

STUDY OF A NEW TYPE OF ACTIVE CARBON CF-1 AS AN ADSORBENT IN GAS CHROMATOGRAPHY

Ladislav FELTL, Jana HRONKOVÁ and Eva SMOLKOVÁ

*Department of Analytical Chemistry,
Charles University, 128 40 Prague 2*

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Dedicated to Professor Dr V. Suk on the occasion of his 60th birthday,

A new type of active carbon, CF-1, was used as the stationary phase in gas chromatography. The adsorption of n-alkanes C_2-C_5 , 1-alkenes C_2-C_4 , acetylene, alcohols, ethyl ethers, CO_2 , H_2S and SO_2 was studied. The measurements were carried out with the original adsorbent and after its reduction with hydrogen at a temperature of $1\ 000^\circ C$. The original and pretreated active carbon were evaluated on the basis of the determined retention data and calculated value of the differential heats of adsorption.

Because of its porosity and consequent large specific surface area, active carbon has been used as a strongly adsorbing substance in various technological fields as well as in gas chromatography, where it is important primarily in the analysis of rare gases, permanent gases and volatile hydrocarbons. As one of the requirements on the column packing in gas chromatography is chemical and geometrical homogeneity of the adsorbent surface, carbonaceous adsorbents prepared by decomposition of a chemically defined substance are preferable to various types of active carbon prepared from natural materials. The high chemical and energetic inhomogeneity of the surface of the active carbon can be decreased by modification of this surface.

This work deals with the properties of wide-pore active carbon CF-1 and the possibility of application of this new active carbon adsorbent in gas chromatography.

EXPERIMENTAL

The adsorption was studied on wide-pore active carbon CF-1, 0.05–0.09 mm fractions with a specific surface of $\sim 120\ m^2\ g^{-1}$ (Polymer Institute, Slovak Academy of Sciences, Bratislava). The adsorbates were model saturated and unsaturated hydrocarbons, methanol, ethanol, diethyl ether, CO_2 , SO_2 and H_2S .

The properties of the original active carbon and carbon from which most of the surface oxides were removed by reduction with hydrogen at $1\ 000^\circ C$ were studied.

A suitable fraction of the adsorbent was packed in columns with an internal diameter of 1 mm and a length of 490 mm. The measurement was carried out on a Hewlett-Packard 5700 A gas chromatograph (USA) with a FID and on a Carlo Erba model C instrument (Italy) with a TCD. The samples were injected with 1 and 10 μl Hamilton syringes.

RESULTS AND DISCUSSION

The specific retention volumes were found at various temperatures and the $\log V_g$ vs $1/T_c$ dependences were plotted (Figs 1–4). The differential heats of adsorption ΔH were found from the slopes of these dependences and are given in Table I together with the heats of adsorption for other types of carbon given in the literature.

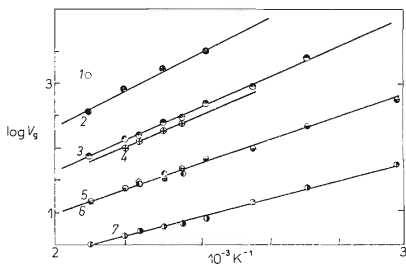


FIG. 1

Dependence of $\log V_g$ on T^{-1} for hydrocarbons on the original active carbon. 1 n-hexane, 2 n-pentane, 3 n-butane, 4 1-butane, 5 propane, 6 propene, 7 ethane

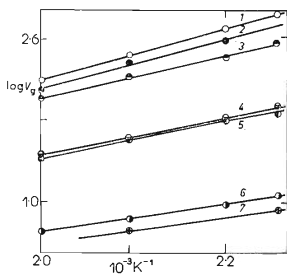


FIG. 2

Dependence of $\log V_g$ on T^{-1} for hydrocarbons of pretreated active carbon. 1 N-butane, 2 1-butene, 3 isobutane, 4 propane, 5 propene, 6 ethane, 7 ethylene

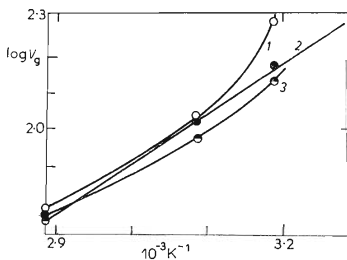


FIG. 3

Dependence of $\log V_g$ on T^{-1} for ethane 3, ethylene 2 and acetylene 1 on the original active carbon

The values of the specific retention volumes V_g and differential heats of adsorption ΔH of the hydrocarbons on the nonspecific carbon surface decrease on passing from the homologous series of n-alkanes to the 1-alkenes. This decrease is a result not only of the decrease in the number of hydrogen atoms in the molecule, but also because the double bond limits the mobility of the carbon chain. It is apparent from the data given in the table that this decrease is greater for the reduced form of the studied carbon than for the original sample, indicating that the surface of the original sample contains polar groups which can interact specifically with the double bond.

Comparison of the retention of ethane, ethylene and acetylene on the two studied samples of active carbon is interesting. The values of the specific retention volumes on the original active carbon increase in the order: ethane, ethylene, acetylene. A change occurs in the elution order on the reduced active carbon: acetylene is eluted first, followed by ethylene and ethane. Similarly, the differential heats of adsorption for the reduced sample increase in the order, acetylene, ethylene, ethane. This fact indicates that the reduction leads to removal of polar groups from the surface of the active carbon, resulting in considerable suppression of the specific interactions, which increased adsorption of molecules with multiple bonds.

