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FLOW PROGRAMMING IN GLASS CAPILLARY COLUMN–ELECTRON CAPTURE GAS CHROMATOGRAPHY BY USING THE VALVE IN THE SPLITTER LINE

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SUMMARY

Flow programming is a useful complement to temperature programming, and in some instances is to be preferred. Using a metering valve in the side outlet of an inlet splitter, the flow-rate in the capillary column can be programmed to follow any desired function. The separation of polychlorinated biphenyls using an exponential flow programme is described as an example.

INTRODUCTION

In the gas chromatographic analysis of many compounds, such as polychlorinated biphenyls (PCBs), there are large differences between the retention times of the individual compounds, which requires the use of programming in order to obtain satisfactory peaks for both fast- and slow-migrating compounds. Temperature programming frequently causes the appearances of ghost peaks arising from impurities in the carrier gas that have been concentrated in the column at the low temperatures used. The electron capture detector is sensitive, especially in trace analysis, to temperature changes, which will cause irregularities of the baseline when the temperature is programmed. We have tested a system for flow programming that differs from the technique with flow restrictors and buffer vessels[1–5]. When a capillary column is used together with an inlet splitter, the valve in the splitter line can be used to programme the flow-rate after any desired function. The flow-rate has been programmed in the range from about 0 to 2 ml/min.

EXPERIMENTAL

Apparatus

A Varian 1700 gas chromatograph equipped with a tritium electron capture detector was used. A system with an injection splitter and a make-up gas entrance to the detector for glass capillary columns was assembled[6] (Fig. 1). The gas flow-rates through the column are controlled with a splitter valve B (Whitey Micro-Metering Swagelok B-22R S4 valve, Oakland, Calif., U.S.A.). The valve has a small flow coefficient which is a linear function of the number of turns opened. One turn of its

micrometer handle is divided into 25 parts, here called x, and the total number of turns is 8. The glass capillary columns are 40–60 m long and have an I.D. of 0.29 mm. They are drawn from Duran glass, washed with hydrofluoric acid, silylated with TMCS (Pierce, Rockford, Ill., U.S.A.) and coated with SF 96 silicone oil[6].

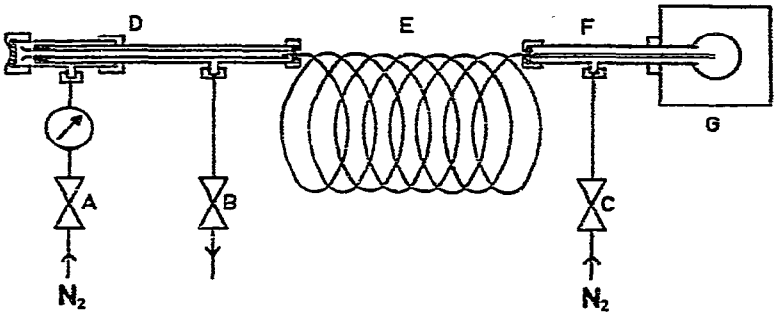

Fig. 1. Schematic diagram of the apparatus. (A) Pressure regulator of the gas chromatograph; (B) splitter outlet valve; (C) make-up gas valve; (D) splitter consisting of a stainless-steel tube with a glass liner, the steel tube being mounted in the ordinary injection port and a 0.2-m silicone tube in the connection between B and D serving as a trap for solvents and solutes; (E) glass capillary column; (F) support for the make-up gas entrance and a straight glass capillary tube to the detector; (G) tritium-source electron capture detector.

Method of use of apparatus

Regulate the inlet pressure with valve A to achieve a suitable flow range for the splitter valve B. Inject the sample and programme the flow by turning the handle of valve B. For exponential programmes, choose the x setting on B from the equation

$$x = ae^{-bt}$$

where a determines the starting flow and b the run time, t.

