CHROMSYMP. 078

ALUMINIUM OXIDE-COATED FUSED-SILICA POROUS-LAYER OPEN-TUBULAR COLUMN FOR GAS–SOLID CHROMATOGRAPHY OF C_1–C_{10} HYDROCARBONS

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SUMMARY

An aluminium oxide-coated fused-silica porous-layer open-tubular column for gas–solid chromatography of C_1–C_{10} hydrocarbons is described. The column is highly efficient and can be operated with nitrogen, helium or hydrogen as carrier gases at temperatures up to 200°C. Humidification of the carrier gas is superfluous. The C_k term in the Van Deemter–Golay equation was estimated and shown to be of the same order of magnitude as the C_g term. The reproducibility of the retention times in both isothermal and temperature-programmed analyses proved to be excellent. The preparation of the column is described in detail and some applications are shown.

INTRODUCTION

Aluminium oxide as the stationary phase in gas–solid chromatography (GSC) was succesfully applied in open-tubular columns as early as 1963 by Kirkland[1]. Relatively short columns 25 ft. long and of I.D. 0.25–0.50 mm allowed the separation of fluorinated hydrocarbons at room temperature. These columns were dynamically coated with a colloidal boehmite suspension.

In the same year, Petitjean and Leftault[2] reported the modification of the inside surface of aluminium tubes of I.D. *ca.* 0.5 mm. A layer of active alumina about 5 μm thick was formed on the inside wall of the column tubing. Schneider *et al.*[3] published a method for the preparation of glass capillary columns dynamically coated with a thixotropic suspension of aluminium oxide in water, leaving a homogeneous layer of aluminium oxide on the inner column wall.

In 1981 we described the preparation of an aluminium oxide-coated fused-silica porous-layer open-tubular (PLOT) column[4]. The columns were coated statically with a stabilized suspension of aluminium oxide. Without additional deactivation, the activity of the aluminium oxide surface causes peak tailing. Deactivation with water[5], potassium chloride[6] or a thin film of a high-boiling liquid[2] has been described.

PREPARATION ON THE COLUMN

The column was prepared according to Schneider et al.[3] with slight modifications. Aluminium hydroxide (Martinal, 95% < 2 μm; COMAG, Amsterdam, The Netherlands) was heated for 24 h at 300°C. Of the aluminium oxide thus obtained, 20 g were added to 70 ml of a 5% (w/v) Dispural solution (Condea Chemie, Hamburg, F.R.G.) in 1% (v/v) acetic acid and the mixture was stirred for 10 min in an ultrasonic bath. After filtering the suspension through a 300-mesh wire sieve, the suspension was allowed to age for 24 h. The suspension obtained showed thixotropic behaviour. A 50 m × 0.32 mm I.D. fused-silica column (Chrompack, Middelburg, The Netherlands) was connected to a 25 m × 0.32 mm I.D. fused-silica buffer capillary column with shrinkable PTFE. A plug of 10 m of 1% (v/v) acetic acid was forced through the column.

Subsequently, a 400 ($\pm$ 1%) μl plug of coating suspension was introduced into the capillary by means of a syringe, and the column inlet was connected to a precision needle valve. The pre-pressure at the needle valve was kept at 50 bar and the flow-rate set at 4 ml/min. The first plug coated about 50% of the capillary. The column was disconnected from the needle .valve, another 400 μl of coating suspension were introduced and the coating procedure was repeated. The second plug of coating suspension coated the fused-silica capillary completely with a homogeneous layer. The buffer column was disconnected and the column was stored for 16 h in a vibration-free location.

The column was then dried in a constant-temperature water-bath by applying a nitrogen pressure of 2 bar. The drying process took about 3 days at 25°C and was followed visually. When it was dry, the column was activated for 3 h heating to 300°C at 10°C/min under 1.0 bar of nitrogen, and subsequently rinsed twice with a 2% (w/v) solution of potassium chloride, forced through the capillary under a nitrogen pressure of 2 bar. The column was dried under a nitrogen pressure of 5 bar for 24 h. Finally, the column was activated at 300°C for 60 min under a carrier gas flow. Columns thus prepared contained 3–4 mg of aluminium oxide per metre.

