

Prediction of Filter Performances against Organic Vapours: Statistical Analysis of Breakthrough Times as a Basis for a Simple Prediction Model

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ABSTRACT

The prediction of the protection efficiency of NBC-respiratory filters against organic vapours is often very difficult, especially when strong physical interactions or chemisorption processes are involved. The presented statistical analysis is an attempt to develop a simple, but reliable, prediction model for breakthrough times. In over 70 experiments run under conditions of the EN 141 guidelines the breakthrough times of 39 organic compounds including alkanes, cyclo-alkanes, alkenes, alcohols, ketones and carboxylic acids have been measured for a given filter type. A linear regression model is then postulated to relate the breakthrough time to the adsorptive properties. For the model, each adsorptive molecule has been considered to be composed of a chemical functional group and a chain radical, resulting in a two dimensional structural code. The number of carbon atoms in the radical-chain and physical properties has been considered as an additional model parameter. General Linear Model (GLM) analysis was run to estimate model performances. We found out, that a simple linear model with only four regressors (two dimensional structural code, number of C atoms in the radical-chain and the saturation pressure) yields satisfactory breakthrough time predictions. Therefore, this study shows that, for a given filter type and well defined testing conditions, satisfactory predictions of breakthrough times of organic vapours are feasible.

Keywords: respiratory filter, breakthrough time, organic vapour, prediction, regression analysis

INTRODUCTION

More and more typical warfare NBC-respirator filters are also intended for use as protection in the case of industrial chemical releases to the atmosphere. It is well known that the protection efficiency of such filters, which relies on physi- and chemisorption processes of the agent on impregnated activated carbon, strongly depends on the type of the agent, as well as on the challenge conditions. For fixed challenge conditions, as for example defined by international norms, the protection efficiency is reflected by the breakthrough time for a given agent. The ability to predict breakthrough curves is therefore predominant. Although "ab-initio" model calculations of breakthrough curves are feasible for purely physisorbed gases and vapours (Wood, 2000; Lavanchy and Stoeckli, 1999; and Lavanchy and Stoeckli, 1997), simple models for the reliable prediction of breakthrough time of industrial toxic agent, especially when strong interactions with the impregnated active carbon are present, are still missing. Due to the inherent complexity of ab-initio models and the need of adequate input parameters it appears that models based

on statistical background may be a valid alternative for breakthrough predictions (Wu *et al.*, 2003). The present paper shows the steps and the results of such an approach for a given respirator filter as a first stage of more complex and extensive study taking place in our establishments.

METHODS

ABC-SF90 filters were challenged under test conditions given by the European Norm EN 141 (CEN/TC 79, 2000) with 39 different organic substances and the corresponding breakthrough time for a breakthrough concentration of 10 ppm recorded. The filters were tested freshly opened without the prior mechanical strain exposure mentioned by the Norm. Table I summarises the filter properties and the test conditions. The ABC-SF90 is a typical combined filter with an active carbon bed of 22 mm depth. The active carbon, known as PLW K 14x35 T is supplied by the Swiss company Dr. Pleisch AG (Mittlere Zelg, 8344 Bäretswil, CH). It is impregnated with a mixture of copper-, chromium- and silver salts as well as triethylenediamine (TEDA). Relating to the test conditions, it is noteworthy to mention, that the challenge concentration according to the EN 141 is defined as 1000 ppm, leading to different mass challenges for each adsorptive. The overall uncertainty of the breakthrough time has experimentally been evaluated in the range of $\pm 15\%$, which also reflects the inhomogeneity of the activated carbon and variations in filter manufacturing.

Table I. Filter properties and test conditions

Filter type	ABC-SF90	
Filter height	72 mm	
Filter diameter	110 mm	
Filter weight	245 g	
Active carbon bed height	~22 mm	
Active carbon bed diameter	~108 mm	
Active carbon bed mass	~110 g	
Active carbon type	PLW K 14x35 T	
Test conditions:	Filter freshly opened (< 4% volatile matter)	
	Air flow rate (constant low)	1.80 m ³ /h
	Humidity of the air flow	70 % r.H.
	Temperature	293.15 K
	Pressure	92500 Pa
	Input concentration	1000 ppm
	Breakthrough concentration	10 ppm
Testing apparatus	described by Arnold and Lavanchy, 1992	

