

CHROMSYMP. 290

## USE OF ZEOLITES ON STANDARD SOLID SUPPORTS IN GAS CHROMATOGRAPHY

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### SUMMARY

The adsorptive and separative properties of cation-modified zeolites of type X applied to the standard solid support Chromaton N AW were studied by gas chromatography and compared with volumetric sorbents. The separation coefficients of individual component pairs, with allowance for analysis time, uniformity criteria and rapid response coefficients of a mixture of C<sub>2</sub>-C<sub>4</sub> hydrocarbon gases, and the heats of adsorption of individual components were calculated for surface-layer sorbents and compared with the corresponding data for volumetric sorbents. The hydrocarbon gas mixture was found to be separated with better separation parameters and at a lower column temperature on surface-layer sorbents.

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### INTRODUCTION

In gas adsorption chromatography, the separation efficiency is defined by the selectivity of the adsorbent used and by the broadening of chromatographic zones. With a given selectivity of the sorbent and at high carrier gas flow-rates, the separation is defined by a mass exchange rate, as the sorption and desorption processes occur almost instantly. The time during which the sorbate molecules remain in the sorbent grains increases, while the mass exchange rate decreases proportionally to the square of the grain diameter<sup>1,2</sup>. Hence the efficiency of gas chromatographic separation increases with decrease in the sorbent grain diameter. However, this increase in separation efficiency is restricted by a strong resistance to the carrier gas flow. For this reason, in gas chromatography it is of interest to use an adsorbent that is an inert carrier, into the pores of which an active sorbent is introduced. An adsorbent of such a type makes it possible to increase the column efficiency without increasing the resistance to the carrier gas flow.

The possibility of using powdery graphitized carbon black introduced into the pores of silica gel in gas chromatography has been shown<sup>3</sup>, and molecular sieves applied on Chromosorb W have been used for air separation<sup>4</sup>. The same method has been used for the separation of aliphatic hydrocarbons C<sub>6</sub>-C<sub>13</sub> on graphitized carbon black applied to Chromosorb W<sup>5</sup>. Sorbents of such a type (surface-layer sorbents) have been considered and classified on the basis of the characteristics of the active porous layer<sup>6-9</sup>.

TABLE I

ADJUSTED RETENTION VOLUMES OF INDIVIDUAL SUBSTANCES ( $V_k$ )

Flow-rate of the carrier gas for specimens containing cations of alkali metals, 50 ml/min (column length 1 m), and for specimens containing cations of alkaline-earth metals, 100 ml/min (column length 0.5 m). s.l.s. = Surface layer sorbent; v.s. = volumetric sorbent.

Specimen	Column temperature 20°C				Column temperature 140°C				
	CO	CH <sub>4</sub>	C <sub>2</sub> H <sub>6</sub>	C <sub>2</sub> H <sub>6</sub>	C <sub>2</sub> H <sub>6</sub>	C <sub>2</sub> H <sub>4</sub>	C <sub>3</sub> H <sub>8</sub>	C <sub>3</sub> H <sub>6</sub>	C <sub>4</sub> H <sub>10</sub>
LiX s.l.s.	1.66	3.33	28.22	3.32	9.96	16.60	79.76	64.70	
LiX v.s.	7.47	15.80	102.56	21.62	58.10	70.55	400.91	360.22	
NaX s.l.s.	35.20	13.28	285.50	9.98	59.58	71.38	345.30	323.50	
NaX v.s.	128.65	50.63	924.62	44.86	142.60	217.46	1453.30	1133.81	
KX s.l.s.	8.67	15.31	269.20	9.17	16.67	47.50	99.17	175.83	
KX v.s.	24.03	45.97	886.67	49.17	119.43	356.67	951.67	1845.83	
CsX s.l.s.	3.33	5.83	131.67	8.33	14.20	53.30	106.50	304.21	
CsX v.s.	24.89	46.89	—	64.20	120.0	497.51	1144.20	3135.01	
MgX s.l.s.	1.58	0.83	4.17	0.83	1.66	4.98	13.28	19.99	
MgX v.s.	4.76	2.35	20.83	5.81	14.91	28.22	86.32	122.01	
CaX s.l.s.	6.67	1.67	16.68	0.85	13.22	14.94	99.60	62.25	
CaX v.s.	25.00	7.50	115.83	10.26	61.42	35.51	327.05	292.99	
SrX s.l.s.	11.60	2.96	42.50	2.49	15.77	19.42	102.92	88.81	
SrX v.s.	26.89	10.28	170.50	5.80	26.56	27.39	343.19	126.99	
BaX s.l.s.	6.84	2.57	64.17	0.83	4.98	6.64	32.87	40.67	
BaX v.s.	27.97	10.84	252.50	8.33	28.32	29.72	246.51	335.32	

