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USE OF HIGH-EFFICIENCY PACKED COLUMNS FOR GAS–SOLID CHROMATOGRAPHY

V. MICROPACKED COLUMNS

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SUMMARY

Micropacked columns are constructed using graphitized carbon black as a support for gas–liquid–solid chromatography. Their effectiveness is evaluated in terms of Van Deemter plots, flow-rates, inlet pressure and column capacity. It is shown that such columns, by choosing an appropriate liquid phase, can be used for a wide range of temperatures and types of compound. Analytical applications connected with the analysis of complex organic mixtures in water are discussed. The problems of the analysis of air pollutants are also considered.

INTRODUCTION

The great number of advantages of coupling gas chromatography with mass spectrometry (GC–MS) have made this technique of more and more use, and many attempts have been made to make the two instruments compatible. These are devoted to the separation of carrier gas from the sample at the interface, and to introducing into the ion source a sufficient amount of sample to obtain clear and reliable mass spectra. Various types of molecular separators are now in use, but each of them shows some defects requiring elimination. Direct coupling of chromatographic columns with MS is possible only if very low flow-rates are employed.

Such flow-rates are possible using classical capillary or support-coated open tubular (SCOT) columns, but the sample amount, especially with complex mixtures, is far from sufficient for small peaks. Furthermore, bleeding of the stationary phase is a serious problem.

For all of these reasons we are developing a column with the following characteristics: (1) Low flow-rate (4 ml/min) at a reasonably high linear gas velocity (10 cm/sec); (2) high performance at a wide range of linear gas velocities; (3) relatively high capacity; (4) low bleeding at high temperature; (5) flexibility of use with heterogeneous compounds; (6) simplicity of construction and reproducibility.

The first two characteristic usually apply to capillary columns, while the third is satisfied by classical packed columns. The remaining requirements, and the third, are very well achieved by using the technique of gas–liquid–solid chromatography (GLSC), as has already been shown[1–4].

The best compromise was found by exploiting the possibilities of micropacked columns, using graphitized carbon black coated with a suitable liquid phase, for GLSC[4].

A recent paper on micropacked columns[5] showed that such columns offer good performance with low flow-rate; furthermore, column length can be reasonably high, so that a number of theoretical plates of the same order of magnitude as those of capillary columns can be attained.

EXPERIMENTAL

Column packing and material

The column packing is graphitized carbon black (Sterling FT; available from Supelco, Bellefonte, Pa., U.S.A., as Carbopack A). This material is treated with hydrogen at high temperature, according to a modification of the procedure previously described[6]. Ultra-pure hydrogen is passed into a cylindrical oven containing a 5-cm-I.D. iron tube in which carbon black is placed. The hydrogen flow-rate is 250 ml/min at room temperature. When all the air is evacuated (about 30 min) the temperature is raised to 1200° (this ensures that a minimum of 1000° is reached in the entire mass of the carbon black). The treatment is continued for 30 h. During cooling hydrogen continues to flow into the oven. A detailed discussion on this hydrogen treatment and its effects on column performance for the elution of polar compounds will be given in a forthcoming paper.

The carbon black was then sieved to 110–125 mesh and coated with 1.5% w/w polymetaphenoxylene dissolved in methylene chloride. Particular care is given to the coating procedure, as described elsewhere[4]. The column material is stainless-steel tubing of 0.7 mm I.D.

Column preparation

The column tubing, straightened as much as possible, is placed in a vertical position, with the terminals blocked in such a way that the tubing undergoes a certain tension. The upper end is connected to a small reservoir containing the column packing, as shown in Fig. 1, while the lower end is closed.

The packing is driven into the column by gently tapping it with a rubber rod. Optimum packing density is achieved when 0.6 g/m are allowed into the column. This is easily controlled in that the packing velocity suddenly becomes much lower. With this procedure, high reproducibility of the columns is attained, while the packing system does not involve sophisticated techniques and can be done in any laboratory without difficulty.

