

Note

Gas chromatographic analysis of light hydrocarbons using aluminium oxide micro-packed columns

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Micro-packed columns filled with various adsorbents have been used successfully to separate different compounds. To increase the efficiency, packing materials with particle size up to $100\ \mu\text{m}^{1-6}$ (and even up to $175\ \mu\text{m}^7$) have been used, namely silica gel¹⁻³, aluminium oxide⁴, graphitized carbon black^{5,6}, molecular sieves⁷ and Porapak⁷. Stainless-steel⁴⁻⁷ and glass³ columns with diameters not larger than 1 mm were used.

Previously we proposed the use of fused-silica capillary micro-packed columns containing activated coal⁸, silica gel^{9,10}, molecular sieves¹⁰ and Porapak⁸, characterized by enhanced efficiency, convenience and possible utilization in solving a wide range of chromatographic problems. Fused-silica capillary micro-packed columns were used by Al-Thamir¹¹ (Chromosorb 102) to analyse natural gases and by Schindler and Wasserfallen¹² (Carbopak modified with Carbowax) to analyse polar compounds.

It was considered of interest to separate mixtures containing saturated and unsaturated C₁–C₆ hydrocarbons with fused-silica capillary columns packed with aluminium oxide.

EXPERIMENTAL

Fused-silica capillaries (length 40–200 cm, I.D. 0.32 and 0.55 mm) with polymeric coatings, both laboratory-made¹³ and produced by Quartz et Silice (Nemours, France), and stainless-steel capillaries (50 cm × 1 mm I.D.) were used. The sorbents were coated on the columns by gas permeable partition using a binding material¹⁴. Aluminium oxide particles with diameters from 40–50 to 100–160 μm were used.

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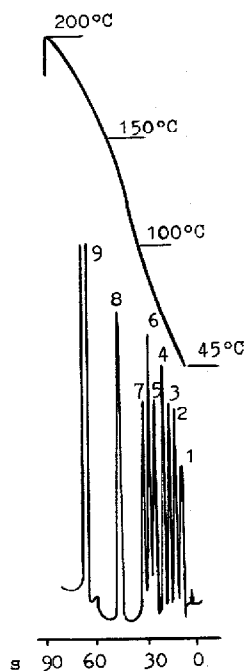


Fig. 1. Separation of C_1 - C_6 hydrocarbons. Stainless-steel column, 50 cm \times 1 mm I.D.; sorbent, aluminium oxide (63-100 μm); column temperature, programmed from 45 to 200°C; carrier gas, hydrogen; inlet pressure, 5 atm. Peaks: 1 = methane; 2 = ethane; 3 = ethylene; 4 = propane; 5 = propylene; 6 = isobutane; 7 = *n*-butane; 8 = *n*-pentane; 9 = *n*-hexane.

An LKhM-8MD gas chromatograph (Khromatograf, Moscow, U.S.S.R.) with a flame ionization detector was used. A stream splitter was used with the fused-silica columns. The carrier gas was nitrogen and the column temperature was 41-55°C.

Mixtures containing C_1 - C_4 and C_1 - C_6 were analysed.

TABLE I

CHARACTERISTICS OF CAPILLARY COLUMNS PACKED WITH ALUMINIUM OXIDE

Sorbate: isopentane.

Column material	Column I.D., d_c (mm)	Al_2O_3 particle diameter, d_p (μm)	Minimum HETP, H_{min} (mm)	Coefficients in Van Deemter equation	
				A (mm)	C (s)
Stainless steel	1	100-160	0.58	—	0.009
	1	63-100	0.27	0.25	0.0011
Fused silica	0.32	89-90	0.46	0.28	0.0009
	0.32	63-90	0.37	0.18	0.00045
	0.32	50-63	0.22	—	—
	0.32	40-50	0.19	—	—
	0.55	40-50	0.24	—	—

RESULTS AND DISCUSSION

A mixture containing nine C_1 – C_6 hydrocarbons was completely separated with a stainless-steel column using temperature programming (Fig. 1). The analysis time was about 1 min; 40 s was sufficient to separate seven C_1 – C_4 hydrocarbons.

Addition of isomeric butenes to the initial mixture led to incomplete peak separation at isothermal conditions. To increase the efficiency of separation it is expedient to use both smaller particles and smaller column diameters.

Data on the efficiency of the columns are given in Table I. The efficiency parameters of the fused-silica columns are higher than those of the stainless-steel column, owing to the smaller particle size and column diameter in the former. The lowest minimum height equivalent to a theoretical plate, H_{\min} , is 0.19 mm for a column of I.D. (d_c) 0.32 mm packed with aluminium oxide particles of diameter (d_p) 40–50 μm . The increase in efficiency is first due to a decrease in the mass-transfer coefficient, C (coefficient in the Van Deemter equation). Higher carrier gas linear flow-rates (and, accordingly, a higher column inlet pressure) can be applied without any serious decrease in efficiency. Eddy diffusion, A , also decreases; note that A is equal to 2–3.5 particle diameters. The efficiency behaviour with both increase in carrier gas flow-rate and sample size was studied. Fig. 2 shows the dependence of \sqrt{H} on sorbate mass, m , at the optimum carrier gas linear flow-rate, u_{opt} , and doubled carrier gas volume flow-rate, u . In both instances the dependence fits well the equation