RESULTS

An application of the described flow programming is illustrated in Fig. 2. It can be seen that the elution can be speeded up in a particular part of the chromatogram. The flow was held constant from the injection to the solvent peak, where it was suddenly decreased and then exponentially programmed. After the exponential part, the flow was once again held constant. When the flow was programmed exponentially in the range 0.1–2 ml/min, the distribution of the peaks in the chromatogram was comparable with that obtained with linear temperature programming from 150 to 215 °C.

A paper describing different applications of the method will be published later.

DISCUSSION

When speaking of flow in gas chromatography, one generally means the flow at the exit of the column. The carrier gas is compressible, which causes a gradient of

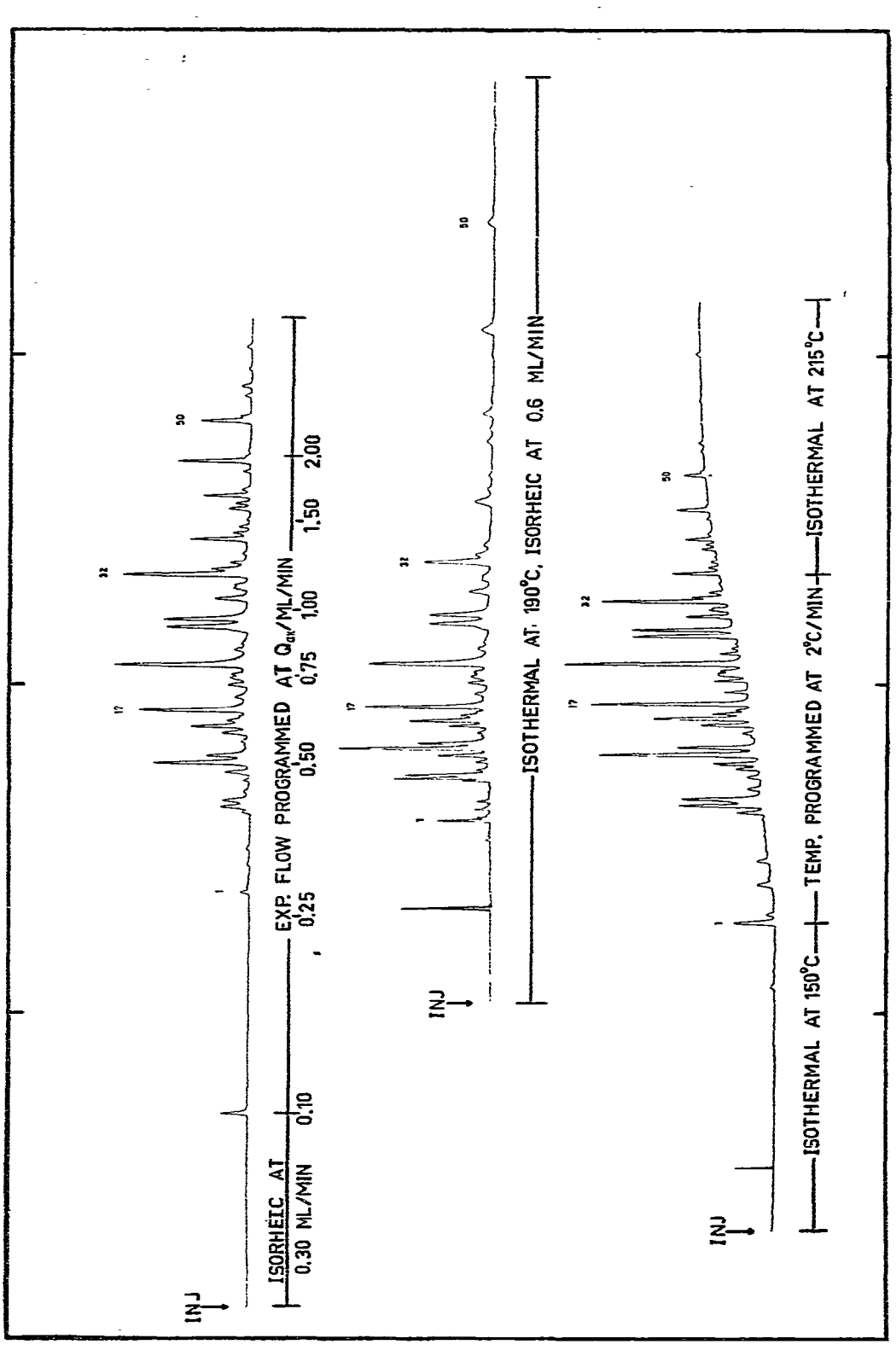

Fig. 2. Electron capture gas chromatogram of PCB oil Clophen A 50, 10 mg/l in hexane. Splitter ratio about 1:100. Injection 5 μl. The column temperature during the flow programming was 190 °C and the flow-rate of carrier gas during the temperature programming was 0.9 ml/min of nitrogen. The identification numbers refer to Jensen and Sundström[7].

gas velocity through the column. When the flow is measured after the detector, Q_{end}, the rate obtained can be corrected from room temperature to the column temperature by the equation