Apparatus

A Carlo Erba Model GI gas chromatograph (Carlo Erba, Milan, Italy), equipped for the use of capillary columns, was used and no further modifications were found necessary. For water detection a microthermal conductivity cell (Gow-Mac, Madison, N.J., U.S.A.) is placed on the chromatograph lid close to the flame ionization detector (FID), so that detector interchange can be easily made.

Fig. 1. Design of the packing reservoir connected to the column.

RESULTS AND DISCUSSION

Column packing characteristics

GLSC with graphitized carbon black has some peculiar features, which have been already shown in other papers of this series and can be summarized as follows: (1) High selectivity for molecular structure; (2) possibility of using a liquid phase below its freezing point without the usual problems encountered in gas–liquid chromatography (GLC); (3) lower bleeding than in GLC for the same liquid phase. In our case bleeding was less than $150 \cdot 10^{-12}$ g/sec at 200° and 2 ml/min (ref. 3); (4) by changing the amount of liquid phase one can make the most convenient column for a certain separation; (5) column packing is very easy because of the absence of a true liquid layer, which usually makes the packing particles stick to each other. These are the reasons for selecting this material for our micropacked columns.

An obvious limitation of GLSC is the higher temperature usually needed to elute certain compounds compared to GLC. All these properties should be kept in mind to understand the usefulness and field of application of this material in GC–MS of complex organic mixtures.

Column efficiency and reproducibility

Van Deemter plots of two columns of different length are shown in Fig. 2. Even though the minimum plate height is apparently slightly higher than that obtained by other authors with micropacked columns, the slope of the linear part of the curves is very low, so that a fast analysis is possible.

The characteristic deep minimum already observed for long GLSC packed columns[7] is also found for the 6.0-m column. Unfortunately a comparison of our results with those of Cramers *et al.*[5] is impossible because these authors do not report H *vs.* $\bar{u}$ curves in their paper.

In Table I comparative data of inlet pressure flow-rate and linear gas velocity using hydrogen as carrier gas are reported. Fast analysis is possible without excessive pressure, the flow-rate at relatively high linear gas velocities being such that no particular problems arise because of excessive pressure in the ion source, if the mass spectrometer is equipped with an efficient differential pumping system.

Reproducibility of Van Deemter plots is within 10% if the packing procedure described here is followed. The optimum packing density is 0.6 g/m of column and column reproducibility is ensured if this value is strictly observed.