EVALUATION

Calculation of C_g and C_k

Theory. Giddings[7] investigated in detail the theory of gas adsorption chromatography and the modifications necessary for the Van Deemter–Golay equation expressing column performance. As there is no liquid phase present, the C_l term was replaced with a mass transfer term for the kinetics of adsorption and desorption, C_k.The plate-height equation for open-tubular adsorption columns is

$$\text{HETP} = \left[\frac{B}{u_0} + C_g u_0 \right] f_1 + C_k u_0 f_2 \tag{1}$$

with

$$f_1 = \frac{9(p^4 - 1)(p^2 - 1)}{8(p^3 - 1)^2}$$

and

$$f_2 = \frac{3(p^2 - 1)}{2(p^3 - 1)}$$

HETP   = height equivalent to a theoretical plate;
$B = 2D_g$ = longitudal gaseous diffusion term;
D_g = gaseous diffusion coefficient;
u_0 = linear gas velocity at column outlet;
C_g = term of resistance to mass transfer in the gas phase;
C_k = term of resistance to mass transfer for adsorption and desorption kinetics.

f_1 and f_2 correct for the effect of the pressure gradient on column efficiency. $p =$ ratio of inlet to outlet pressure (p_i/p_0). If $x = u_0/D_g$, eqn. 1 becomes

$$\frac{H}{f_1} = H_g(x) + \frac{C_k x f_2 D_g}{f_1} \tag{2}$$

where H is HETP and $H_g(x)$ is a function of x.

D_g is calculated according to Fuller et al.[8]. For two different types of carrier gas, H/f_1 can be plotted as a function of x. Also, $f_2 D_g/f_1$ can be plotted as a function of x. C_k can be calculated according to the equation

$$C_k = \frac{\left(\dfrac{H}{f_1}\right)_A - \left(\dfrac{H}{f_2}\right)_B}{x\left[\left(\dfrac{f_2 D_g}{f_1}\right)_A - \left(\dfrac{f_2 D_g}{f_1}\right)_B\right]} \tag{3}$$

where A = carrier gas A and B = carrier gas B. C_g can also be calculated according to eqn. 1.

Results. C_g and C_k values were calculated for 1,3-butadiene at 130°C with helium and nitrogen as the carrier gas. With D_g (C_4H_6, He) = 0.579 cm²/sec and D_g (C_4H_6, N_2) = 0.178 cm²/sec, H/f_1 and $f_2 D_g/f_1$ can be plotted against $x = u_0/D_g$. For the values x = 200, 250, 300, 350 and 400 cm⁻¹ C_k was calculated from eqn. 3 to be $1.8 \cdot 10^{-4}$ sec.

C_g was calculated from eqn. 1 to be $4.6 \cdot 10^{-4}$ sec for nitrogen and $1.3 \cdot 10^{-4}$ sec for helium.

It can be concluded that C_k and C_g are of the same order of magnitude.

Choice of carrier gas

Hydrogen. Ettre[9] reported the hydrogenation of unsaturated hydrocarbons on aluminium oxide-coated columns with hydrogen as the carrier gas and oven temperatures above 100°C.

Two unsaturated hydrocarbons, propyne and 1,3-butadiene, were analysed on

TABLE I

PEAK AREA (A) OF PROPYNE RELATIVE TO THAT OF PROPANE AT 200°C

Column: 50 m × 0.32 mm I.D. Al_2O_3-coated fused-silica PLOT. Carrier gas: hydrogen.

P_i (atm)	Reaction time (min)	$\dfrac{A_{propyne}}{A_{propane}}$	Relative standard deviation (%)	n
0.25	1.301	0.22	2.2	4
0.50	2.625	0.21	2.7	4
1.0	5.393	0.21	3.9	4
2.0	9.719	0.22	10.1	5

a 50 m × 0.32 mm I.D. aluminium oxide-coated fused-silica PLOT column at 200°C, the maximum isothermal operating temperature of the column with hydrogen as the carrier gas. At column inlet pressures of 0.25–2.0 bar, a gas mixture containing these two unsaturated hydrocarbons and the saturated hydrocarbon propane was analysed. The peak areas of propyne and 1,3-butadiene were related to propane (see Tables I and II).

The reaction times (retention times) were varied between approximately 1 and 10 min without a significant change in the relative peak areas of propyne and 1,3-butadiene. It can be concluded that no hydrogenation of unsaturated hydrocarbons occurs at 200°C. For this reason, hydrogen is well suited for the rapid analysis of light hydrocarbons (see also *Applications*).

Helium and nitrogen. H versus $\bar{u}$ curves for 1,3-butadiene with helium or nitrogen are shown in Fig. 1. The optima of the H vs. $\bar{u}$ curves for helium (44 cm/sec) and nitrogen (24 cm/sec) are due to the relatively high D_g values for 1,3-butadiene at 130°C.