Breakthrough times recorded as indicated, together with the properties of the test substances, form the basic data for the statistical analysis according to the following concept. Each adsorptive molecule is considered to be composed of a chemical functional group and a chain radical leading to the classification schema shown in Table II. As an example, 2-hexanone may be split into a methyl ketone- and a butyl radical. It is assumed that the functional group mainly contains the strong interaction or chemisorption properties, whereas physisorption properties should predominate in the chain radicals. The definitions of the functional groups are partly voluntary and not in full agreement with international chemical syntax

rules. They are defined in order to represent similar size fragments, such as for example methanol and methyl ketone. In addition, ethyl and vinyl radicals were introduced for reasons of consistency as pseudo-functional groups. The radical chains are primarily characterised by their total number of carbon atoms. They are further subdivided as shown in Table II in relation to their molecular structure. Table II gives the number of experiments run for a given “functional group – radical type” combination. Unfortunately, the data are not evenly distributed, which reduces to some extent the generality of the following results. This could especially be the case for carboxylic acids and the tertiary alkanes. Some molecules can be fragmented in different ways so that the total number of combinations exceeds the number of experiments.

Table II. Classification schema of the adsorptives and number of data points per class

Radical	Chemical functional group					
	Ethyl	Ethylene in cycle	Vinyl	Methanol	Methyl ketone	Carboxylic acid
n-alkyl	15	4	4	7	4	3
1-alkenyl	0	2	0	3	2	0
i-alkyl	7	2	2	2	2	0
t-alkyl	1	0	3	0	0	0
Methyl & alkyl (2 radicals)	3	0	9	2	0	0

This classification schema allows us to postulate the following linear regression model for the relation between adsorptive properties and the observed breakthrough times.

$$tb = x_0 + x_1 \cdot p_{sat} + x_2 \cdot CinR + x_{3i} \cdot R_{typ} + x_{4j} \cdot Funct + \varepsilon \quad (1)$$

where

- x_0 - x_4 = unknown parameters
- tb = breakthrough time [min] (response variable)
- p_{sat} = saturation pressure of the adsorptive [Pa]
- CinR = number of carbon atoms in the radical
- R_{typ} = type of the radical (as defined in Table II; class variable)
- Funct = functional group (as defined in Table II, class variable)
- ε = random effect [min]

The model is defined as a linear combination of the chemical functional groups (Funct), the radical types (R_{typ}) as well as the total number of carbon atoms in the radicals (CinR). Furthermore, the saturation pressure of the adsorptive (p_{sat}) has been introduced as an additional specific variable. Prior to solving the model by regression analysis, five experiments were randomly selected and withdrawn from the dataset. The purpose was to use them for the subsequent validation of the model.

The remaining data was considered as the training set and subjected to a general linear model analysis using the GLM-Procedure of the program "SAS for Windows", Version 6.12 (SAS Institute Inc., Cary, NC, USA).

RESULTS

Table III summarises the results of the breakthrough time measurements. It also lists the saturation pressure at 293.15K (STN data base DIPPR, Pennsylvania State University, USA) as well as the classification parameters used for each adsorptive. A test of the normal distribution of the breakthrough times gives the following values: mean = 180 min; sigma = 73 min; skewness = 0.32; kurtosis = -0.022. The data is not ideally normal distributed, but is still acceptable for the proposed regression analysis.

Table III. Breakthrough times and properties of the adsorptives used in this study