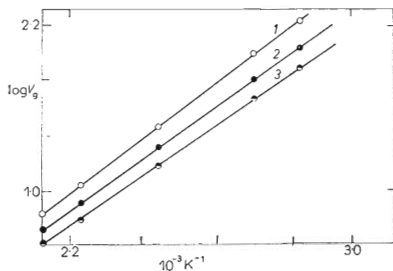


FIG. 4

Dependence of $\log V_g$ on T^{-1} for ethane 1, ethylene 2 and acetylene 3 on pretreated active carbon

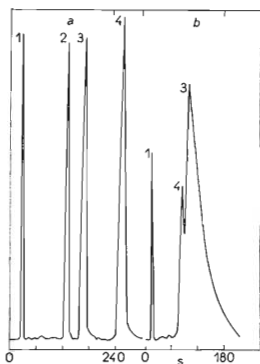


FIG. 5

Chromatograms of methane 1, acetylene 2, ethylene 3 and ethane 4 at 70°C on the original (b) and pretreated (a) active carbon

TABLE I
Heats of adsorption of hydrocarbons on active carbon

Hydrocarbon	ΔH measured, kJ mol^{-1}		ΔH published, kJ mol^{-1}						
	active carbon (ox) 70°–200°C	active carbon (red) 170°–220°C	Saran carbon	JADO carbon ^a 1 053	JADO carbon ^a 1 051 polar	CMS C ^b	CMS 4 ^c	czech. carbon 63 ^c	Barnebey carbon ^d
n-Pentane	63.09 ± 3.5	—	—	—	—	—	—	—	—
n-Butane	54.9 ± 3.2	57.36 ± 1.28	—	—	—	55	—	—	—
Isobutane	—	47.8 ± 1.4	—	—	—	—	—	—	—
1-Butene	52.3 ± 0.9	55.45 ± 2.25	—	—	—	—	—	—	—
Propane	42.06 ± 2.0	42.1 ± 0.95	39.8	45.0 ± 0.8	45.7 ± 0.8	45–46	50.7	45.5	49.5
Propene	42.06 ± 2.0	40.15 ± 0.95	—	44.9 ± 0.7	45.6 ± 0.8	—	40.6	36	44.5
Ethane	29.95 ± 4.4	29.88 ± 0.19	29.2	34.6 ± 1	33.2 ± 0.8	36	36.9	30.5	33.5
Ethylene	—	27.78 ± 0.19	—	33.1 ± 1.1	32.0 ± 1.5	—	26.4	22.6	32.2

^a Ref.^{2, b} ref.^{3, c} ref.^{4, d} ref.⁵.

In the interpretation of the measured values, it was important to determine the effect of changes in the specific surface area of the studied adsorbent. Consequently, the specific surface of the active carbon was determined by the thermal desorption method; the values determined were $120 \text{ m}^2 \text{ g}^{-1}$ for the original sample, which increased to $630 \text{ m}^2 \text{ g}^{-1}$ after reduction by hydrogen at $1\,000^\circ\text{C}$. The specific retention volumes V_S , related to a unit surface area of the adsorbent are given in Table II. If only a geometric change in the surface area were involved, the V_S values for the original and reduced active carbons would be approximately the same. The values given in Table II, however, indicate that the V_S value on the thermally treated carbon is always lower. The greatest differences were observed for specifically interacting unsaturated hydrocarbons, indicating that, in addition to an increase in the geometric surface area of the carbon, polar groups were also removed from the surface. The decrease in V_S observed also for nonspecifically interacting alkanes can be attributed to structural changes in the adsorbent (a change in the porosity).

Interesting results were obtained in study of the sorption of CO_2 , SO_2 and H_2S . While these gases were eluted from the column containing the original sample of active carbon within 3 min, after reduction the sulphur-containing compounds were irreversibly adsorbed in the temperature interval $40 - 120^\circ\text{C}$. Irreversible adsorption can be explained by uncovering and freeing of a large number of pores in which the ability to catalyze the reaction of hydrogen sulphide with sulphur dioxide can become important; the sulphur formed is deposited in the pores of the active carbon. It fol-

TABLE II

Specific retention volumes V_S of some hydrocarbons on the original (orig) and reduced (red) active carbon at various temperatures

Hydrocarbon	$V_S \cdot 10^3, \text{ ml m}^{-2}$					
	70°C		180°C		200°C	
	orig	red	orig	red	orig	red
Ethane	159	53	13.2	4.36	9.6	3.17
Ethylene	164	33.5	—	—	—	—
Acetylene	175	24.8	—	—	—	—
Propane	—	—	63.8	29.2	42.2	19.2
Propene	—	—	63.8	28.2	42.2	19.1
Butane	—	—	373	223	218	131
1-Butene	—	—	299	182	182	107

lows from the data measured that sulphur-containing gases are best separated on the original active carbon. The pretreated sample could be used for desulphuring gases in industrial practice.

All the results confirm that the sample pretreatment resulted in not only an increase in the geometric surface area of the active carbon, but also considerable removal of the active sites partaking in the specific interactions. It can be assumed that graphitization of the studied adsorbent at temperatures close to 3 000°C could yield an adsorbent with a high degree of homogeneity.

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