Owing to the decrease in the diffusion paths inside the grain and the corresponding decrease in the diffusion time of the substance being chromatographed, in surface-layer sorbents the adsorptive and separative processes occur in the surface layer with a small depth equal to the thickness of the active sorbent layer.

Zeolites as surface-layer sorbents were used for the first time by Bombaugh<sup>4</sup>. In gas chromatography, zeolites are mainly used for the separation and determination of low-boiling gases and their separative ability depends on the type of a zeolite and its cation-exchange form.

Using gas chromatography, we have studied the adsorptive and separative properties of cation-modified zeolites of type X, containing cations of alkali and alkaline-earth metals and applied to the standard solid support Chromaton N AW.

## EXPERIMENTAL

The cation-modified forms of zeolites were prepared by a known method<sup>10</sup>. The chemical composition of the specimens studied was as follows:

- (1)  $0.96 \text{ Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 2.23 \text{ SiO}_2 \cdot 3.08 \text{ H}_2\text{O}$ ;
- (2)  $0.52 \text{ Li}_2\text{O} \cdot 0.37 \text{ Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 2.26 \text{ SiO}_2 \cdot 3.04 \text{ H}_2\text{O}$ ;
- (3)  $0.68 \text{ K}_2\text{O} \cdot 0.18 \text{ Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 2.28 \text{ SiO}_2 \cdot 2.80 \text{ H}_2\text{O}$ ;
- (4)  $0.50 \text{ Cs}_2\text{O} \cdot 0.42 \text{ Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 2.23 \text{ SiO}_2 \cdot 2.73 \text{ H}_2\text{O}$ ;
- (5)  $0.62 \text{ MgO} \cdot 0.38 \text{ Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 2.35 \text{ SiO}_2 \cdot 3.94 \text{ H}_2\text{O}$ ;
- (6)  $0.77 \text{ CaO} \cdot 0.19 \text{ Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 2.28 \text{ SiO}_2 \cdot 3.78 \text{ H}_2\text{O}$ ;
- (7)  $0.74 \text{ SrO} \cdot 0.22 \text{ Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 2.19 \text{ SiO}_2 \cdot 3.53 \text{ H}_2\text{O}$ ;
- (8)  $0.84 \text{ BaO} \cdot 0.14 \text{ Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 2.29 \text{ SiO}_2 \cdot 3.52 \text{ H}_2\text{O}$ .

The procedure for preparing surface-layer sorbents has been described earlier<sup>11</sup>.

The studies were carried out on an LKhM 8MD, Model 5, chromatograph with a  $1 \text{ m} \times 3 \text{ mm}$  I.D. column. The solid support was Chromaton N AW with grains of size 0.315–0.2 mm, retaining about 16% of the zeolite powder on its surface<sup>10</sup>. When the zeolite powder is shaken with the large-pore solid support, it enters the macropores of the support and is retained there by adhesive forces, which determine the strength of the surface layer of the sorbent. The flow-rate of the carrier gas (helium) was 50–100 ml/min. A catharometer was used as a detector. As the model mixture we used the mixture of  $\text{C}_1$ – $\text{C}_4$  hydrocarbon gases, carbon monoxide and also a mixture of  $\text{C}_5$ – $\text{C}_8$ . The studies were conducted under isothermal conditions. When comparing sorbents, columns of the same length and diameter were used.

## RESULTS AND DISCUSSION

The main gas chromatographic characteristics of surface-layer sorbents were studied and compared with those of volumetric sorbents. With surface-layer sorbents, the amount of active adsorbent per unit volume of the column is considerably less than that with the usual volumetric sorbents. Accordingly, the retention value for columns with surface-layer sorbents is less than that for columns with volumetric sorbents. The adjusted retention volumes of individual components on the specimens studied are given in Table I.

