

PROTECTION PERFORMANCE OF THE SWISS ARMY NBC-CANISTER AGAINST INDUSTRIAL TOXIC AGENTS

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Abstract

NBC-canisters are combined particle and gas filters. The high efficiency particle filter element gives good protection against dusts and aerosols. However, the protection performance of the gas filter element, consisting of chemically impregnated, activated carbon, strongly depends on the type of the agent to be eliminated, as well as on the challenge conditions.

The protection performance of the Swiss army respirator canister has been measured against relevant industrial agents, incl. alcohols, ketones and carboxylic acids, totally more than 50 compounds. Specific properties of the test equipment used are briefly described.

The influence of molecular structure and physical properties of homologous series of alcohols, ketones and carboxylic acids on the adsorption capacity is shown and discussed. The observed sorption capacity against those organic compounds with boiling points above 65 °C correlates quite well to the limiting micropore volume as calculated by Dubinin's theory assuming physical adsorption.

Once more it is seen, that for chemicals with boiling points above 65 °C at challenge concentrations below 0.5 % by volume, a satisfactory protection level is achieved. For agents with low boiling points, especially in presence of water, the protection level may be poor and has to be specifically evaluated.

Introduction

In the last few years, more than 10'000 accidents with industrial chemicals, and emissions to the environment, have been reported in PCFACTS, a database for hazardous materials accidents from TNO Netherlands. In this context, protection performance data of respiratory protection filters against specific gases or vapors are asked. In Switzerland one is interested in protection data for the Swiss army NBC-canister because of the wide spread availability to the population as civil protection device.

These canisters are combined particle and gas filters, consisting of a glass fiber paper and a bed of chemically impregnated activated carbon. They are adequate to industrial respiratory protection filters of A2B2-P3 type according to the European standard EN 141.

The high efficiency particle filter element gives good protection against dusts and aerosols. The gas filter performance however strongly depends on the type and concentration of the chemicals to be eliminated, as well as on air climate and flow conditions. Thus, at least for agents with low boiling points, performance data specifically must be evaluated.

Experimental

The filter test apparatus is constructed mainly of glass, to avoid corrosion problems in the used highly humid test climate and to see condensation effects. A wide variety of gaseous or liquid test agents can be added to the test air stream and the system is equipped with appropriate analytical instruments for break-through detection. A sketch of the apparatus is given in figure 1. The compounds tested are listed in table 1.

For the results presented in this work, the following detection methods have been used:

- Process gas chromatography, 1 ccm gas sample loop, 1.8m x 0.53 mm HP-1 column, isothermal run, nitrogen carrier, flame ionization detector. This holds for alcohols and ketones and dichloromethane
- Continuous stripping of the sample air stream in water and titration to a constant pH of 9.5 with 0.01 molar NaOH. This was used for carboxylic acids.
- Commercial amperometric cell for sulfur dioxide.