Reproducibility of retention behaviour

Water strongly influences the retention behaviour of alumina[4]. It is obvious that an absolutely water-free carrier gas is a necessity if high reproducibility of retention times is required. A molecular sieve containing moisture filter was placed in

TABLE II

PEAK AREA (A) OF 1,3-BUTADIENE RELATIVE TO THAT OF PROPANE

Conditions as in Table I.

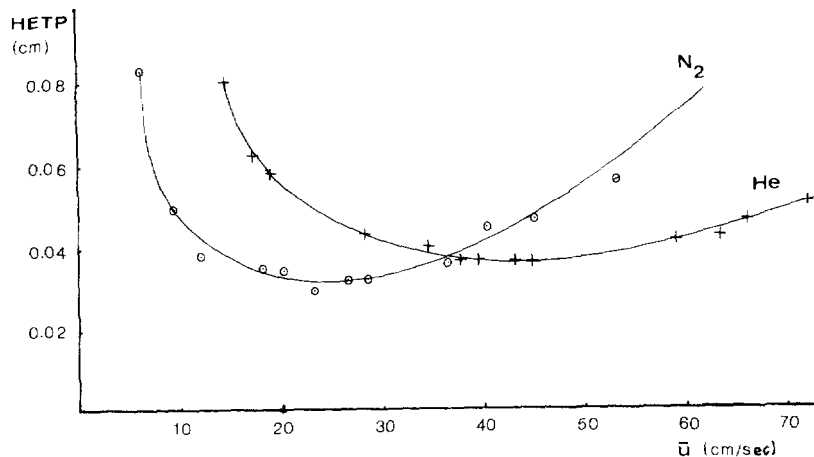| P_i (atm)	Reaction time (min)	$\dfrac{A_{1,3\text{-}butadiene}}{A_{propane}}$	Relative standard deviation (%)	n
0.25	1.350	0.94	2.5	4
0.50	2.722	0.91	5.1	4
1.0	5.591	0.91	2.7	4
2.0	10.079	0.92	2.0	5

Fig. 1. *H versus ū* curves for helium and nitrogen. Capillary column: 50 m × 0.32 mm I.D. Al$_2$O$_3$-coated fused-silica, temperature: 130°C. Test compound: 1,3-butadiene.

TABLE III

RETENTION CHARACTERISTICS OF TEN SUCCESSIVE ISOTHERMAL ANALYSES AT 130°C

Column: see text. Carrier gas: 1.0 bar nitrogen.

Hydrocarbon	Mean retention time (sec)	Standard deviation (sec)	Retention index	Standard deviation
Propane	251.1	0.2	300.00	—
Propene	277.7	0.2	345.63	0.02
Propadiene	312.4	0.6	381.97	0.03
Propyne	528.2	0.5	481.31	0.04

TABLE IV

RETENTION CHARACTERISTICS OF TEN SUCCESSIVE TEMPERATURE-PROGRAMMED ANALYSES FROM 70°C TO 200°C (RATE 7.5°C/min)

Column: see text. Carrier gas: 1.0 bar nitrogen.

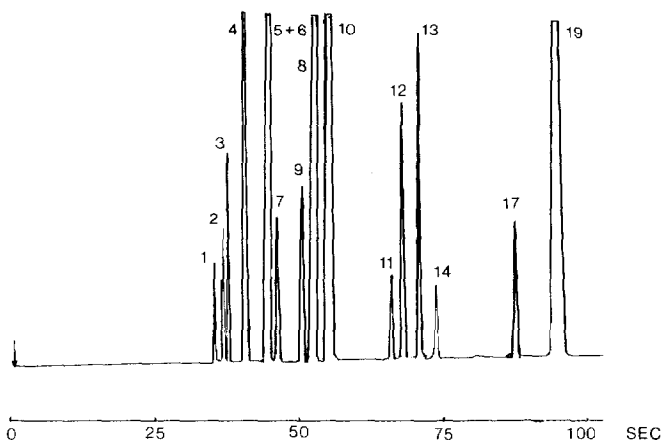| Hydrocarbon	Mean retention time (sec)	Standard deviation (sec)	Retention index	Standard deviation
Propane	286.7	0.3	300.00	—
Propene	363.3	0.3	342.79	0.02
Propadiene	439.2	0.3	385.15	0.02
Propyne	705.1	0.4	—	—

Fig. 2. Analysis of C_1-C_4 hydrocarbons within 100 sec. Column: 50 m × 0.32 mm I.D. Al_2O_3-coated fused-silica. Temperature: 130°C. Carrier gas: 3 bar hydrogen. Split injection. Detection: $8 \cdot 10^{-12}$ A f.s. For peak identification see Fig. 3.

the carrier gas line. A mixture of propane, propene, propadiene and propyne was analysed on a 50 m × 0.32 mm I.D. aluminium oxide-coated fused-silica PLOT column. Retention times and retention indices were measured for ten consecutive isothermal analyses at 130°C and ten temperature-programmed analyses from 70°C to 200°C at 7.5°C/min.

