2. Wold S, Esbensen K, Geladi P. Principal Component Analysis. Chem. Intell. Lab. Syst. 1987; 2: 37 – 52.
3. Dunn III WJ, Wold S, Edlund U, Hellberg S, Gasteiger J. Multivariate Structure-Activity Relationships Between Data from a Battery of Biological Tests and an Ensemble of Structure descriptors: The PLS method. Quant. Struct.-Act. Relat. J. 1984, 131-137.

Table 1. Training-sets of compounds for experimental evaluation of break-through profiles in activated carbon.

Number	Halogenated hydrocarbons	Number	Amines	Number	Ketones and aldehydes
44	2,2-Difluoropropane	2	Allylamine	1	Acetone
11	1,2-Dichloroethane	28	Diallylamine	61	Acrolein
9	Bromomethane	36	Diisobutylamine	27	Cyclopentanone
70	1-Bromopropane	46	N,N-Dimethylethylamine	4	Diethyl ketone
71	2-Bromopropane			6	Diisopropyl ketone
19	1,2-Dibromoethane				
81	Iodobutane				

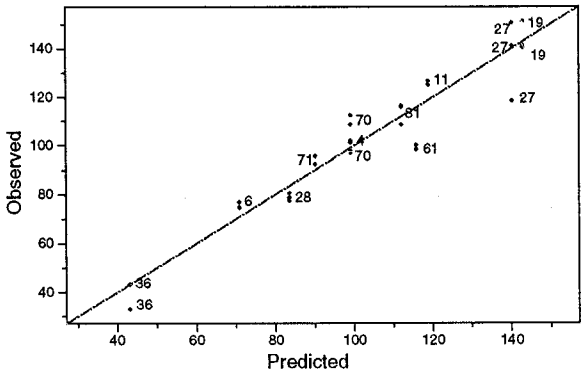

Figure 1. Observed versus predicted 1 % break-through time for dry Norit carbon. (For compound numbering see Table 1).

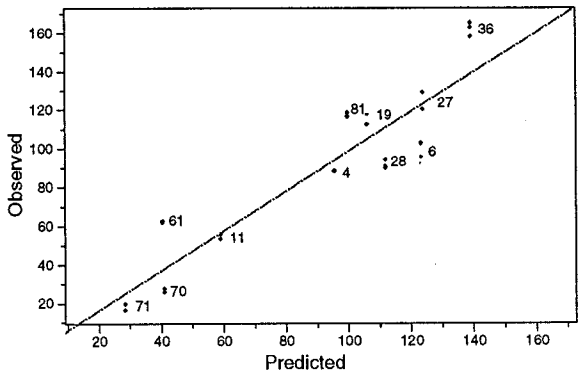

Figure 2. Observed versus predicted 1% break-through time for prewetted Norit carbon.