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Note

On the possibility of increasing the effectiveness of chromatographic columns filled with zeolites

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At present synthetic zeolites are used particularly in the U.S.S.R. for the separation of different complex gas mixtures¹. In most papers^{1–3} devoted to the application of zeolites in gas chromatography (GC), different methods of filling the columns with volumetric sorbents are considered. In certain cases this leads to an increase in the time of analysis, to asymmetric peaks and the necessity of comparatively high oven temperatures.

The use of modified zeolites described as surface-layer sorbents avoids the above disadvantages^{4,5}. Surface-layer sorbents comprise an adsorbent (active agent) coated with a thin layer, similar to the liquid phase on the inert solid carrier in gas-liquid chromatography (GLC), and are not mixtures of the adsorbent and solid carrier. Therefore, the nature of the solid carrier at which the active agent is retained by adhesion forces defines the amount of the adsorbent coated. Chromosorb W retains at its surface about 32% of zeolite powder, while Chromaton N retains only 17%. The thin layer of the active agent thus plays an important rôle in the processes of chromatographic separation in this case.

It was established, on the other hand, that the use of "active" carrier gases such as carbon dioxide also increases the effectiveness of chromatographic columns⁶.

The present note describes the results of an investigation of the combined effects of carbon dioxide as carrier gas and variation of the surface-layer filling on the separation of a C₁–C₄ hydrocarbon gas mixture.

EXPERIMENTAL

Investigations were carried out on a LKhM 8MD chromatograph, with a column of 0.5 m × 3 mm I.D. Zeolite NaY granules, 0.5–1.0 mm, prepared without binding, and zeolite dust, 0.25–0.30 mm, coated on the solid carrier Chromosorb W, were used⁶. The amount of zeolite coated on the solid carrier was about 30% of the latter's weight. The sorbents were activated by heating at 400°C for 4 h. The working

temperature of the column was varied over the range 20–200°C, under isothermal conditions. A thermal conductivity detector was employed. Apart from carbon dioxide, nitrogen and helium were used as the carrier gas, for comparison. The gas velocity was 50 ml/min throughout the experiments. To estimate the effect of the above two factors, *i.e.*, the carrier gas nature and the character of the adsorbent, on the process of separation of the hydrocarbon gas mixture, the retention times of the hydrocarbons, t_R , asymmetry coefficients, \bar{v} , of individual peaks and the number of theoretical plates per m of the chromatographic column were determined.

RESULTS AND DISCUSSION

Table I shows the retention times of individual hydrocarbons. There is a decrease in retention time for all hydrocarbons upon changing from a volumetric to a surface-layer column packing, independent of the nature of the carrier gas. In addition, the nature of the carrier gas itself considerably affects the magnitude of the retention times, which decrease in the order: helium, nitrogen, carbon dioxide. A similar dependence is exhibited by the asymmetry coefficients of the peaks of certain hydrocarbons (Table II). The most symmetrical peaks are obtained with carbon dioxide as carrier gas and a surface-layer column packing.

Calculation of the number of theoretical plates per m of the column also showed, that the most effective column is that filled with zeolite, coated on the solid carrier and with carbon dioxide as carrier gas (Table III).

Hence, the use of surface-layer sorbents in gas chromatography with carbon dioxide as carrier gas allows a considerable decrease in the analysis time for hydrocarbon gas mixtures with appearance of symmetrical peaks at lower column tempera-

TABLE I

EFFECT OF THE NATURE OF THE CARRIER GAS ON THE RETENTION TIMES OF C₁–C₄ HYDROCARBON GASES ON ZEOLITE NaY

Column temperature (°K)	Components of hydrocarbon gas mixture	Retention time, t_R (sec)					
		Helium		Nitrogen		Carbon dioxide	
		Vol.	Surf. layer	Vol.	Surf. layer	Vol.	Surf. layer
293	CH ₄	17	5	36	5	9	5
	C ₂ H ₆	115	10	108	10	50	8
	C ₃ H ₈	848	48	—	47	353	20
	C ₄ H ₁₀	—	329	—	—	4228	93
	C ₂ H ₄	1308	70	—	80	208	14
	C ₃ H ₆	—	—	—	—	2248	85
373	CH ₄	12	5	10	4	7	4
	C ₂ H ₆	46	7	41	7	25	5
	C ₃ H ₈	241	15	210	14	102	11
	C ₄ H ₁₀	1350	65	1005	62	555	40
	C ₂ H ₄	225	14	181	10	71	9
	C ₃ H ₆	2008	73	1315	68	450	36

TABLE II

ASYMMETRY COEFFICIENTS, \bar{v} , OF PEAKS OF HYDROCARBON GASES ON ZEOLITE ADSORBENT NaY AT 333°K

Components of hydrocarbon gas mixture	Asymmetry coefficients, \bar{v}					
	Helium		Nitrogen		Carbon dioxide	
	Vol.	Surf. layer	Vol.	Surf. layer	Vol.	Surf. layer
CH ₄	0.67	0.77	0.70	0.80	0.85	0.92
C ₂ H ₆	0.61	0.67	0.61	0.67	0.84	0.90
C ₃ H ₈	0.36	0.60	0.50	0.60	0.75	0.80
C ₄ H ₁₀	—	0.55	—	0.45	0.64	0.70
C ₂ H ₄	0.23	0.33	0.26	0.40	0.80	0.82
C ₃ H ₆	—	0.31	—	—	0.54	0.60

TABLE III

DEPENDENCE OF THE NUMBER OF THEORETICAL PLATES ON THE NATURE OF THE CARRIER GAS AND THE COLUMN PACKING WITH ZEOLITE NaY AT 373°K

Components of hydrocarbon gas mixture	Number of theoretical plates, <i>N</i>					
	Helium		Nitrogen		Carbon dioxide	
	Vol.	Surf. layer	Vol.	Surf. layer	Vol.	Surf. layer
CH ₄	180	433	176	442	990	1020
C ₂ H ₆	444	461	469	521	690	735
C ₃ H ₈	208	474	365	532	372	800
C ₄ H ₁₀	385	565	272	625	676	877
C ₂ H ₄	238	465	444	559	452	833
C ₃ H ₆	308	595	166	662	380	952

tures than in the case of the use of carrier gases such as helium or nitrogen and volumetric sorbents.

Obviously, this is caused by the fact that carbon dioxide plays a rôle not only as the carrier gas, but also as a displacer; in addition, on the surface-layer sorbents the sorption and adsorption processes occur only in the thin layer of the active sorbent. As a result, an increase in the effectiveness of the chromatographic column is obtained.

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