For isothermal analyses the maximum standard deviation of the retention time was 0.6 sec (relative standard deviation, 0.2%) for propane, and the maximum standard deviation in the retention index was 0.04 index unit for propyne. For temper-
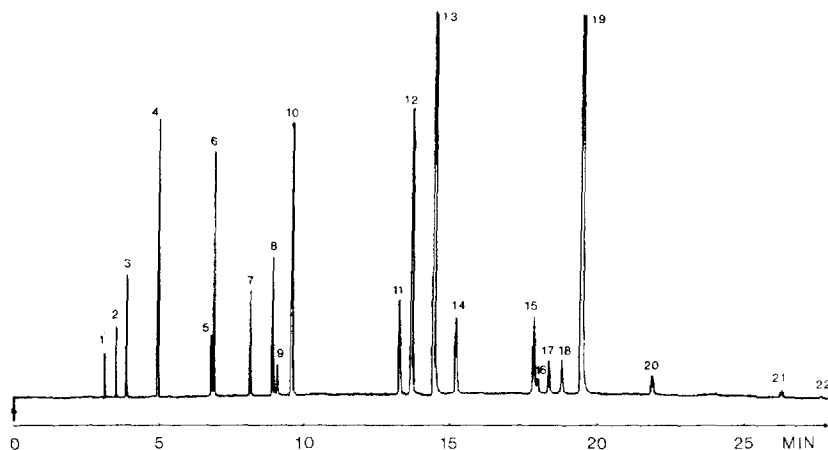

Fig. 3. Separation of C_1-C_5 hydrocarbons. Column: 50 m × 0.32 mm I.D. Al_2O_3-coated fused-silica. Temperature programmed from 70 to 200°C at 3°C/min. Carrier gas: 1.0 bar nitrogen. Split injection. Detection: flame-ionization detector, $4 \cdot 10^{-12}$ A f.s. Peaks: 1 = methane; 2 = ethane; 3 = ethene; 4 = propane; 5 = cyclopropane; 6 = propene; 7 = ethyne; 8 = isobutane; 9 = propadiene; 10 = n-butane; 11 = trans-2-butene; 12 = 1-butene; 13 = isobutene; 14 = cis-2-butene; 15 = isopentane; 16 = 1,2-butadiene; 17 = propyne; 18 = n-pentane; 19 = 1,3-butadiene; 20 = 3-methyl-1-butene; 21 = vinylacetylene; 22 = ethylacetylene.
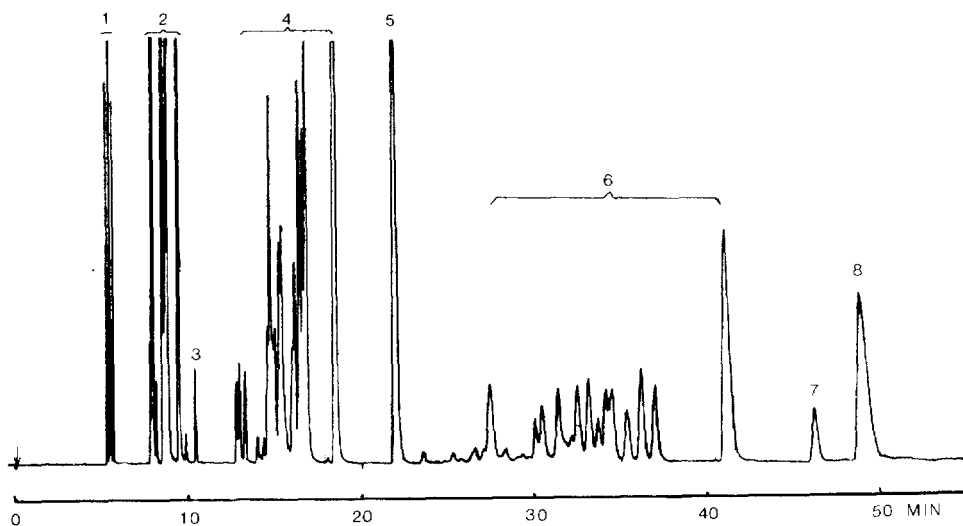
Fig. 4. Analysis of benzene and toluene in naphtha. Column: 50 m × 0.32 mm I.D. Al$_2$O$_3$-coated fused-silica. Temperature: 190°C. Carrier gas: 1.5 bar helium. Split injection. Detection: flame-ionization detector, 4 · 10^{-12} A f.s. Peaks: 1,2,4,6-aliphatic hydrocarbons (hexane, heptanes, octanes and nonanes, respectively); 3 = benzene; 5 = toluene; 7 = ethylbenzene; 8 = m- + p-xylene.