$$Q_{end.\ corr.} = Q_{end} \cdot \frac{T_c}{T_r} \tag{1}$$

where T_c and T_r are the absolute temperatures in the column and outside the chromatograph, respectively. It can further be converted into an average flow by a compressibility correction factor[8,9]:

$$Q_{av.,\ cal.} = Q_{end.\ corr.} \cdot \frac{3}{2} \cdot \frac{(p_i/p_0)^2 - 1}{(p_i/p_0)^3 - 1} \tag{2}$$

where p_i and p_0 are the pressures at the inlet and outlet of the column, respectively.

In our experiments, we measured Q_{end} and calculated an average flow-rate, $Q_{av.,cal.}$, from eqns. 1 and 2 and from experimental data on the column temperature and pressure drop. The average flow-rate must be used when the column efficiency is determined[2]. The ratio of the column volume and the retention time of the unretained solvent can be used as the average flow-rate, $Q_{av.,exp.}$ (Fig. 3). Under the conditions of our experiments, the error is negligible when the solvent peak is used instead of the air peak.

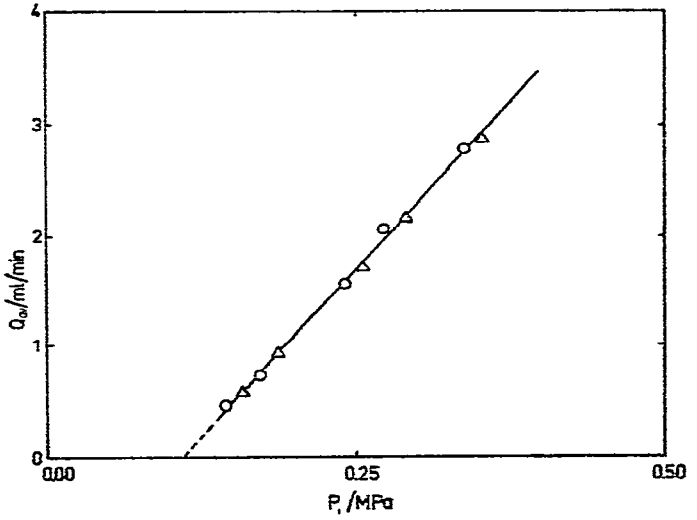

Fig. 3. Comparison of average flow-rate measured from the column volume and the retention time of the air (solvent) peak (△), with the average flow-rate calculated from the flow at the exit of the column (○).

