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CONTRIBUTION TO THE STUDY OF MICROPACKED COLUMNS IN GAS CHROMATOGRAPHY

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SUMMARY

Several chromatographic columns made from glass tubes of I.D. 0.5–1 mm and with solid support particle sizes of 100–120 and 120–140 mesh were evaluated. The effect of liquid film thickness, column diameter, permeability and particle diameter to column diameter ratio on column efficiency is discussed. The pressure drop at the optimum gas velocity per unit column length and per theoretical plate is considered. A column is discussed with 6250 theoretical plates per metre, and others, less efficient per unit length, with a total of about 60 000 theoretical plates which can be run at about 7 kg/cm^2 if nitrogen is used.

INTRODUCTION

One of the major advances in the separation of substances after the onset of gas chromatography was the development in 1958 of capillary columns[1], which had such high separation powers that they seemed likely to bring to an end the use of traditional packed columns. Halász and Heine, however, warned in 1967[2] that the best results would be obtained with the type of column most suited to a particular problem. Nowadays chromatographers have various posibilities to choose from, with the following columns in order of increasing gas flow resistance: thin-layer capillary columns (1958); thick-layer capillary columns (1979); porous-layer capillary columns (1963); packed capillary columns (1963); packed columns of small diameter (1963); and conventional packed columns (1952).

Increasing resistance to the gas flow implies a parallel increase in the head gas pressure per unit length necessary to obtain the optimum flow-rate, and therefore the practical maximum length of a column diminished in the same order as above, with a concomitant decrease in the number of theoretical plates that can be obtained in the column. On the other hand, the load capacity of the different column types increases in the same order. Packed capillary columns and packed columns of small

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diameter represent the borderline between two ways in which the gas flows along the column in contact with the stationary phase: laminar flow parallel to the tube axis, with a considerable resistance to mass transfer in the gas phase (open-tubular columns), or passing through small multiple channels that facilitate the gas-phase mass transfer (classical packed columns). Packed capillary columns[2,3] and small-diameter packed columns[2,4,5] offer intermediate properties between the two flow regimes. The important difference between the two is not the diameter of the column, but rather the ratio of particle diameter to column inner diameter (d_p/d_c), which makes the chromatographic behaviour of the two types different. Packed capillary columns, with a d_p/d_c ratio between 0.2 and 0.5, have a loose packing, whereas small-diameter packed columns are tightly packed, with values of d_p/d_c of the order of 0.1 or lower[2]. Cramers and Rijks[6] proposed the name micropacked columns for packed columns of I.D. below 1 mm and d_p/d_c below 0.3.

Attempts to improve the efficiency of small-diameter packed columns have followed two different approaches: either using large particle diameters so that the special characteristics of the flow pattern found in packed capillary columns could be obtained or approximated[7–9], or seeking a flow pattern similar to that found in conventional packed columns[10,11] by using smaller particle diameters. The efficiencies obtained with the first procedure are lower, with reported values of the mean height equivalent to a theoretical plate ($\bar{H}$) varying from 0.26 to 0.6 mm. Packing the column with small-diameter particles produce values of $\bar{H}$ of the order of 0.1 mm. Jonker *et al.*[12] seem to have achieved the lowest value of $\bar{H}$ recorded with a value of 0.02 mm for tubes of 1.2 mm I.D. diameter and particles of 0.01 mm diameter, normally used in high-performance liquid-chromatography. This type of column needs a head pressure of about 200 atm/m, which imposes a limit on the length of the column. Following the same idea, Berezkin *et al.*[13] obtained a value of $\bar{H}$ of 0.09 mm for a head pressure of the order of 25 atm/m. Obviously, with this specific pressure drop columns cannot be very long.