Adsorptive	Breakthrough time [min]	p_{sat} (293K) [Pa]	Chemical functional group	Radical	Number C in the radical
Butanol	326	930	Methanol	n-alkyl	3
1-Buten-3-one	278	12558	Methyl ketone	1-alkenyl	2
1-Hexene	186	24653	Vinyl	n-alkyl	4
1-Hexene	195	24653	Vinyl	n-alkyl	4
Pentanol	302	2811	Methanol	n-alkyl	4
Pentanol	304	2811	Methanol	n-alkyl	4
Pentanol	301	2811	Methanol	n-alkyl	4
1-Penetene	159	85081	Vinyl	n-alkyl	3
1-Penetene	156	85081	Vinyl	n-alkyl	3
2,2-Dimethylbutane	150	42738	Ethyl	t-alkyl	4
2-Butanol	266	2449	Methanol	Methyl & alkyl	3
2-Butanone	235	12314	Methyl ketone	n-alkyl	2
2-Hexanone	245	1552	Methyl ketone	n-alkyl	4
2-Methyl-1-butene	160	81310	Vinyl	Methyl & alkyl	3
2-Methyl-1-butene	150	81310	Vinyl	Methyl & alkyl	3
2-Methyl-1-butene	155	81310	Vinyl	Methyl & alkyl	3
2-Methyl-1-propanol	300	1395	Methanol	i-alkyl	3
2-Methyl-2-butene	168	62456	Vinyl	Methyl & alkyl	3
2-Methyl-2-butene	177	62456	Vinyl	Methyl & alkyl	3
2-Methyl-2-butene	168	62456	Vinyl	Methyl & alkyl	3
2-Methylpentane	174	28149	Ethyl	i-alkyl	4
2-Propanol	264	6058	Methanol	Methyl & alkyl	2
Acetone	148	30752	Methyl ketone	n-alkyl	1
2-Propen-1-ol	338	18654	Methanol	1-alkenyl	2
2-Propen-1-ol	343	18654	Methanol	1-alkenyl	2
2-Propen-1-ol	333	18654	Methanol	1-alkenyl	2
3,3-Dimethyl-1-butene	151	57507	Vinyl	t-alkyl	4
3,3-Dimethyl-1-butene	161	57507	Vinyl	t-alkyl	4
3,3-Dimethyl-1-butene	152	57507	Vinyl	t-alkyl	4
3-Methyl-1-butanol	308	427	Methanol	i-alkyl	4

3-Methyl-1-butene	125	120330	Vinyl	Methyl & alkyl	3
3-Methyl-1-butene	130	120330	Vinyl	Methyl & alkyl	3
3-Methyl-1-butene	131	120330	Vinyl	Methyl & alkyl	3
3-Methyl-butane-2-one	231	6903	Methyl ketone	i-alkyl	3
4-Methyl-1-pentene	163	36184	Vinyl	i-alkyl	4
4-Methyl-1-pentene	161	36184	Vinyl	i-alkyl	4
4-Methyl-pentane-2-one	234	2651	Methyl ketone	i-alkyl	4
5-Hexen-2-one	265	869	Methyl ketone	1-alkenyl	4
2-Pentanone	253	4739	Methyl ketone	n-alkyl	3
Formic acid	156	5687	Carboxylic acid	n-alkyl	0
Butane	91	207987	Ethyl	n-alkyl	2
Butane	80	207987	Ethyl	n-alkyl	2
Butane	87	207987	Ethyl	n-alkyl	2
Cyclohexene	214	11918	Ethylene in cycle	1-alkenyl	4
Cyclohexene	212	11918	Ethylene in cycle	1-alkenyl	4
Cyclopentane	158	42333	Ethylene in cycle	n-alkyl	3
Cyclopentane	150	42333	Ethylene in cycle	n-alkyl	3
Cyclopentane	142	42333	Ethylene in cycle	n-alkyl	3
Cyclopentane	155	42333	Ethylene in cycle	n-alkyl	3
Acetic acid	98	2079	Carboxylic acid	n-alkyl	1
Ethanol	250	7928	Methanol	n-alkyl	1
Hexane	187	20266	Ethyl	n-alkyl	4
Hexane	203	20266	Ethyl	n-alkyl	4
Hexane	174	20266	Ethyl	n-alkyl	4
Hexane	180	20266	Ethyl	n-alkyl	4
Hexane	180	20266	Ethyl	n-alkyl	4
iso-Butane	74	315208	Ethyl	Methyl & alkyl	2
iso-Butane	74	315208	Ethyl	Methyl & alkyl	2
iso-Butane	73	315208	Ethyl	Methyl & alkyl	2
iso-Pentane	138	87035	Ethyl	i-alkyl	3
iso-Pentane	142	87035	Ethyl	i-alkyl	3
iso-Pentane	185	87035	Ethyl	i-alkyl	3
iso-Pentane	192	87035	Ethyl	i-alkyl	3
iso-Pentane	198	87035	Ethyl	i-alkyl	3
iso-Pentane	182	87035	Ethyl	i-alkyl	3
Methanol	45	16842	Methanol	n-alkyl	0
Methylcyclopentane	186	18332	Ethylene in cycle	i-alkyl	4
Methylcyclopentane	177	18332	Ethylene in cycle	i-alkyl	4
Pentane	166	68400	Ethyl	n-alkyl	3
Pentane	132	68400	Ethyl	n-alkyl	3
Pentane	140	68400	Ethyl	n-alkyl	3
Pentane	168	68400	Ethyl	n-alkyl	3
Pentane	171	68400	Ethyl	n-alkyl	3
Propane	27	953257	Ethyl	n-alkyl	1
Propane	27	953257	Ethyl	n-alkyl	1
Propanol	310	2753	Methanol	n-alkyl	2
Propionic acid	93	496	Carboxylic acid	n-alkyl	2

