

GAS CHROMATOGRAPHY ON SMALL DIAMETER COLUMNS*

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(Received September 8th, 1964)

Packed columns of usually 4–6 mm inner diameter and capillary columns of diameter less than 1 mm find application in gas chromatography practice. Progress during the last two years in the sphere of increasing chromatographic resolution is related to the development of small diameter columns. Principal trends of work in this sphere were as follows:

(1) Formation of adsorbing layer on the capillary column inner wall by etching^{1–4}, the resulting large surface being coated with liquid film.

(2) Formation of an adsorbing layer by coating the wall with an active solid powder^{5,6}.

(3) Formation of an adsorbing layer by coating the wall with an active solid dispersed in a sol⁷.

(4) Formation of a liquid film by coating the wall with powdered support impregnated with the stationary liquid⁸.

(5) Filling a glass column with an active solid packing, then drawing out the column, decreasing its diameter, and pressing in active solid particles into the wall⁹.

(6) Filling the column with an inert support followed by treating the latter and the column inner wall with a solution of the stationary liquid (frontal method)^{10,11}.

The aim of the above modifications is to increase the sorptive surface and to decrease column interstitial volume. This allows an increase in column selectivity without lowering efficiency in terms of H (height equivalent to a theoretical plate) and makes it possible in a number of cases to carry out an analysis on a short column. Maximum efficiency of $H = 0.2$ – 0.3 mm has been obtained by the authors using small diameter modified columns. But analysis using these columns presents certain difficulties and requires experience.

One more trend in the development of capillary columns consists in increasing the inner diameter up to 1.6 or even 2.5 mm^{12–17}. The increase of sorptive capacity allows operation with samples large enough for the use of a thermal conductivity cell. In addition, there is the possibility of using very high velocities of carrier gas in long columns without substantial pressure gradients.

The advantages and disadvantages of capillary and packed columns are sufficiently discussed in the literature¹⁸.

* This paper was submitted to the Fifth International Symposium on Gas Chromatography, held at Brighton, England, on September 8th to 10th, 1964. As it did not quite fit into the scheme for the formal morning sessions it was preprinted separately and distributed as a basis for discussion at the informal afternoon sessions. It was not read or formally presented at the symposium and will not appear in the final reprints.

In the choice of the optimum technique in the chromatographic process the following factors are particularly important: column selectivity, column efficiency, pressure drop, and the obtaining of reproducible data.

The selectivity coefficient of the column may be defined from the ratio:

$$K_c = \frac{\Delta\Gamma_0}{\Gamma_0} = \frac{\Delta\Gamma}{\Gamma + \frac{\kappa}{\kappa_1}} \quad (1)$$

where:

$\Delta\Gamma_0$ = difference of Γ_0 (overall Henry coefficients of adjacent components of sample);

$\Delta\Gamma$ = difference of Γ (true Henry coefficients);

κ = gas portion of the column volume, κ_1 = portion of column volume occupied by stationary liquid.

The overall Henry coefficient is the ratio in a unit volume of the column of the total quantity of solute to the amount of solute in the gas phase. The true Henry coefficient is the ratio of the concentration of solute in the liquid phase to the concentration in gas phase.

It is quite evident that the K_c value will approach its asymptotic value $k_c = \Delta\Gamma/\Gamma$, when the κ/κ_1 value decreases. Thus, the most selectivity is provided by the packed columns.

To attain maximum efficiency it is necessary to have a large sorptive surface and a small thickness of liquid film, which can be obtained in different ways. In particular, a large surface is more readily obtained in packed columns.

The pressure drop per unit length is substantially lower for capillaries than for packed columns and this allows the use of capillary columns of greater length than packed columns.

Finally, it is evident that a packed column is much more readily reproducible than a capillary column. This is one of the chief reasons for using only packed columns in process chromatographs.