$$\sqrt{H} = \sqrt{H_0} + \lambda m$$

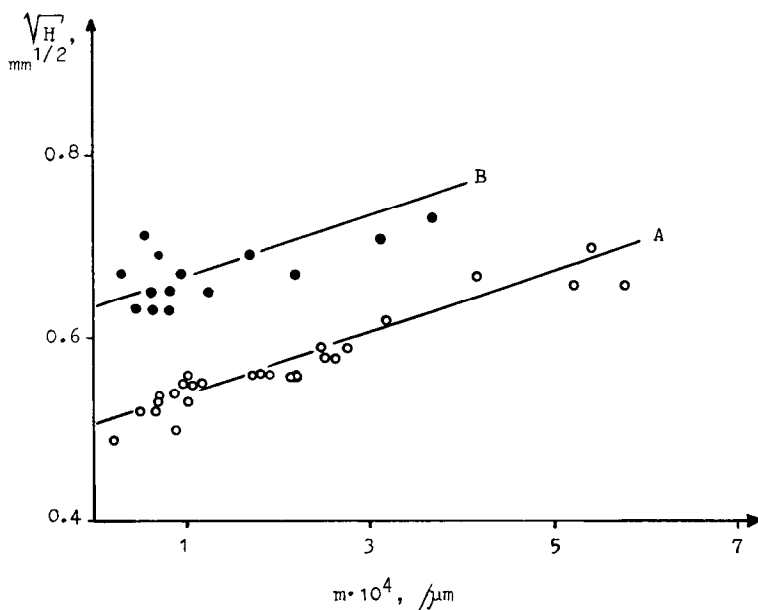


Fig. 2. Relationship between the sample (pentane) size, m , and efficiency characteristic, \sqrt{H} . Column, fused silica (73 cm \times 0.32 mm I.D.); sorbent, aluminium oxide (63–90 μm); sample, n -pentane– n -hexane (1:9, w/w); column temperature, 77°C. (A) $u_{\text{opt}} = 5.1$ cm/s; (B) $u = 11.8$ cm/s.

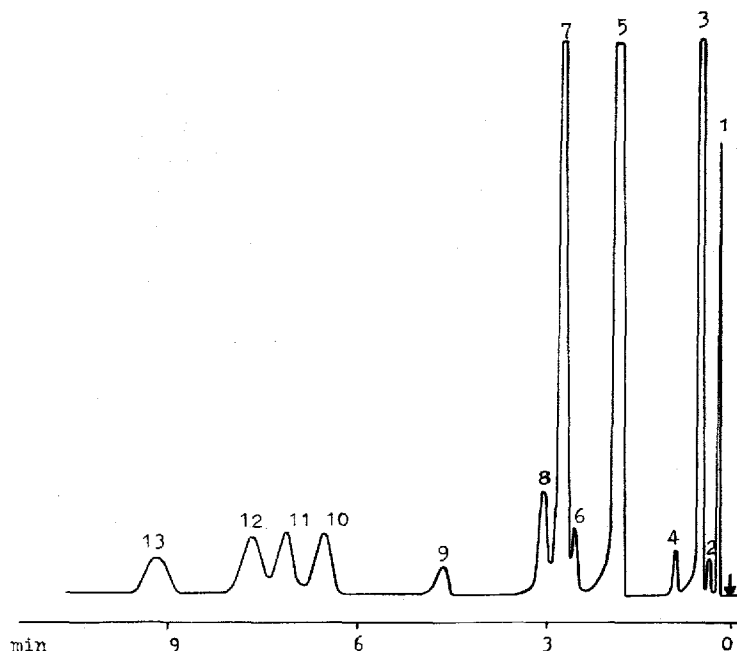


Fig. 3. Separation of saturated and unsaturated C_1 - C_4 hydrocarbons. Column, fused silica (115 cm \times 0.32 mm I.D.); sorbent, aluminium oxide (40-50 μ m); column temperature, 45°C; inlet pressure, 1.0 MPa. Peaks: 1 = methane; 2 = ethane; 3 = ethylene; 4 = propane; 5 = propylene; 6 = isobutane; 7 = cyclobutane; 8 = *n*-butane; 9 = cyclobutene; 10 = 1-butene; 11 = *trans*-2-butene; 12 = isobutene; 13 = *cis*-2-butene.

where H_0 is the H value when $m = 0$ and λ is a proportionality factor¹⁵. H_0 increases with the increase in carrier gas flow-rate, but λ hardly changes.

To separate mixtures of saturated and unsaturated C_1 - C_4 hydrocarbons containing cyclobutene and all the isomeric butenes, a fused-silica capillary column with small inner diameter packed with small particles was used (Fig. 3). The specific efficiency was not less than 5200 effective theoretical plates. The inlet pressure was about 1.0 MPa but when carbon dioxide was used instead of nitrogen a lower inlet pressure was sufficient.

In conclusion, a satisfactory separation of 10-13 components was achieved in about 7 min.

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