ature-programmed analyses the reproducibility was even better (see Tables III and IV).

Applications

The column described is a powerful tool for the rapid separation of light hydrocarbons. Fig. 2 shows the isothermal analysis of a C$_1$–C$_4$ hydrocarbon mixture with hydrogen as the carrier gas within 100 sec. If greater resolution is required, a
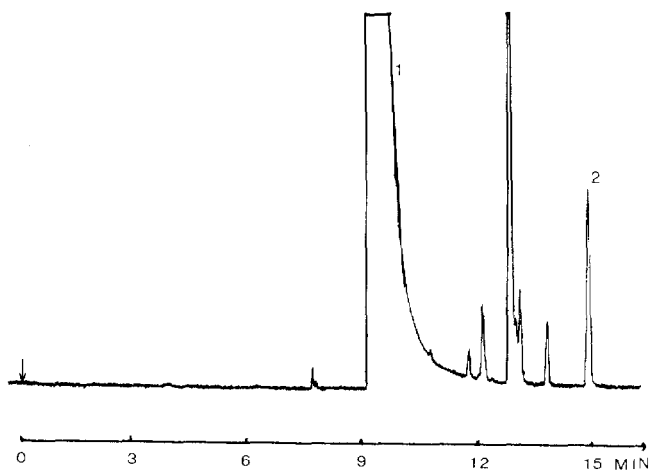

Fig. 5. Analysis of 100 ppm of benzene in cyclohexane. Column: 50 m × 0.32 mm I.D. Al$_2$O$_3$-coated fused-silica. Temperature: 200°C. Carrier gas: 1.0 bar nitrogen. Split injection. Detection: flame-ionization detector, 2 · 10^{-12} A f.s. Peaks: 1 = cyclohexane; 2 = benzene.

temperature programme is used, for example from 70 to 200°C, as shown in Fig. 3, which illustrates the separation of 22 C_1–C_5 hydrocarbons.

The elution pattern may be varied by adjusting the temperature programme. Even the analysis of heavier components, such as aromatics and aliphatic hydrocarbons up to C_9, is feasible. Fig. 4 shows the isothermal analysis of naphtha at 190°C. An interesting detail is the noninterference with the benzene and toluene peaks. Another specific application is the determination of low levels of benzene in cyclohexane. Fig. 5 shows the isothermal analysis of 100 ppm of benzene in cyclohexane at 200°C. Benzene concentrations as low as 10 ppm can be determined by split injection. For quantitation of lower concentrations (0.1–10 ppm) on-column or splitless injection is used.

REFERENCES

1 J. J. Kirkland, *Anal. Chem.*, 35 (1963) 1295–1297.
2 D. L. Petitjean and C. J. Leftault, *J. Gas Chromatogr.*, 1 (1963) 18–21.
3 W. Schneider, J. C. Frohne, H. Bruderreck, *J. Chromatogr.*, 155 (1978) 311–327.
4 R. de Nijs, *J. High Resolut. Chromatogr. Chromatogr. Commun.*, 4 (1981) 612–615.
5 H. Bruderreck, *Erdöl Kohle*, 16 (1963) 847–850.
6 C. G. Scott and C. S. G. Phillips, in A. Goldup (Editor), *Gas Chromatography 1964*, Institute of Petroleum, London, 1965, p. 266.
7 J. C. Giddings, *Anal. Chem.*, 36 (1964) 1170–1175.
8 E. N. Fuller, P. D. Schettler and J. C. Giddings, *Ind. Eng. Chem.*, 58 (1966) 19–27.
9 L. S. Ettre, *Open Tubular Columns in Gas Chromatography*, Plenum Press, New York, 1965, pp. 108–109.