The GLM-analysis for the postulated model (1) leads to $R^2 = 0.844$, a coefficient of variation (C.V.) of 17.42 and a root mean square error of 31.46 for the total of 72 observations. The parameter estimates are given in Table IV. Figure 1 shows the measured breakthrough times versus their individual predictions for all experiments.

Table IV. Results of the GLM-Analysis

Regression model		$tb = x_0 + x_1 \cdot p_{\text{sat}} + x_2 \cdot \text{CinR} + x_{3i} \cdot R_{\text{typ}} + x_{4j} \cdot \text{Funct} + \varepsilon$ [min]			
x_0 [min]	69.55				
x_1 [min•Pa ⁻¹]	-87.4·10-6		x_2 [min]	29.14	
x_3 [min]	n-Alkyl	0	x_4 [min]	Ethyl	0
	1-Alkenyl	59.86		Ethylene in cycle	-10.50
	i-Alkyl	3.10		Vinyl	5.84
	t-Alkyl	-31.06		Methanol	129.27
	Methyl & alkyl	-7.925		Methyl ketone	67.86
				Carboxylic acid	17.22

Keeping in mind an uncertainty of up to 15% for experimental breakthrough times, the data is in fairly good agreement with only two exceptions, namely methanol and formic acid. According to our classification, these molecules have no carbon on the radical and contain only the functional group. Therefore, they must be considered in this context as atypical organic compounds. Figure 1 also shows that the predicted breakthrough times of the five experiments initially removed from the analysis and represented by squares, the validation data, lies well along the 45° line. This strongly supports the predictive power of the model.

It should be mentioned that other simple models have also been tested, but were not superior. Amongst others, adding the Dubinin-affinity coefficient β (Wood, 2001) to the present model leads to similar results but not to a fundamental improvement ($R^2 = 0.849$, C.V. = 17.26). A generalized inverse method had to be used in order to solve the system of equations and some estimates are biased. This makes any interpretation of the results for deductions of general physical and chemical rules very speculative.

Nevertheless, the increasing effect of the estimates for the carboxylic acid, the methyl ketone and methanol makes sense in that the polar interactions with the adsorbent, the strong sorption interaction contribution, increase within the series. The positive contribution of the alkenyl radicals could be related to π -electrons interactions with the carbon surface. The strong negative estimate for tertiary-alkyl radicals may correspond to steric effects. Finally, on the basis of the present analysis, the predicted breakthrough time increases by about 30 min per additional carbon atom in the radical chain.

CONCLUSIONS

By a suitable classification of molecular properties and the use of a statistical regression analysis, a simple model has been developed with a high prediction capability of filter sorption performance for organic compounds. In spite of the obvious advantages, some constraints and limitations should be

considered. Firstly, the data is limited to a given type of filter. Secondly, the regression parameters apply only for the experimental conditions of the present study. Finally, other functional groups, such as amines or halogenated compounds, have not yet been included in the analysis.