THEORETICAL

The factors that affect the separation efficiency in packed column technology have been extensively studied by Giddings[14]. Optimization of resolution should be partially based on a consideration of the equation describing the height equivalent to a theoretical plate (H):

$$H = \frac{2vD_g}{u} + \frac{(1-R)2v_lD_l}{Ru} + \frac{w\,d_p^2}{D_g}\cdot u + \frac{q(1-R)d_l^2}{D_l}\cdot u + \frac{1}{\dfrac{1}{2\lambda d_p} + \dfrac{D_g}{wd_p^2\,u}} \qquad (1)$$

where v is the obstruction factor for the mobile phase, D_g and D_l are the solute diffusion coefficients in the gas and liquid phases, respectively, u is the linear gas velocity, R is the ratio between the velocities of the solute band and the gas in the column, v_l is the obstruction factor for the liquid phase, d_p is the particle diameter, d_l is the liquid phase film thickness, λ is a constant depending on the packing geometry, w is a parameter related to the gas velocity distribution inside the column

and q is the gas flow per unit area of column cross-section, proportional to pressure drop per unit length.

This equation is sometimes written as

$$H = \frac{B_g + B_l}{u} + (C_g + C_l)u + \frac{1}{\frac{1}{A} + \frac{1}{C_g u}} \quad (2)$$

In order to improve the packed column performance, the mass transfer terms (C_g and C_l) must be decreased. Therefore, attention should be paid to all parameters affecting them: uniformity of the packing may decrease the C_g term by a factor as high as ten[14]. A decrease in the particle diameter would increase the column efficiency but severe practical difficulties such as impossible pressure drops or even difficulties in packing the column with very small particles will place a limit on the improvements that can be obtained in this way.

On the other hand, considering the problem from a different point of view, Halász and Heine[2] decided that under certain circumstances it may be more practical to have a loose packing of the column with fewer theoretical plates per metre but with a much lower pressure drop per unit length, thus allowing the construction of much longer columns with more theoretical plates and the possibility of higher gas velocities, which would make analyses much faster. This is the goal with packed capillary columns. Therefore, there is another property of chromatographic columns that must be considered, *viz.*, permeability, the facility with which a column allows the gas to pass through it. This can be calculated using the Kozeny–Carman expression for spherical particles

$$K = \frac{d_p^2 \, \varepsilon^3}{180(1-\varepsilon)^2} \quad (3)$$

According to this expression, permeability is independent of the column inner diameter as long as the particle diameter (d_p) and the porosity (ε) (the fraction of the cross-sectional area occupied by the gas) remain constant. The equation is valid for small values of d_p/d_c. Therefore, in order to prepare efficient packed columns, attention should be paid to factors that affect efficiency, such as support characteristics, inner diameter of the tube and uniformity and thickness of the liquid film, in addition to those which modify the permeability.

EXPERIMENTAL

Solid support

Volaspher A-2[15], 100–120 and 120–140 mesh (125–150 and 100–125 μm) was used throughout. Polar liquids were used on a non-silanized support, prepared by treating silanized Volaspher A-2 with concentrated hydrochloric acid at 70°C for 1 h followed by washing. Fine particles were eliminated in all instances by floatation in ethanol, and the powder was dryed for 1 h under a stream of nitrogen.

Preparation of the packing

The stationary phase was dissolved and mixed with the solid in a round-bottomed flask that had indentations to facilitate homogenization of the mixture while the flask turned. The operation was carried out at room temperature under vacuum. In this way air was eliminated from the solid[16] and the resultant liquid film was more uniform.

Filling the columns

All columns were made of glass tubing that was drawn and coiled while empty. The packing was introduced under pressure while ultrasonic vibration was applied. Short columns were filled at a constant pressure of about 8 kg/cm^2. Long columns were filled at low pressures for the first few turns, increasing the pressure gradually until about 8 kg/cm^2 at the end. In all instances the column was placed with the turns parallel to the table-top[6]. Columns were conditioned in the normal way.

The gas chromatograph

Experiments were carried out in a Hewlett-Packard 5830A apparatus. Split injection was employed and a make-up gas was added before gases leaving the column reached the flame-ionization detector.