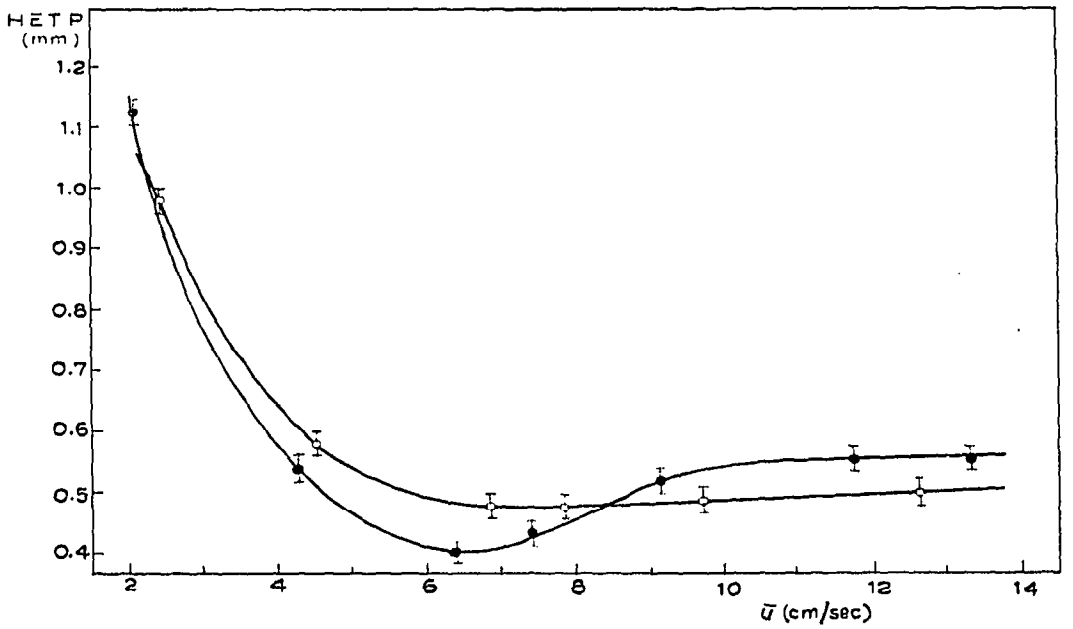

Fig. 2. HETP *vs.* $\bar{u}$ plots for *n*-heptane at 50° on micropacked columns. Column packing: hydrogen-treated Sterling FT + 1.5% P.M.P., 110–125 mesh. ○, Column length 1.5 m; ●, column length 6.0 m.

Packing size, as expected, has a decisive effect on column efficiency and permeability, but the shape of the particles of carbon black also causes limitation of the latter. 110–125 mesh was found to be the best compromise between column efficiency and permeability. However, further studies are needed to establish the possibility of making longer columns. Under these conditions a larger particle size might be necessary.

Elution of water

The problem of water elution is important to everybody interested in the

TABLE I

KINETIC FEATURES OF MICROPACKED COLUMNS

Temperature, 50°. P = Inlet pressure; Φ = flow-rate; $\bar{u}$ = linear gas velocity.

Column A (1.5 m)			*Column B (6.0 m)*		
P (kg/cm²)	Φ (ml/min)	$\bar{u}$ (cm/sec)	P (kg/cm²)	Φ (ml/min)	$\bar{u}$ (cm/sec)
0.3	1.0	2.4	1.0	0.5	2.1
0.6	1.7	4.6	2.0	1.4	4.3
0.9	2.3	6.8	3.0	2.7	6.3
1.2	3.0	7.8	4.0	3.5	7.4
1.5	3.9	9.6	5.0	5.4	9.1
2.0	5.5	12.6	6.0	7.7	11.7
2.5	7.8	17.4	7.0	10.0	13.2
3.0	10.2	20.2			

analysis of organic compounds dissolved or suspended in water. In this case one needs to elute large amounts very quickly and at low temperatures.

The usual GLC supports act as strong adsorbents of water and as a result water is eluted with a persistent tail, which is in many cases responsible for the unsatisfactory behaviour of polar compounds on the chromatographic column. In addition, polar liquid phases may be destroyed if water is retained by the column at high temperatures, so that a complex extraction procedure is often needed prior to the chromatographic analysis.

A satisfactory solution of these problems was found to be the use of hydrogen-treated graphitized carbon black and a very slightly polar liquid phase, polymetaphenoxylene. Millard *et al.*[8] showed that the adsorption isotherm of water is fairly