The components elute on surface-layer sorbents in the same order as on volu-

metric sorbents, whereas the temperatures of the inversion points for the ethylene-propane and butane-propylene pairs on the respective sorbents coincide, from which it follows that the main separation process proceeds not throughout the whole volume of the zeolite grains but when the extent of filling of the cavities is low.

On of the basic characteristics justifying the use of various sorbents in gas chromatography is their separative ability, which is quantitatively defined by the separation coefficient<sup>12</sup>. When we compare columns of the same length containing surface-layer and volumetric sorbents, it is difficult to compare the separations because for volumetric sorbents the separation coefficients will be higher, but the analysis time will be longer (Fig. 1). Table II gives the values of the characteristic  $K/t_R$  values, which are the ratios of the separation coefficients to the mean retention time of a component for two neighbouring peaks and which defines the separative ability of the column with the analysis time taken into account<sup>9</sup>. It can be seen that the separative ability with allowance for the analysis time is considerably higher for surface-layer sorbents than for volumetric sorbents.

With a volumetric filling of the column the separation of mixtures of heavier hydrocarbons ( $C_5-C_9$ ) on zeolites is difficult because of the strong adsorption of the components, whereas at high temperatures, because of catalytic transformations, a model mixture containing  $C_5-C_8$  hydrocarbons was separated on the surface-layer sorbents. The separation coefficients of individual component pairs on the specimens studied are given in Table III. The coefficients take into consideration the effect of the column efficiency and selectivity on the completeness of separation.

The quality and rate of separation of multi-component mixtures can be evaluated by means of the rapid response coefficient,  $\lambda$  ( $\text{sec}^{-1}$ )<sup>12</sup>. This coefficient is of the generalized type and is defined by the selectivity of the sorbent with respect to the

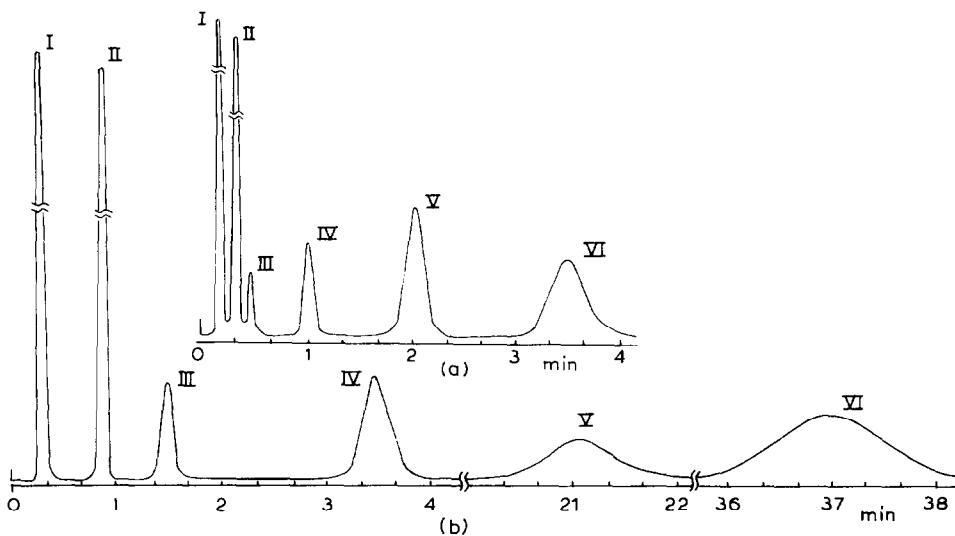


Fig. 1. Chromatogram of the separation of a mixture of  $C_1-C_4$  hydrocarbon gases on zeolite KX: (a) surface-layer sorbent; (b) volumetric sorbent. Column temperature,  $160^\circ\text{C}$ ; activation temperature,  $300^\circ\text{C}$ . Peaks: I = methane and carbon monoxide; II = ethane; III = ethylene; IV = propane; V = propylene; VI = butane.

TABLE II

COMPARISON OF SEPARATION COEFFICIENTS RELATIVE TO THE MEAN RETENTION TIME ( $K_1/t_R$ ) OF SEPARATE COMPONENT PAIRS

Column temperature: 140°C.