RESULTS

Effect of liquid film thickness on column efficiency

The number of theoretical plates per metre depends on the liquid loading, as may be observed in Fig. 1, where two stationary phases of different polarity are shown. Column efficiency was measured on peaks corresponding to *n*-alkanes with a capacity factor of approximately 3. The highest efficiency was obtained with a liquid loading of *ca.* 4% in both instances, which corresponds to an average film thickness of about 0.04 μm. For higher loadings, the efficiency decreased quickly. Lower column efficiencies were found with polar liquid stationary phases, as may be

Fig. 1. Dependence of specific efficiency on liquid loading. d_c = 1.0 mm; L = 2 m; d_p = 0.113 mm; carrier gas, N_2. ○, non-polar phase (SE-30); □, polar phase (Carbowax 20M).

TABLE I

SPECIFIC EFFICIENCY OF SIMILAR COLUMNS WITH DIFFERENT STATIONARY PHASES

Common characteristics: d_p = 0.113 mm; d_c = 1.0 mm. Carrier gas, N_2. Column length, 2 m. $p_i/p_o(\bar{u}_{op})$ is the inlet to outlet pressure ratio at optimum gas velocity. N/m is the number of theoretical plates per metre, at $\bar{u}_{op}$.

Stationary phase	*Liquid load (%, w/w)*	p_i/p_o $(\bar{u}_{op})$	N/m
SE-30	3.5	1.7	4000
Carbowax 20M	4	1.8	3800
Fractonil III	5	2.2	3300
Triton X	5	2.0	3000
OV-225	5	1.9	2800
Fomblin Y	5	2.3	2400
Carbowax 300	5	1.8	2000
OV-275	5	1.7	2000

deduced from Table I. The effect has also been observed with mixed stationary phases.

Effect of column diameter on column efficiency

A number of columns of different diameter were prepared using a solid support of a size of 100–125 μm and a liquid loading of 4% of OV-1. The effect of column diameter on the number of theoretical plates per metre of column under these conditions is shown in Fig. 2. The lower limit of column diameter depends on the difficulty of filling a tube smaller than 0.5 mm with the support employed. The dependence of column efficiency on d_p/d_c is shown in Fig. 3, which seems to place a lower limit on the specific efficiency of large-diameter columns made with this packing of *ca.* 2000 theoretical plates per metre.

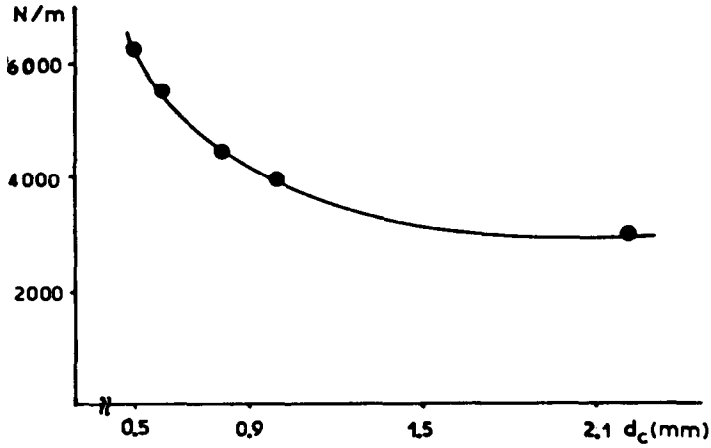


Fig. 2. Specific efficiency of different columns of 4% OV-1 on 120–140-mesh Volaspher A-2. L = 3 m; carrier gas, N_2.

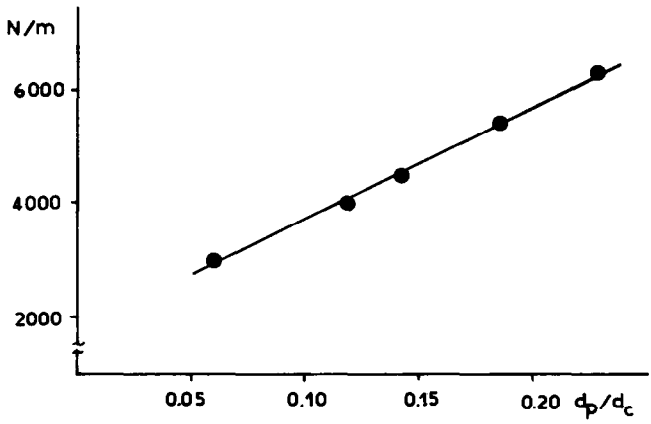


Fig. 3. Dependence of specific efficiency of the columns shown in Fig. 2 on d_p/d_c.