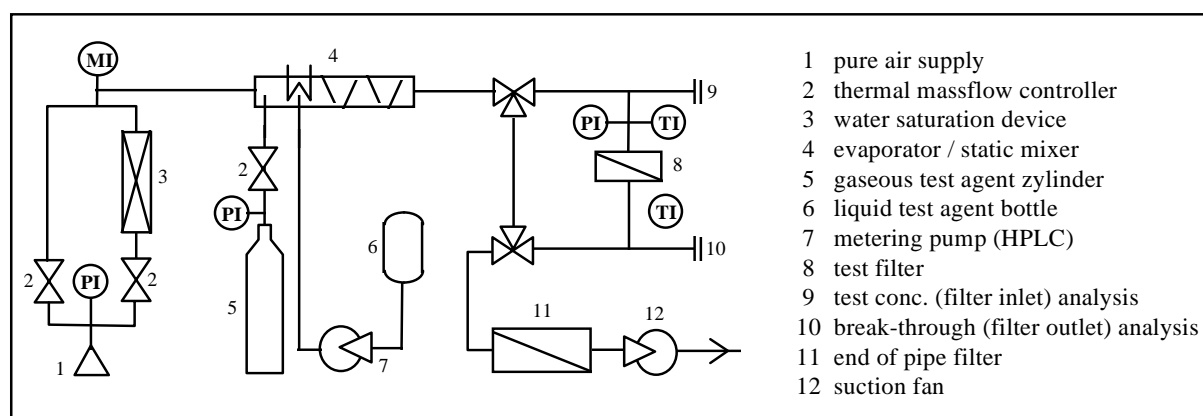


figure 1 : functional scheme of the test equipment for filter testing

table 1: alphabetic list of compounds tested

Acetaldehyde	Cyanogen chloride	Hydrogen chloride	Nitrogendioxide
Acetic acid	Cyclohexanone	Hydrogen cyanide	Pentane
Acetone	Dichloromethane	Hydrogen sulfide	2-Pentanol
Acrolein	1,1-Dichloroethene	Mercury	2-Pentanone
2-Aminobutane	Dichloromethane	Methanol	Phosgene
Ammonia	Diethylamine	3-Methyl-1-butanol	2-Propanol
1-Butanol	Diethylether	2-Methyl-1-propanol	1-Propanol
2-Butanol	Dimethoxymethane	3-Methyl-butane-2-one	Propionic acid
2-Butanone	Dimethylether	4-Methyl-pentane-2-one	Sulfur dioxide
3-Butene-2-ol	Ethanol	Methylacetate	Tetrachloromethane
1-Butene-3-one	Formic acid	Methylamine	trans-1,2-
Dichloroethene			
Chlorine	2-Hexanone	Methylformiate	2,2,2-Trifluoroethanol
Chloroform	5-Hexene-2-one	Methyliodide	Vinylchloride

Results

Main influence factors of challenge conditions

By the amount of adsorbent in the filter a limited maximum adsorption capacity is given. Thus the lifetime of the filter depends, in a first approximation, in a reciprocal way on the massflow of the compounds adsorbed. This massflow is given by the challenge concentration and the air flow rate. As an example see Methanol in table 2.

In presence of water, the remaining filter capacity for the challenge compound may be reduced by co-adsorption of water. This effect is especially strong for chemically inert compounds with a low boiling point, as illustrated for Dichloroethane in table 2.

For reactive compounds eliminated by chemisorption processes, water is not only a competitor in the adsorption step but also may be a reactant in the following chemical process. This may lead to a better filter performance under humid challenge conditions. A typical example is sulfur dioxide (table 2).

The observed adsorption capacity generally is reduced with an increased air flow rate for kinetic reasons

table 2: results under varying concentration, flow or humidity (test air temperature 20 °C)

compound	test air flow rate [m ³ /h]	test air humidity [%rH]	canister precondition	challenge concentr. [g/m ³]	breakthr. time [Minutes]	canister load [g]
Methanol	2	50	48 h in humid air	1.4	32	1.5
Methanol	2	50	48 h in humid air	3.5	19	2.3
Methanol	2	50	48 h in humid air	7.0	14	3.3
Methanol	2	50	48 h in humid air	14.0	9	4.3
Methanol	4	50	48 h in humid air	7.0	4	1.8
Dichloromethane	2	dry	48 h in dry air	7.6	77	9.7
Dichloromethane	2	dry	freshly opened	7.6	71	8.9
Dichloromethane	2	50	48 h in humid air	7.6	54	6.8
Dichloromethane	2	50	freshly opened	7.6	41	5.2
Dichloromethane	2	70	48 h in humid air	7.6	7	0.9
Dichloromethane	2	90	48 h in humid air	7.6	4	0.5
Sulfur dioxide	2	0	48 h in dry air	2.4	30	2.4
Sulfur dioxide	2	30	48 h in humid air	2.4	39	3.1
Sulfur dioxide	2	60	48 h in humid air	2.4	63	5.0
Sulfur dioxide	2	75	48 h in humid air	2.4	81	6.5
Sulfur dioxide	2	90	48 h in humid air	2.4	76	6.1

To enable a comparison of the filter performance against different vapours we used standard test conditions as given in European standard 141 for respiratory protection filters. That is: test air flow rate of 30 l/min, test air climate of 20°C and 70%rH, challenge concentration 1000 PPM for alcohols and ketones resp. 5000 PPM for carboxylic acids, breakthrough concentration 100 PPM, test filters freshly opened for the test.