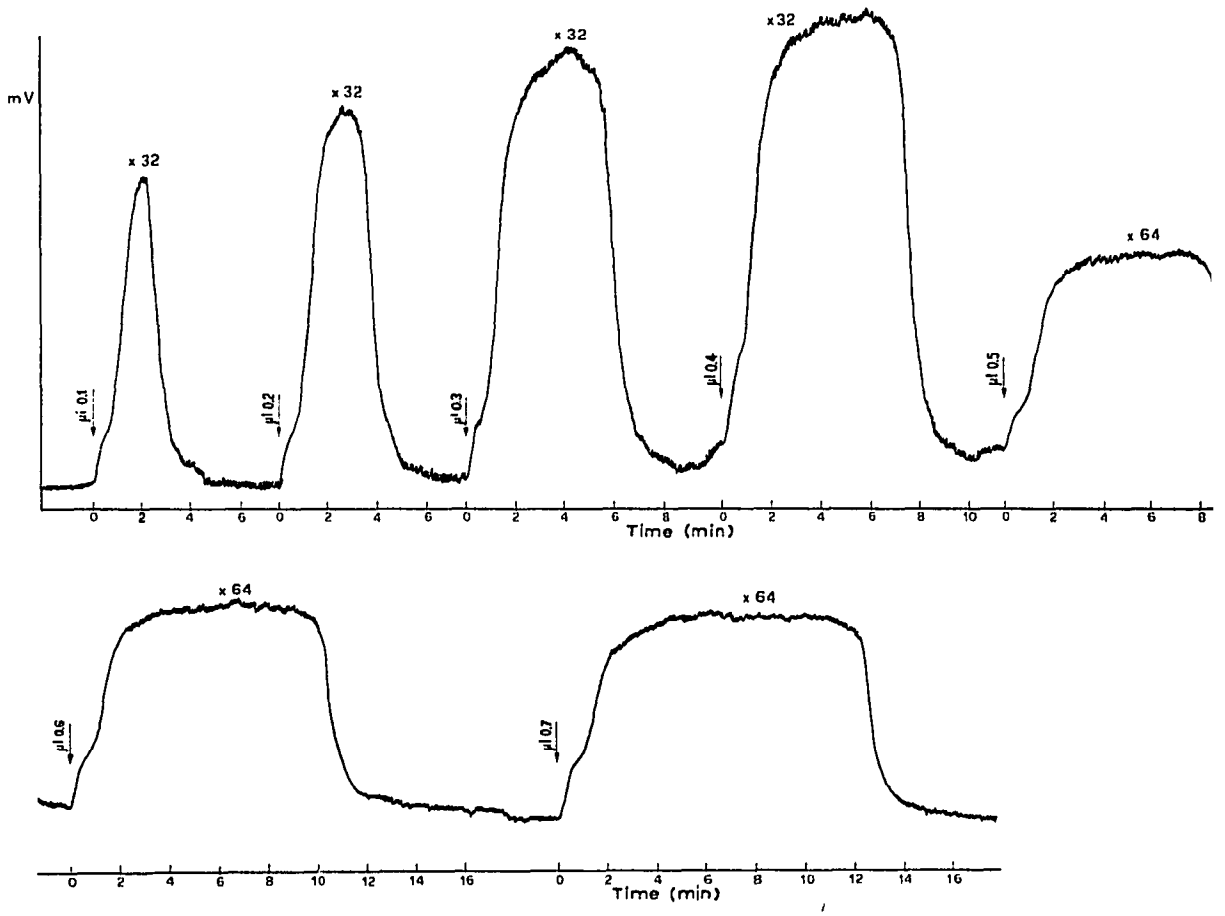

Fig. 3. Chromatogram showing the elution of different amounts of water on a micropacked column. Column length, 1.5 m; inlet pressure, 1.0 kg/cm²; temperature, 50°. Column packing as in Fig. 2.

linear on hydrogen-treated graphitized carbon black and that the heat of adsorption is so low that water is practically unadsorbed at 50°.

In Fig. 3 the elution of water is shown with increasing amounts injected. The major feature of this chromatogram is the sharp decrease of the detector signal at the end of the peak, while the capacity ratio is less than 1. In this way all the compounds heavier than C_4 hydrocarbon are eluted after water even at room temperature. It is also noticeable that large amounts of water are completely eluted after 12 min on a micropacked column, showing that this time just about corresponds to the column volume occupied by water vapour.

Analytical applications

A test mixture of different organic functional groups is shown in Fig. 4. It is worth noting that compounds of quite different nature (*e.g.* *p*-cresol and indole) are eluted linearly by means of this column. Temperature programming does not influence column performance, as shown by the fact that at least fifty analyses were performed without any damage to the column. The peculiar characteristics of GLSC are shown by the good separation obtained between *o*- and *p*-cresols and 2-methyl-1- and 3-methyl-1-butanols.