TABLE II

PERMEABILITY (K) OF SOME COLUMNS

Common characteristics: 4% OV-1 on 120–140-mesh Volaspher A-2. Column length: 3 m.

d_c	d_p/d_c	*Packing density* (g/cm^3)	ε	$K \cdot 10^7$	p_i/p_o (p_o = 1 atm)	$\bar{u}_{op}$ (cm/s)
0.5	0.23	0.411	0.211	10.56	2.5	4.4
0.6	0.19	0.460	0.107	1.10	2.3	3.8
0.8	0.14	0.475	0.087	0.56	2.3	3.4
1.0	0.11	0.478	0.047	0.08	2.5	3.3

Effect of permeability on various experimental parameters

Columns of different diameter, prepared with the same packing of 4% OV-1 on 120–140-mesh support, and of length 3 m allowed us to study the packing density, porosity, permeability and head pressures necessary to run the column at the optimum gas velocity. Table II gives a summary of the results.

DISCUSSION

From the point of view of the specific efficiency (plates/metre), the best column is one of I.D. 0.5 mm, whose characteristics are summarized in Table III. Despite the low packing density, an efficiency of 6250 plates/metre was measured at a capacity factor of *ca.* 3. This high efficiency was achieved by paying attention to the term C_g in eqn. 2. The procedure followed for filling the column limits the practical maximum column length to about 5 m. Therefore, about 30000 theoretical plates could be achieved with a working head pressure of nitrogen of the order of 4 kg/cm^2, which is easily handled on any gas chromatograph and without special injection difficulties. Such numbers of theoretical plates are more than sufficient for many separation problems. Table IV compares various columns, cited in the literature, with special

TABLE III

CHARACTERISTICS OF THE MOST EFFICIENT COLUMN

Characteristic	*Value*
Packing	4% OV-1 on 120–140-mesh Volaspher A-2
I.D.	0.5 mm
Column length	3 m
d_p/d_c	0.23
Packing density	0.411 g/cm^3
Porosity, ε	0.21
Permeability, K	$10.56 \cdot 10^{-7}$ cm^2
$\bar{u}_{op}$ (N_2)	4.4 cm/s
p_i/p_o at $\bar{u}_{op}$	2.5
$\bar{H}$ at $\bar{u}_{op}$	0.16 mm
$C_g + C_l$	$4.17 \cdot 10^{-4}$ s

attention to the pressure needed, specific efficiency and length or pressure necessary to achieve 10^4 theoretical plates. Although the column shown in Table III has neither the highest efficiency nor the lowest pressure drop per metre, it shows a good equilibrium between performance and pressure drop, with a clear advantage if the cost of one theoretical plate in terms of head pressure is considered.

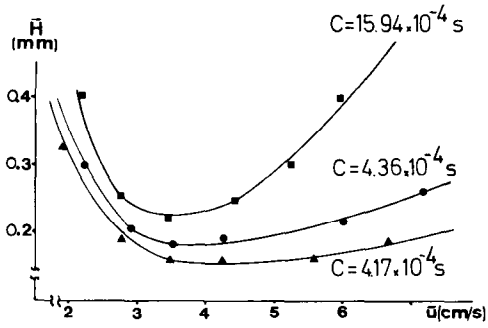
According to Cramers and Rijks[6], all columns shown in Figs. 2 and 3 (Table II) with I.D. between 0.5 and 1.0 mm may be considered as micropacked columns as they have an I.D. below 1.0 mm and d_p/d_c values below 0.3. In these, a gradual increase in the column efficiency may be observed as the column diameter decreases (Fig. 3) without much change in the column head pressure needed, as may be deduced from Table II. However, if other characteristics are considered, differences can be observed. The ratio d_p/d_c is close to 0.2 for the 0.5 and 0.6 mm I.D. columns, which would make them packed capillary columns[2], whereas the 0.8 and 1.0 mm I.D. columns should be considered as micropacked. An evaluation of the C terms in eqn. 2, as shown in Fig. 4 for the 0.5, 0.6 and 0.8 mm I.D. columns, again shows a clear