The filter capacity, expressed as adsorbate volume, is used as yardstick for the comparison of the filter performance against different gases.

Comparison of homologous organic compounds

To study the relation of adsorption performance to molecular structure and functional groups we have started to measure homologous series of organic compounds. The objective is to find more detailed rules which may allow to predict the sorption performance even for compounds with critical sorption behaviour.

The results of homologous alcohols, ketones and carboxylic acids are summarized in table 3 and displayed in figures 2a through 2c.

table 3: adsorption data of some alcohols, ketones and carboxylic acids

Experiment (test conditions as given above)			Properties					Derived values			
compound name	test conc. [% vol.]	break through time [min]	mol. weight [g/mol]	liquid density [kg/m ³]	boiling point [°C]	saturat. vapour pressure [mbar]	Beta []	test conc. [g/m ³]	observed adsorbate volume on canister [cm ³]	relative vapour pressure $p_{\text{test}}/p_{\text{sat}}$	equilibrium adsorbate volume of canister [cm ³]
Methanol	0.1	45	32.0	791	65	128	0.48	1.22	2.1	0.007	7.3
Ethanol	0.1	250	46.1	789	79	77	0.70	1.75	16.6	0.012	24.9
1-Propanol	0.1	310	60.1	804	97	19	0.94	2.28	26.4	0.049	42.7
1-Butanol	0.1	326	74.1	810	117	7	1.18	2.81	34.0	0.133	48.8
2-Methyl-1-propanol	0.1	300	74.1	798	108	12	1.18	2.81	31.7	0.078	47.3
2-Butanol	0.1	266	74.1	808	100	17	1.16	2.81	27.8	0.055	45.9
3-Butene-2-ol	0.1	292	74.1	836	97		0.96	2.81	29.5		
3-Methyl-1-butanol	0.1	308	88.2	809	132	3	1.17	3.34	38.2	0.310	50.6
2-Pentanol	0.1	284	88.2	810	118	5	1.17	3.34	35.2	0.186	49.6
Propanone	0.1	148	58.1	790	56	233	0.78	2.20	12.4	0.004	20.8
2-Butanone	0.1	235	72.1	804	80	105	0.97	2.74	24.0	0.009	33.3
2-Pentanone	0.1	253	86.1	809	102	16	1.15	3.27	30.7	0.058	46.0
2-Hexanone	0.1	245	100.2	810	127	3.5	1.35	3.80	34.5	0.266	50.6
1-Butene-3-one	0.1	278	70.0	855	81	100	0.80	2.66	25.9	0.009	27.5
3-Methylbutane-2-one	0.1	231	86.1	804	95	56	1.13	3.27	28.2	0.017	40.5
5-Hexene-2-one	0.1	265	98.2	841	130		1.29	3.72	35.2		
4-Methylpentane-2-one	0.1	234	100.2	799	116	20	1.34	3.80	33.4	0.047	46.8
Cyclohexanone	0.1	287	98.2	948	156	4.5	1.22	3.72	33.8	0.207	49.9
Formic acid	0.5	156	46.0	1220	101	43	0.48	8.73	33.5	0.108	34.5
Acetic acid	0.5	98	60.1	1049	118	16	0.70	11.39	31.9	0.291	48.6
Propionic acid	0.5	93	74.1	993	141	5	0.94	14.06	39.5	0.930	51.5

Discussion

In addition to the expected correlation of the measured sorption capacity to the molecular weight, in the diagrams 2a through 2c the following effects can be seen:

- Carbon chain structure: the alcohols and ketones with linear carbon structure show a slightly better sorption capacity than those with branched.
- Position of functional group: the primary alcohols clearly show a superior sorption capacity in comparison to the secondary.
- Double bonds: the alcohol and the two ketones with a double bond show a slightly higher sorption capacity than their homologues with saturated carbon chain.
- Functional groups: distinct differences in the sorption capacity for compound classes are observed.