Specimen	$K_1/t_R$				
	$C_2H_6-C_2H_4$	$C_2H_4-C_3H_8$	$C_3H_8-C_3H_6$	$C_3H_6-C_4H_{10}$	$C_3H_8-C_4H_{10}$
LiX v.s.	0.0405	—	0.011	0.001	0.006
LiX s.l.s.	0.143	—	0.0675	0.008	0.011
NaX v.s.	0.092	0.01	0.021	0.002	0.008
NaX s.l.s.	0.122	0.0135	0.053	0.005	0.015
KX v.s.	0.040	0.029	0.012	0.004	0.060
KX s.l.s.	0.095	0.07	0.034	0.015	0.097
Cs v.s.	0.029	0.024	0.009	0.004	0.007
Cs s.l.s.	0.061	0.11	0.036	0.019	0.016
MgX v.s.	0.036	0.026	0.037	0.007	0.015
MgX s.l.s.	—	—	0.143	0.033	0.060
CaX v.s.	0.1	—	0.012	0.005	0.031
CaX s.l.s.	—	—	0.064	0.016	0.080
SrX v.s.	0.035	0.008	0.017	0.002	0.019
SrX s.l.s.	0.054	0.02	0.028	0.007	0.027
BaX v.s.	0.064	0.035	0.015	0.003	0.016
BaX s.l.s.	0.83	0.064	0.049	0.006	0.043

worst separable pair, by the sorption capacity and efficiency of the column and by the uniformity of distribution of peaks on the chromatogram. Rapid response coefficients and uniformity criteria for some specimens are compared in Table IV. The uniformity criterion ( $\bar{A}$ ), characterizing the distribution of peaks on the chromatogram, is analogous to the selectivity coefficient for the separation of a multi-component mixture<sup>12</sup>.

It can be seen from Table V that the hydrocarbon gas mixture separates with

TABLE III

SEPARATION COEFFICIENTS OF SEPARATE COMPONENT PAIRS ON SURFACE-LAYER SORBENTS

Column temperature: 250°C.

Binary mixture	$K_1$							
	LiX	NaX	KX	CsX	MgX	CaX	SrX	BaX
<i>n</i> -Pentane- <i>n</i> -hexane	1.45	1.93	2.40	2.59	0.94	1.10	1.78	1.70
<i>n</i> -Hexane- <i>n</i> -heptane	1.68	2.00	2.40	3.36	1.61	1.63	2.30	1.80
<i>n</i> -Heptane- <i>n</i> -octane	2.82	—	—	3.77	—	1.70	—	—
<i>n</i> -Pentane-2-pentene	0.59	1.73	1.14	1.78	—	—	—	3.31
<i>n</i> -Hexane-1-hexene	1.71	1.69	1.73	0.42	—	—	—	2.85
Cyclohexane-cyclohexene	0.93	2.90	2.58	1.13	—	—	—	—
Cyclohexane- <i>n</i> -hexane	0.96	0.64	1.33	1.61	—	—	—	—
Cyclohexane-benzene	1.88	2.40	2.86	—	—	—	—	—
2-Pentene-1-hexene	1.76	1.703	1.60	0.64	—	—	—	1.90

TABLE IV

COMPARISON OF UNIFORMITY CRITERIA ( $\bar{\lambda}$ ) AND RAPID ACTION COEFFICIENTS ( $\lambda$ ) FOR A MIXTURE OF GASES HYDROCARBON C<sub>2</sub>-C<sub>4</sub> ON SPECIMENS CONTAINING CATIONS OF ALKALINE-EARTH METALS