TABLE IV

CHARACTERISTICS OF SOME COLUMNS REPORTED BY DIFFERENT WORKERS

d_p *(mm)*	$\bar{H}_{min}$ *(mm)*	d_p/d_c	p/m *(atm)*	$N/atm\ m$	$L/10^4$ *T.P.** *(m)*	$p_o/10^4$ *T.P.** *(atm)*	*Ref.*
0.175	1.0	0.70	1	1000	10	10	17
0.150	0.26	0.17	3	1282	2.6	7.8	7
0.140	0.50	0.18	1	2000	5	5.0	9
0.125	0.60	0.39	0.5	3333	6	3.0	8
0.113	0.16	0.23	0.8	7813	1.6	1.3	This work
0.030	0.1	0.03	7	1430	1	7	11
0.030	0.1	0.03	8	1250	1	8	10
0.025	0.09	0.067	25	440	0.9	22.5	13
0.010	0.02	0.008	240	208	0.2	48.0	12

* T.P. = theoretical plates.



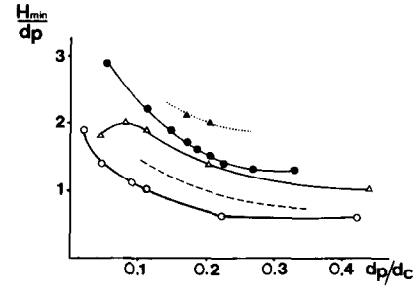


Fig. 4. Plot of $\bar{H}$ *versus* average linear gas velocity for the columns in Table II. ■, 0.8; ●, 0.6; ▲, 0.5 mm I.D. The C terms in eqn. 2 are shown.

Fig. 5. Dependence of $\bar{H}_{min}/d_p$ on d_p/d_c. ▲, Chromosorb P with OV-1 ($d_l \approx 0.04$ μm) (this work); ●, Volasphere A-2 with OV-1 ($d_l \approx 0.04$ μm) (this work); △, Chromosorb P without stationary phase[19]. ○, glass beads without stationary phase[19]. Broken line, calculated for Volaspher A-2 without stationary phase.

distinction between the two smaller columns and the 0.8 mm I.D. column, which has a C term about four times as large. A change in column I.D. from 0.8 to 0.5 mm brings about a decrease in the value of $\bar{H}$ at the optimum gas velocity from 0.22 to 0.16 mm while increasing the optimum gas velocity from 3.4 to 4.2 cm/s, thus decreasing analysis time by nearly 20%, as had been suggested by Kaiser[18].

The dependence of H on d_p/d_c was first considered by Sternberg and Poulson[19], who used solid particles without a liquid coating. Their findings are presented in Fig. 5 compared with our results. The curves corresponding to Chromosorb P and glass beads without any liquid coating show the dependence of the C_g term in eqns. 1 and 2 on d_p/d_c, and the curves corresponding to our results show the effect of d_p/d_c on both the C_g and C_l terms in these equations. If the ratio between the $\bar{H}/d_p$ values corresponding to coated Chromosorb P (our points) and uncoated Chromosorb P[19] is assumed to hold for coated and uncoated Volaspher A-2, the dotted line shown in the Fig. 5 may be drawn, corresponding to an uncoated porous spherical support, with a behaviour close to that of spherical glass beads and superior to what can be expected from a non-spherical support such as Chromosorb P.

TABLE V

CHARACTERISTICS OF LONG MICROPACKED COLUMNS

N/m = theoretical plates per metre.