From the above it follows that to obtain high resolution the use of short packed columns is quite feasible. Decreasing the inner diameter enables the analysis time to be shortened and reduces the wall effect on peak spreading. An additional increase of efficiency is obtained by the reduction of the sorbent particles and by the use of small samples if a flame ionization detector is used (although the use of a thermal conductivity cell is possible). Further, due to the small sorptive capacity, the temperature may be lowered resulting in an additional increase in the selectivity coefficient.

In this connexion the examination of packed columns of less than 1 mm inner diameter was of interest. These columns, simple both in operation and design, possess valuable properties which enlarge the gas chromatographic possibilities. They have the advantages of satisfactory reproducibility, a proportionately small gas volume, and a reasonably uniform sorptive capacity throughout. All this favours the wide use of such columns in laboratory and process chromatographs. Also, low heat inertia due to the increased proportion of metal in the column section is an advantage in programmed temperature applications.

All experiments were done using either a Beckman flame ionization detector

and a recorder with a pen speed of 0.25 sec full scale, or a Gasofract 300 B (Dr Virus KG) with a flame ionization detector. Gaseous and liquid samples were injected by a microsyringe, a splitter being used if necessary. In the present work capillaries of 0.7–0.9 mm inner diameter were used. Column packings were obtained by coating the 0.10–0.14 and 0.14–0.20 mm fractions of Celite or Chromosorb W with various

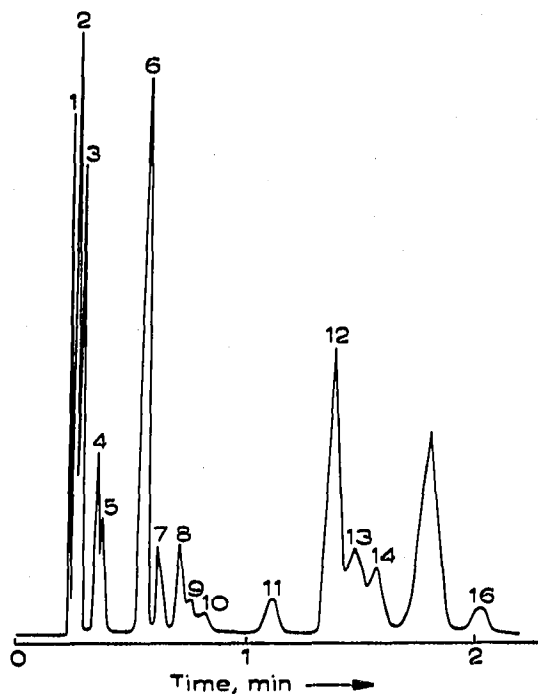


Fig. 1. Chromatogram of C_1 – C_5 hydrocarbons mixture on the 1.25 m \times 0.9 mm column. Quantity of column packing (20% w/w *n*-heptadecane on Celite) 0.390 g. Inlet pressure 2 kg/cm², temperature 38°. 1 = Methane; 2 = ethylene; 3 = ethane; 4 = propylene; 5 = propane; 6 = isobutane; 7 = isobutene + 1-butene; 8 = *n*-butane; 9 = *trans*-2-butene; 10 = *cis*-2-butene; 11 = 3-methyl-1-butene; 12 = isopentane; 13 = 1-pentene; 14 = 2-methyl-1-butene; 15 = *n*-pentane; 16 = 2-methyl-2-butene.

non-volatile liquids in the conventional manner. Columns were packed by two techniques. In the first a small flask containing column packing is joined to one end of the straightened column. The lower end of the column is closed by a small piece of metal gauze held in place by a very short length of capillary, which is attached to the main column by a metal collar. This end of the column is weighted by a hollow bolt and blind nut retained by the collar. Filling is done by tapping the lower end on a solid surface. Recently, column-filling has been done by another technique using a specially designed device involving a tripod and vibrator. Column filling is speedy taking only a matter of minutes.

The results of this research indicate that in the analysis of gaseous and liquid hydrocarbons efficiencies may be attained corresponding to $H = 0.22$ – 0.3 mm even with considerable inlet pressures (of the order of 2–3 kg/cm²); the reproducibility of the small diameter columns both in packing density and efficiency proved quite satisfactory.