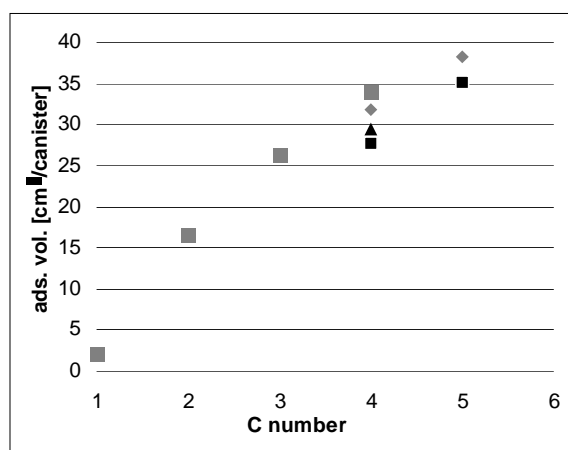


Figure 2 a : alcohols

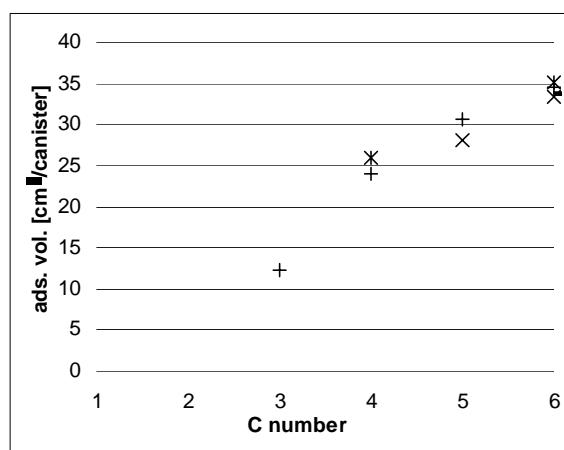


Figure 2 b : ketones

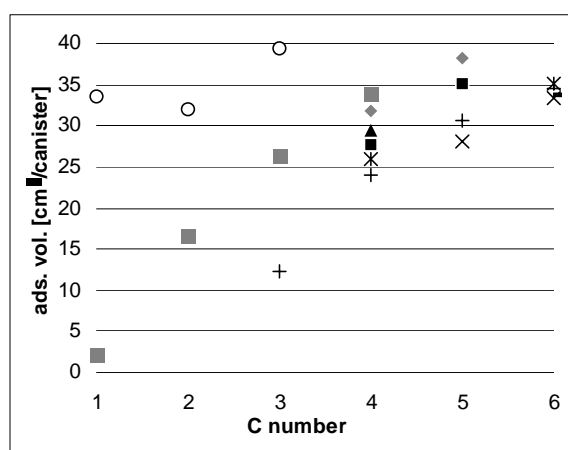
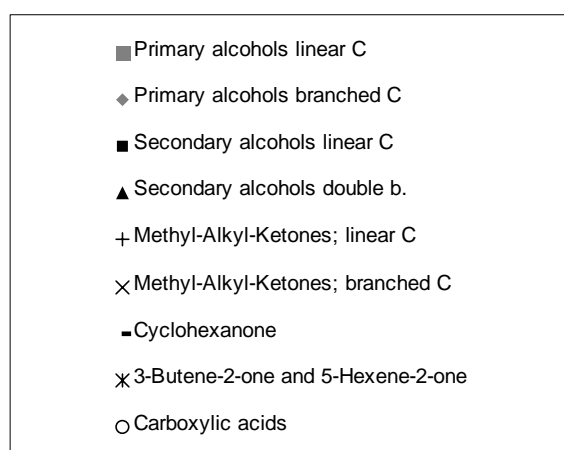


Fig. 2 c : alcohols, ketones and carbox. acids



Legend to figures 2a ... 2c, 3 and 4

For a more detailed data analysis, additional measurements will be needed. The relatively high sorption capacity against formic acid is assumed to be due to a chemical reaction on the impregnated carbon, as will be discussed later.

Correlation of the observed adsorption capacity to physical properties

The diagram of the measured filter capacity versus the boiling point in figure 3 shows a linear correlation over the majority of the measured compounds, regardless of their functional groups and structure, at least above a boiling point of 65 °C. This is not very surprising since physical adsorption seems to be predominant.