By coupling the selectivity of carbon black and high column efficiency a wide range of analytical applications is possible with this type of column.

In Fig. 5 the analysis of a cracking naphtha, C_3–C_{11}, is reported. 5 μl of the mixture were injected and column efficiency was unaffected by overloading. This represents a very good column capacity, as we found that the same mixture injected in a SCOT column gave analogous results only if 0.5 μl was injected. A capacity more than 100 times with respect to classical capillary columns was attained, 130 peaks were detected and the same number was found with a capillary column.

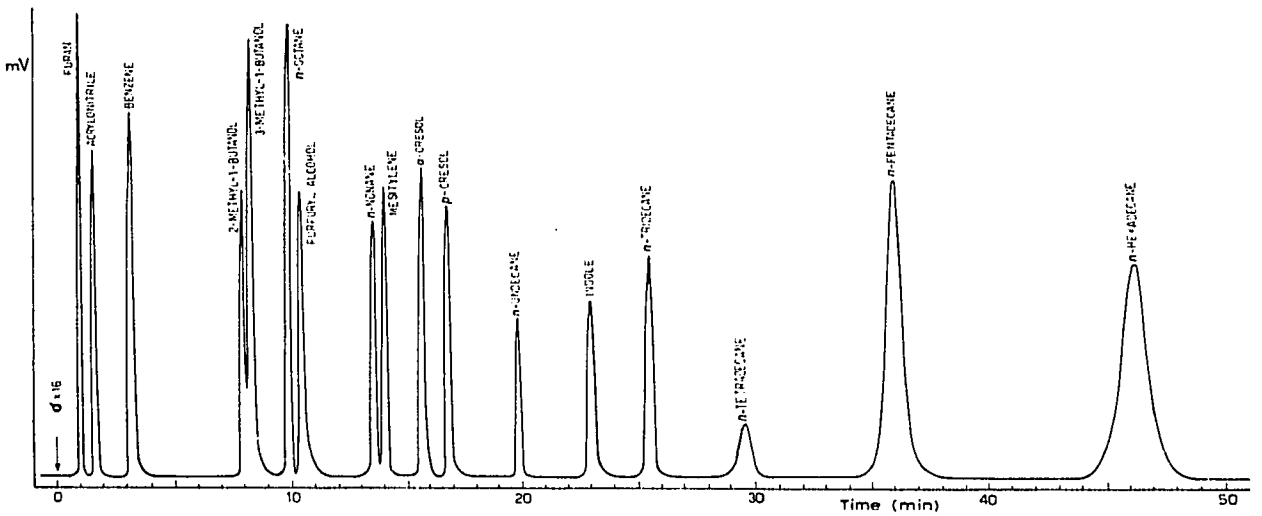

Fig. 4. Chromatogram of a test mixture. Column, see Fig. 3; inlet pressure, 1.0 kg/cm²; temperature 50° for 10 min, then programmed at 4°/min to 200°.