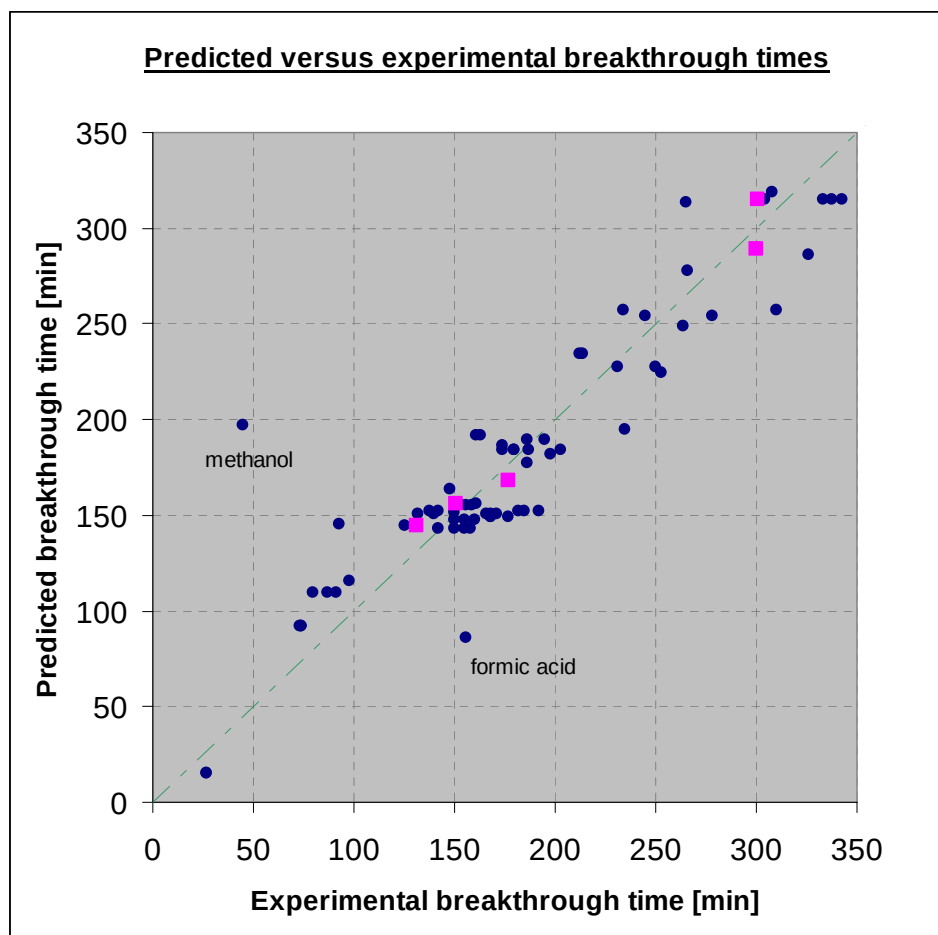


Figure 1. Predicted versus experimental breakthrough times. Circles represent fitted data and squares represent the predicted data of the five experiments not used for the analysis.

These limitations are not as restrictive as may appear at first. The respirator filter type used in this study is of a typical design. Therefore, with some experience, extrapolation to other, similar filter systems may be made without a great loss of accuracy. The limitation to given experimental conditions is inherent to the use of testing norms and generally accepted for filter evaluation. Lastly, the method shown here can easily be applied to different sets of experimental data, if available. It is planned to extend our experimental measurements to amines, which will lead to an additional functional group in the present regression model. A similar approach on a data set of over 570 experiments, including various filter types and testing conditions, is under investigation.

REFERENCES

- Arnold W and Lavanchy A. (1992) Schutz gegen industrielle Schadstoffe durch den ABC-Schutzfilter 74. *Chimia* 1992, 46, 79-83.
- CEN/TC 79. (2000) Respiratory protective devices - gas filters and combined filters - requirements, testing, marking. NE 141 (2000-02-00).
- Lavanchy A and Stoeckli F. (1997) Dynamic adsorption of vapour mixtures in active carbon beds described by Myers-Prausnitz and Dubinin theories. *Carbon* 1997, 35 (10-11), 1573-1579.
- Lavanchy A and Stoeckli F. (1999) Dynamic adsorption, in active carbon beds, of vapour mixtures corresponding to miscible and immiscible liquids. *Carbon* 1999, 37 (2), 315-321.
- Wood GO. (2000) Reviews of models for adsorption of single vapors, mixtures of vapors, and vapors at high humidities on activated carbons for applications including predicting service lives of organic vapor respirator cartridges. LA-UR-00-1531, Los Alamos National Laboratory.
- Wood GO. (2001) Affinity coefficients of the Polanyi-Dubinin adsorption isotherm equations. *Carbon* 2001; 39:343-356.
- Wu JF, Hammarstrom L-G, Claeson O, Fangmark IE. (2003) Modelling the influence of physico-chemical properties of volatile organic compounds on activated carbon. *Carbon* 2003; 41:1322-1325.