An even better correlation shows the experimental (dynamic) filter capacity to the equilibrium adsorbate volume of the filter as calculated by the Dubinin expression. This is shown in figure 4. Here, additionally to the ratio of the challenge concentration to the volatility (saturation conc.), physical properties of a given compound are taken into account by the affinity coefficient β . β is the ratio of the parachor of the particular compound to the parachor of Benzene. The parachor is derived from molecular weight, density and surface tension, or by the increment addition method from the molecular structure.

The slope of 0.7 of the linear regression in figure 4 means, that in average the observed dynamic capacity is 70 % of the equilibrium capacity. This confirms the rough empirical rule, that about 2/3 of the total canister capacity may be exploited under dynamic conditions.

The relatively high capacity observed for Formic acid may be due to additional chemical reaction on the impregnated active carbon, and possibly this also holds for 3-Butene-2-on.

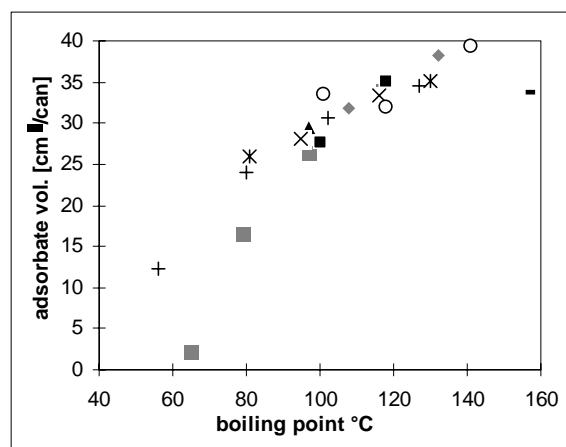


Fig. 3 : alcohols, ketones and carbox. acids

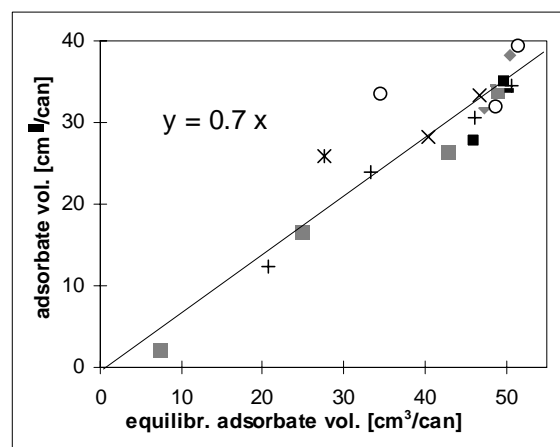


Fig. 4 : alcohols, ketones and carbox. acids

Conclusions

For compounds with boiling points above 65 °C, the adsorption performance can be predicted in a satisfactory manner by known physical adsorption theories.

That means, physical adsorption is predominant. Chemical aspects of functional groups may be neglected. Thus, the transfer of the findings on higher homologues with boiling points above 65 °C to compounds with lower boiling points is limited by the fact, that chemical effects can not be detected, which might be important for the lower homologues.

In general, for compounds with boiling points below 65 °C the physical adsorption performance is unfavorable because of lower physical adsorption power. In humid air this is worse due to the strongly reduced ability to displace adsorbed water.

In order to achieve a satisfying protection level against specific compounds with low boiling points, such as hydrogen cyanide (and other cyanogen compounds), phosgene and arsine, the active carbon in the Swiss NBC-canisters is impregnated with chromium-, copper- and silver-salts. The agents to be eliminated are chemically bound to the impregnates or chemically degraded to harmless compounds.

In opposition to the uniform physical adsorption process, chemisorption and catalysis are based on a diversity, respectively variety of rather specific complex processes, which, in general are not sufficiently known to allow an overall prediction of the protection performance. Thus, regarding the elimination of high volatile agents on impregnated carbons by chemisorption processes, specific experiments, considering the full range of the affecting parameters, are indispensable to get data for the filter performance under practical challenge conditions.