This permitted the use of columns 0.14–1.25 m long for a rapid detailed analysis of pyrolysis gases, pentane–amylene fractions, and other mixtures involving com-

ponents up to C_{10} . As an example Fig. 1 shows a chromatogram of a C_1 - C_6 hydrocarbons mixture, obtained with a 1.25 m column at 38° . In this case 16 components are separated in about 2 min; however, a further increase of carrier gas (nitrogen) flow-rate permits a reduction of the analysis time to 70 sec, the quality of resolution being only slightly lowered.

An analysis of paraffins and olefins with the same carbon number on a non-polar stationary phase is a complicated problem; nevertheless this problem can be solved for C_6 - C_8 hydrocarbons using a length of only 14 cm of 0.9 mm diameter column packed with 15% *n*-hexadecane or squalane, which carries out the separation in less than 8 min. On 1 m column the resolution is unnecessarily good (Fig. 2).

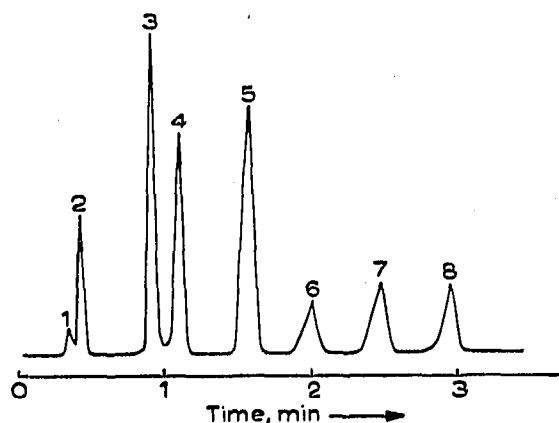


Fig. 2. Analysis of synthetic blend on the 1 m column. Inlet pressure 3 kg/cm², temperature 50° . 1 = 1-pentene; 2 = *n*-pentane; 3 = 1-hexene; 4 = *n*-hexane; 5 = benzene; 6 = cyclohexane; 7 = 1-heptene; 8 = *n*-heptane.

When the partition coefficient of components is highly different, short columns naturally provide a rapid and complete resolution. Thus, for the separation of hexane, benzene, and toluene mixtures in 25 sec, a 38 cm column proved to be sufficient.

The application of small diameter packed columns opens a prospect for the development of techniques for the analysis of such complex mixtures as liquid petroleum products. Thus, a chromatogram of straight-run gasoline hexane fraction containing 20 peaks can be obtained in 5 min on a 52 cm column¹⁹.

Fig. 3 shows a chromatogram of a mixture of oxygen-containing compounds and hydrocarbons obtained on the 30 cm column in about 3.5 min.

In papers recently published^{10,11} packed capillary columns of 0.5 and 0.25 mm diameter with efficiencies up to 1500 theoretical plates per meter have been described. They were prepared by passing a solution of the stationary phase through a capillary filled with a solid support, both the packing and the wall being coated with liquid. In our opinion, confirmed experimentally, the preparation technique used in the present paper is quite simple and allows the packing of columns of the highest efficiency.

For a rapid analysis of substances with greatly different partition coefficients the use of short capillary columns is of considerable interest. Thus, Fig. 4 shows a chromatogram of a benzene, toluene, and *p*-xylene mixture, obtained on a 130 cm column of 0.9 mm inner diameter coated with *n*-heptadecane in 10 sec at room temper-

ature and at a carrier gas flow of the order of 200 ml/min. A complete resolution at very high gas velocities can be attained using a small film thickness. This results in a decrease of the liquid mass transfer term of the HETP equation and flattens the slope of the HETP vs. gas velocity curve after the minimum position. Thus a rise in flow