<i>Model mixture</i>	<i>Column temperature (°C)</i>	<i>Specimen</i>	$\bar{\lambda}$	$\lambda$ ( $\text{sec}^{-1}$ )
C <sub>2</sub> H <sub>6</sub> -C <sub>2</sub> H <sub>4</sub> -C <sub>3</sub> H <sub>8</sub> -C <sub>3</sub> H <sub>6</sub> -C <sub>4</sub> H <sub>10</sub>	200	MgX v.s.	0.087	0.861 · 10 <sup>-4</sup>
	100	MgX s.l.s.	0.093	0.936 · 10 <sup>-4</sup>
C <sub>2</sub> H <sub>6</sub> -C <sub>3</sub> H <sub>8</sub> -C <sub>2</sub> H <sub>4</sub> -C <sub>4</sub> H <sub>10</sub> -C <sub>3</sub> H <sub>6</sub>	200	CaX v.s.	0.039	0.708 · 10 <sup>-4</sup>
	100	CaX s.l.s.	0.042	0.752 · 10 <sup>-4</sup>
C <sub>2</sub> H <sub>6</sub> -C <sub>3</sub> H <sub>8</sub> -C <sub>2</sub> H <sub>4</sub> -C <sub>4</sub> H <sub>10</sub> -C <sub>3</sub> H <sub>6</sub>	200	SrX v.s.	0.027	0.011 · 10 <sup>-4</sup>
	100	SrX s.l.s.	0.0364	0.058 · 10 <sup>-4</sup>
C <sub>2</sub> H <sub>6</sub> -C <sub>2</sub> H <sub>4</sub> -C <sub>3</sub> H <sub>8</sub> -C <sub>3</sub> H <sub>6</sub> -C <sub>4</sub> H <sub>10</sub>	200	BaX v.s.	0.0309	0.196 · 10 <sup>-4</sup>
	100	BaX s.l.s.	0.0544	0.633 · 10 <sup>-4</sup>

better separation parameters and at a lower column temperature on surface-layer sorbents than with volumetric filling of the columns with zeolite.

The coefficients of asymmetry of individual components on the specimens containing cations of alkali metals are given in Table V. When using surface-layer sorbents, the chromatographic peaks are more symmetrical because the sorption and desorption processes occur only in a thin layer of an active sorbent. It is just the symmetry of peaks that points to adsorption equilibrium.

When using surface-layer sorbents there is no need to choose temperature intervals with more symmetrical peaks in order to calculate heats of adsorption, whereas there is such a need with volumetric sorbents. Heats of adsorption calculated by the chromatographic method correspond only to energies of interaction between the adsorbent and the adsorbate and do not contain an additional energy of interaction between molecules of the adsorbate. As shown in Table VI, the heats of adsorption calculated for individual components on both surface-layer and volumetric sorbents are in good agreement, which also proves that the separation process does not proceed throughout the whole volume of the zeolite grains but when the extent of filling of the cavities is low.

TABLE V

ASYMMETRY COEFFICIENTS OF SORBATES ( $K_a$ ) ON VARIOUS SPECIMENS

Column temperature: 140°C.

<i>Sorbent</i>	$K_a$							
	<i>LiX</i> <i>v.s.</i>	<i>LiX</i> <i>s.l.s.</i>	<i>NaX</i> <i>v.s.</i>	<i>NaX</i> <i>s.l.s.</i>	<i>KX</i> <i>v.s.</i>	<i>KX</i> <i>s.l.s.</i>	<i>CsX</i> <i>v.s.</i>	<i>CsX</i> <i>s.l.s.</i>
C <sub>2</sub> H <sub>6</sub>	1.20	1.01	1.09	1.01	1.02	1.00	1.17	1.07
C <sub>2</sub> H <sub>4</sub>	1.60	1.40	1.33	1.07	1.25	1.12	1.22	1.02
C <sub>3</sub> H <sub>8</sub>	1.33	1.25	1.25	1.05	1.37	1.25	1.54	1.12
C <sub>3</sub> H <sub>6</sub>	1.37	1.23	1.30	1.13	1.05	1.00	1.32	1.14
<i>n</i> -C <sub>4</sub> H <sub>10</sub>	1.25	1.12	1.25	1.12	1.58	1.22	1.16	1.11