Stationary phase	*Liquid load (%, w/w)*	d_p	d_c	p_i/p_o ($\bar{u}_{op}$)	*Carrier gas*	*L (m)*	*N/m*
OV-1	4	0.113	0.8	7.0	N_2	13	4600
Superox 20M	3	0.137	0.9	5.0	N_2	10	2900
Superox 20M + SE-30	4	0.137	0.9	5.0	H_2	11	3400
OV-101	15	0.137	0.9	5.0	H_2	10	2400
Superox 20M	10	0.137	0.9	4.0	H_2	10	2000
Superox 20M + SE-30	8	0.137	0.9	5.0	H_2	9	2900

Bearing in mind the relationship between efficiency, permeability, stationary phase load, particle and tube diameters, sample capacity, head pressure needed and construction facility, other columns could be used to advantage for particular problems, even if they may not be considered as the best overall micropacked columns possible. Table V lists several columns made from 0.8 and 0.9 mm I.D. tubing of length 9–13 m. The lower specific efficiencies may be compensated for with a greater length, resulting in columns with a sufficient number of theoretical plates and larger sample capacity.

Comparing the two OV-1 columns in Tables III and V, it can be seen that the latter has a lower specific efficiency but about twice as many theoretical plates as the longest column which could be made with the characteristics of the former, working at a head pressure of nitrogen of 7 kg/cm^2, which is not too high for commercial gas chromatographs but which could be made lower if hydrogen is used as the carrier gas, with the additional advantages of a higher analysis speed.

In some particular instances, a higher sample capacity must be achieved by increasing the stationary phase percentage, even if a lower specific column efficiency is obtained. As can be seen in Table V, an increase in Superox 20M from 3 to 10% lowers the efficiency from 2900 to 2000 theoretical plates per metre, but if this can

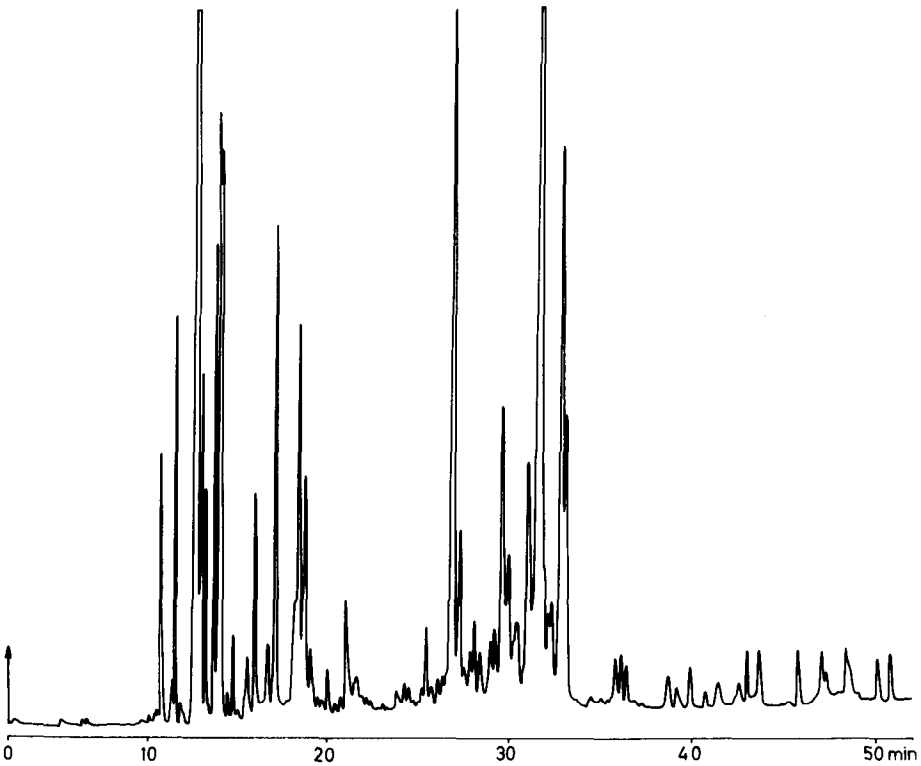


Fig. 6. Chromatogram of extract of *Santolina rosmarinifolia* obtained on a 4% SE-30 on Volaspher A-2 (120–140-mesh) column (5.5 m × 1.0 mm I.D.). Carrier gas, H_2 (8 cm/s). Temperature, programmed from 40°C at 5°C/min to 200°C.

be compensated for with a greater column length, the result may still be a very reasonable column. As already mentioned, these lower specific column efficiencies were the norm with polar liquid stationary phases (see Table I). Mixed stationary phase columns, made by mixing two liquids of different polarity and covering the solid support with the mixture (homogeneous mixed stationary phase), show specific efficiencies between the values corresponding to the individual stationary phase columns. Once again, the normal dependence of column efficiency on the amount of stationary phase on the support may be observed, with the lowest value of $\bar{H}$ at a *ca.* 4% loading.