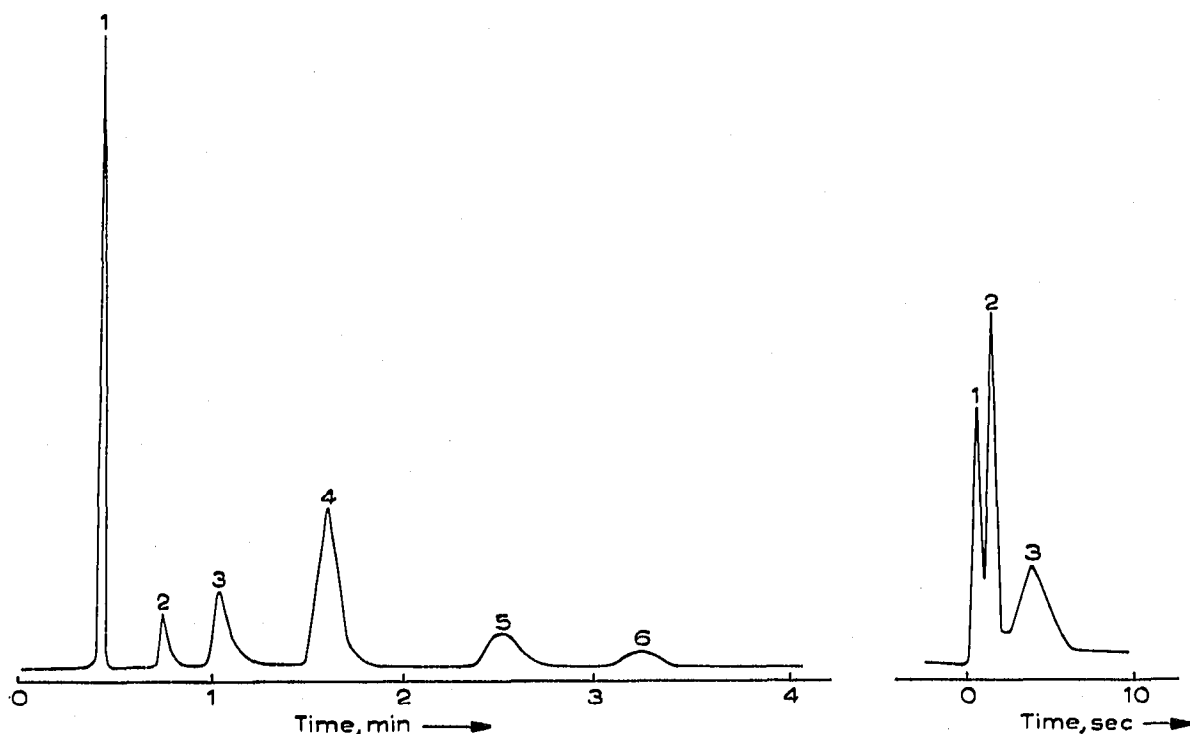


Fig. 3. Analysis of a mixture of oxygen-containing compounds and hydrocarbons on the 30 cm \times 0.7 mm column with 15% w/w *n*-heptadecane on Celite (0.10–0.12 mm). Temperature 26°. 1 = Ethylene; 2 = acetone; 3 = allyl alcohol; 4 = methyl ethyl ketone; 5 = tetrahydrofuran; 6 = *n*-hexane.

Fig. 4. Chromatogram obtained on the 1.3 m \times 0.9 mm capillary column coated with *n*-heptadecane. 1 = Benzene; 2 = toluene; 3 = *p*-xylene.

rate increases the HETP only to a very slight extent, but since the selectivity coefficient remains constant the high resolving power is retained.

Thus, small diameter short chromatographic columns are very powerful tools for the analysis of diverse organic mixtures and merit more extensive use.

SUMMARY

The principal trends of work in the sphere of increasing chromatographic resolution are considered. Short packed columns of inner diameter less than 1 mm are shown to possess high efficiency and resolving power. Examples are given indicating the possibility of using small diameter columns for the rapid analysis of various gaseous and liquid mixtures. Since small diameter packed columns can be readily and satisfactorily reproduced, their application in process chromatographs is feasible.

It is shown that with short capillary columns operating at low temperatures very high carrier-gas velocities can be used in some cases.

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