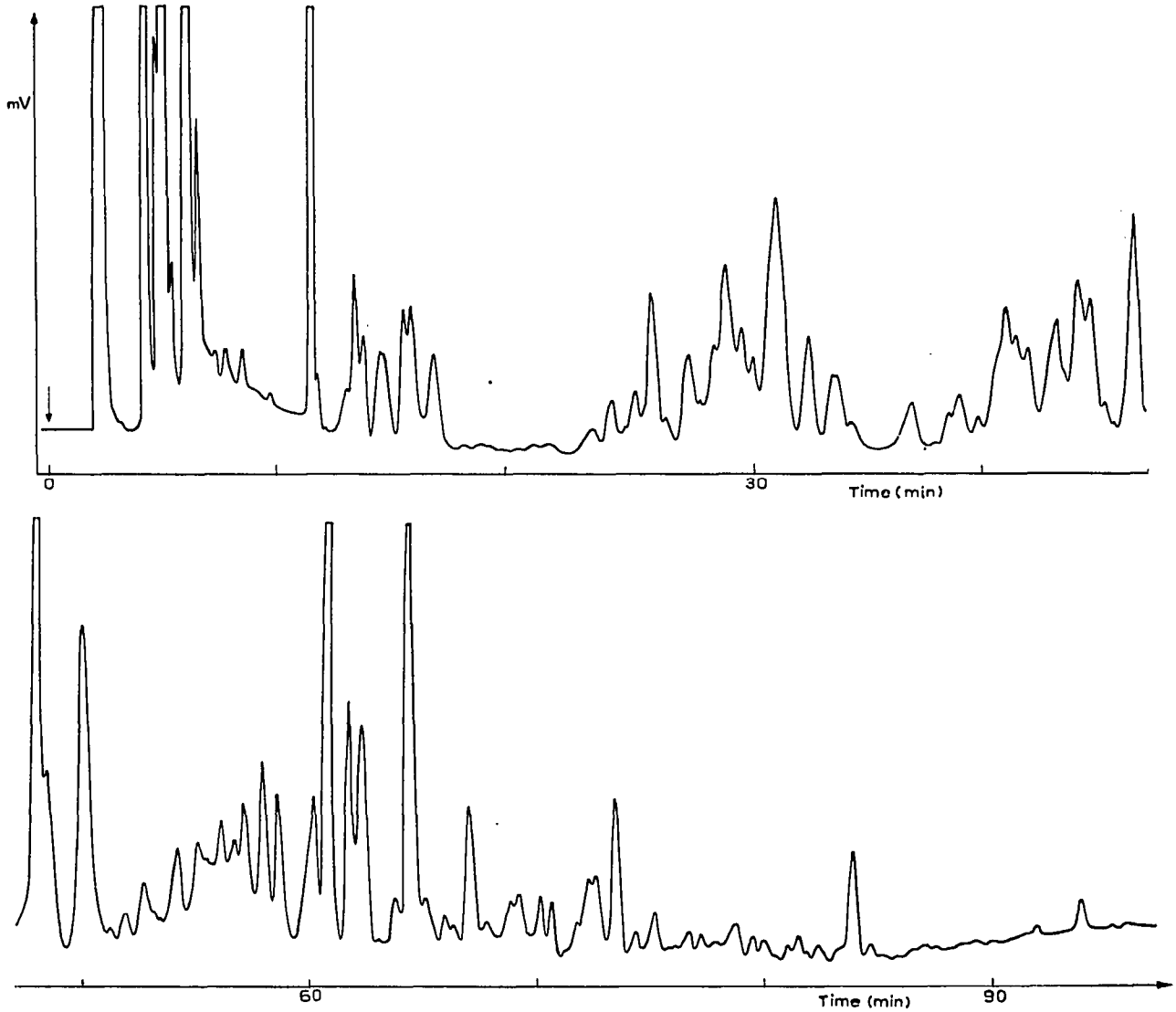

Fig. 5. Chromatogram of a cracking naphtha, C_3–C_{11}. Column: 6 m, micropacked, containing hydrogen-treated Sterling FT + 1.5% P.M.P., 110–125 mesh. Inlet pressure, 5.0 kg/cm^2; temperature, 30° isothermal for 10 min, then programmed at 2°/min to 220°.

In Fig. 6 an example of an analytical application is given. 25 l of polluted air were sampled in the proximity of a petroleum products stocking area. Pollutants were collected by passing the air into a short column (3 cm × 0.4 cm I.D.) containing activated charcoal and than extracted with CS_2 (Merck, Darmstadt, G.F.R.).

The results of this work again show the potentiality of GLSC with graphitized carbon black. Furthermore, micropacked columns may cover a rather difficult field in GC–MS, because they yield both high efficiency and high column capacity.