Columns of the type shown here may be used to solve problems of some complexity. Figs. 6 and 7 show two examples of short columns with a non-polar liquid stationary phase applied to complex separations. Fig. 8 shows the separation of the components of a wine extract on an OV-275 column only 2 m long.

To summarize, if a good solid support is used and the coating procedure produces a homogeneous thin layer of stationary phase, then it is not necessary to have very low values of d_p/d_c, as values between 0.11 and 0.23 produce columns with 4000–6000 theoretical plates per metre with reasonable head pressures. All columns prepared in our laboratories and described in this paper have specific pressure drops below 1 atm/m.

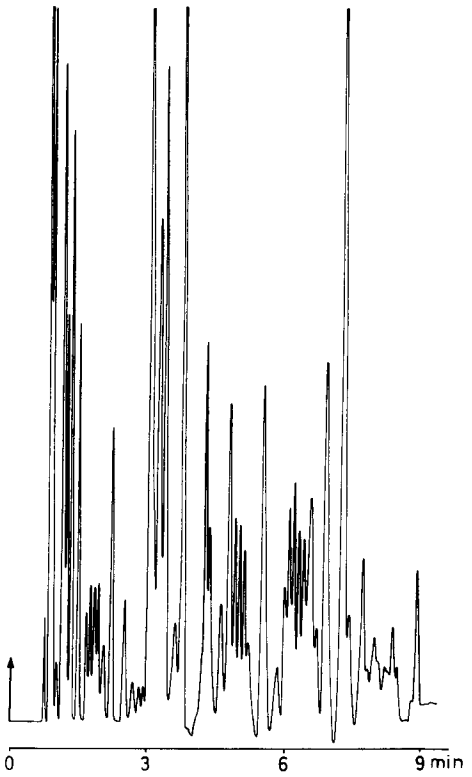


Fig. 7. Chromatogram for direct injection of naphtha into a 4% OV-1 on 120–140-mesh Volaspher A-2 column (3 m × 0.5 mm I.D.). Carrier gas, N_2 (4.5 cm/s). Temperature, programmed from 60°C at 10°C/min to 210°C.

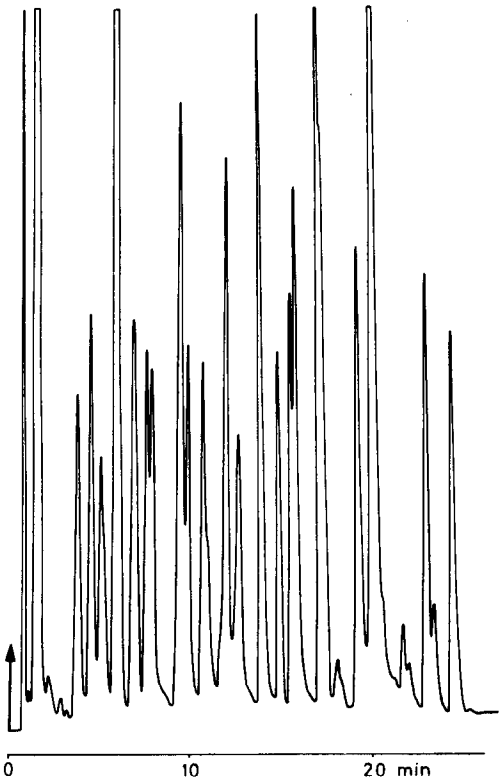


Fig. 8. Chromatogram of an organic extract of a wine obtained on a 5% OV-275 on Volaspher A-2 (120–140-mesh) column (2 m × 1 mm I.D.). Carrier gas, N_2 (4 cm/s). Temperature, programmed from 70°C at 5°C/min to 200°C.

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