TABLE VI  
HEAT OF ADSORPTION (Q) OF INDIVIDUAL SUBSTANCES DETERMINED BY GAS CHROMATOGRAPHY

Specimen	Q (kcal/mol)				ΔQ (kcal/mol)			
	CH <sub>4</sub>	C <sub>2</sub> H <sub>6</sub>	C <sub>2</sub> H <sub>4</sub>	C <sub>3</sub> H <sub>8</sub>	C <sub>3</sub> H <sub>6</sub>	C <sub>4</sub> H <sub>10</sub>	C <sub>2</sub> H <sub>4</sub> - C <sub>2</sub> H <sub>6</sub>	C <sub>3</sub> H <sub>6</sub> - C <sub>3</sub> H <sub>8</sub>
LiX, v.s.	4.4	5.26	9.52	7.30	10.85	9.35	4.26	3.55
LiX, s.l.s.	-	5.89	9.33	7.35	11.30	10.15	3.44	3.95
NaX, v.s.	4.53	6.47	10.36	7.67	11.46	10.20	3.89	3.79
NaX, s.l.s.	3.97	6.49	9.23	8.24	11.19	10.85	2.74	2.96
KX, v.s.	4.64	7.07	8.14	9.63	10.11	10.93	1.07	0.48
KX, s.l.s.	4.09	6.54	8.52	8.88	9.96	10.70	1.98	1.08
CsX, v.s.	4.96	7.32	7.52	9.73	9.85	10.96	0.2	0.12
CsX, s.l.s.	4.36	6.68	7.43	9.14	9.61	10.87	0.75	0.47
MgX, v.s.	3.56	5.73	8.92	6.63	8.85	8.73	3.19	2.22
MgX, s.l.s.	3.68	5.65	8.89	6.52	8.79	8.70	3.24	2.27
CaX, v.s.	4.28	5.82	10.24	6.76	10.27	8.02	4.42	3.52
CaX, s.l.s.	4.08	5.66	10.14	6.72	10.08	7.87	4.48	3.36
SrX, v.s.	5.25	6.84	11.12	8.92	11.57	10.23	4.28	2.65
SrX, s.l.s.	5.13	6.74	11.10	8.80	11.79	9.89	4.36	2.99
BaX, v.s.	4.80	6.81	10.16	9.78	10.48	10.05	3.35	0.69
BaX, s.l.s.	4.89	6.78	10.14	9.86	10.75	9.94	3.36	0.89

TABLE VII  
CONVENTIONAL CHROMATOGRAPHIC POLARITY OF SURFACE-LAYER SORBENTS

Form of zeolite	Adjusted retention volume		$\log \left( \frac{V'_{R1}}{V'_{R2}} \right)$	Adjusted retention volume		$\text{Log} \left( \frac{V'_{R1}}{V'_{R2}} \right)$
	$C_2H_4$	$C_2H_6$		$C_3H_6$	$C_3H_8$	
LiX	9.69	3.32	0.477	79.76	16.0	0.682
KX	16.67	9.17	0.259	99.17	47.50	0.324
NaX	59.58	9.98	0.776	345.3	17.38	0.684
CsX	14.20	8.33	0.232	106.5	53.3	0.301
MgX	1.66	0.83	0.301	13.28	4.98	0.425
CaX	13.22	0.85	1.19	99.60	14.94	0.825
SrX	15.77	2.49	0.802	102.92	19.92	0.713
BaX	4.98	0.83	0.778	32.87	6.64	0.694

On the basis of the studied chromatographic properties of various cation-exchange forms of zeolite of type X applied to Chromaton N AW, an attempt was made to classify adsorbents by their relative chromatographic polarities as suggested by Rohrschneider<sup>13</sup> for liquid stationary phases used in gas-liquid chromatography. As a characteristic of polarity we took the logarithm of the ratio of the retained volumes of two substances with different electron molecular structures on the studied forms of zeolite of type X. For the surface-layer sorbents studied the values of  $\log (V'_{R1}/V'_{R2})$  for the ethylene-ethane and propylene-propane pairs are given in Table VII. The relative chromatographic polarities decrease in the order  $CaX > SrX > BaX > NaX > LiX > MgX > KX > CsX$ .

A knowledge of the relative chromatographic polarities of sorbents allows one to choose the appropriate cation-exchange form of a zeolite for the separation of various mixtures depending on the nature of their components, and also to evaluate to some extent the character of the intermolecular interactions in the chromatographic column.

In conclusion, the use of surface-layer sorbents makes it possible to shorten the analysis time, to lower the column temperature, to increase the number of substances that can be analysed on zeolites and to eliminate the broadening of chromatographic zones.

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