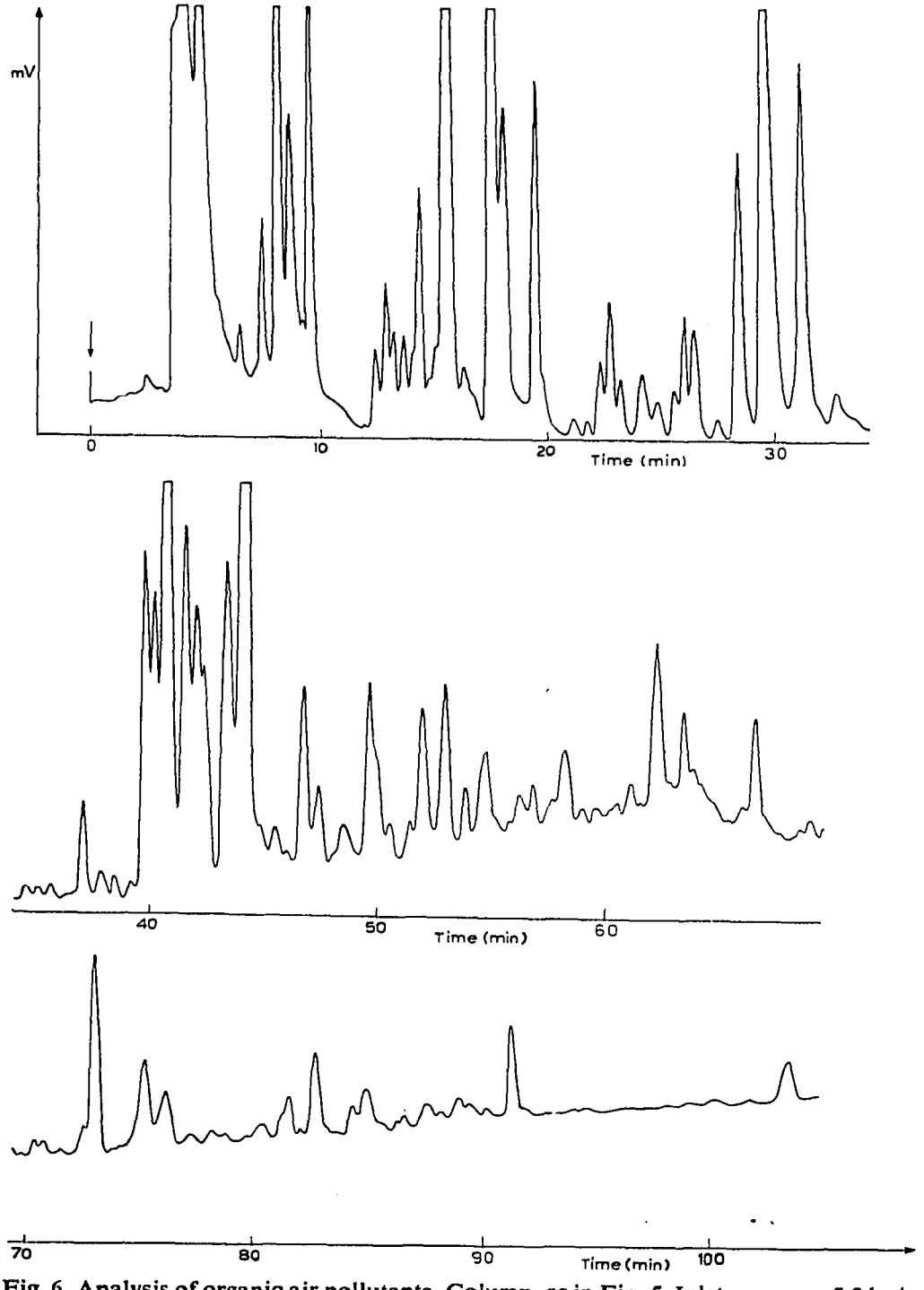

Fig. 6. Analysis of organic air pollutants. Column, as in Fig. 5. Inlet pressure, 5.0 kg/cm^2; temperature, 30° for 1 min, then programmed at 2°/min to 220°.

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