The relationship between $Q_{av.}$ and p_i is derived from the Poisseuille equation and the expression for the compressibility correction factor. For a compressible gas

$$Q = Kp_i^2 \tag{3}$$

where Q is the flow of the gas and K is a constant of proportionality related to the

length and diameter of the tube and the viscosity of the gas. The gas flow at the exit of the column follows eqn. 3, and eqn. 2 can therefore be expressed as

$$Q_{av.} = \frac{3}{2} \cdot KC_p p_i \tag{4}$$

The coefficient

$$C_p = \frac{p_o}{\left[1 + \frac{p_o^2}{p_i(p_i + p_o)}\right]} \tag{5}$$

approaches p_o when p_i/p_o is increased. The gas flow in the column can be approximated and looked upon as a theoretical flow of an incompressible fluid. Hence this hypothetical linear velocity or volumetric flow-rate can be regarded as constant over the entire length of the column.

In Fig. 3, $Q_{av.}$ is plotted as a function of p_i. The experimental and the calculated data will fit the same curve. An average flow-rate can evidently be determined in both ways.

The flow in the capillary column can be fully controlled and regulated with the valve B in the splitter line. Consequently, any change in flow-rate with time can be obtained in the range from about 0 to 2 ml/min. As the peaks from a homologous series of solutes in isothermal chromatography are exponentially distributed in time, it seems natural also to programme the flow exponentially. Thus the flow-rate will change with time according to

$$Q = Ae^{Bt} \tag{6}$$

were A is the starting flow and B the time constant. The relationships between $Q_{av.,exp.}$ and the splitter valve readings x are illustrated in Fig. 4 for three different inlet pressure levels. The curves are used for calibration of the splitter valve. From the experimentally found relationship

$$Q_{av.\ exp.}^{-1/2} = Cx \tag{7}$$

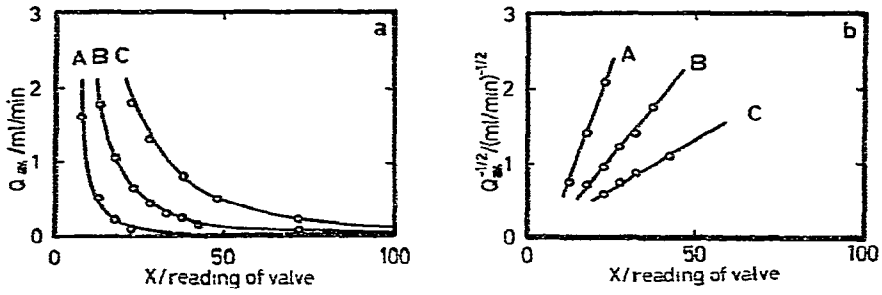

Fig. 4. (a) Relationship between flow-rate and splitter valve reading at three pressure levels, where $P_A < P_B < P_C$. (b) Calibration graphs for determination of the constant C in eqn. 7.

(Fig. 4b) and eqn. 6, the valve setting x is derived as a function of time:

$$x = ae^{-bt} \tag{8}$$

C is an instrumental constant that depends mainly on the inlet pressure, the column temperature and the column dimensions. Now,

$$a = \frac{1}{C\sqrt{A}} \tag{9}$$

gives the starting position of x and

$$b = \frac{C}{2} \tag{10}$$

decides the length of time the programme will take.

In flow programming, it is very important to consider the influence of the flow-rate in the column on the separation efficiency. To characterize the column efficiency during a flow programme sequence, both the height equivalent to a theoretical plate (HETP) and the height equivalent to an effective theoretical plate (HEETP) have been plotted against the average flow-rate in the usual manner proposed by Golay[10] (Fig. 5). The values of the equivalent heights were calculated from chromatograms for a chlorinated hydrocarbon mixture, and plotted against the partition ratios. Fig. 6 illustrates the method we used for determining the equivalent heights. When the partition ratio is greater than 3, the equivalent heights approach a constant value. In Fig. 5, we took the mean of the equivalent heights from the components with partition ratios greater than 3. As can be seen in Fig. 5, the efficiency decreased by about 50% when the flow was programmed from 0.1 to 2 ml/min.

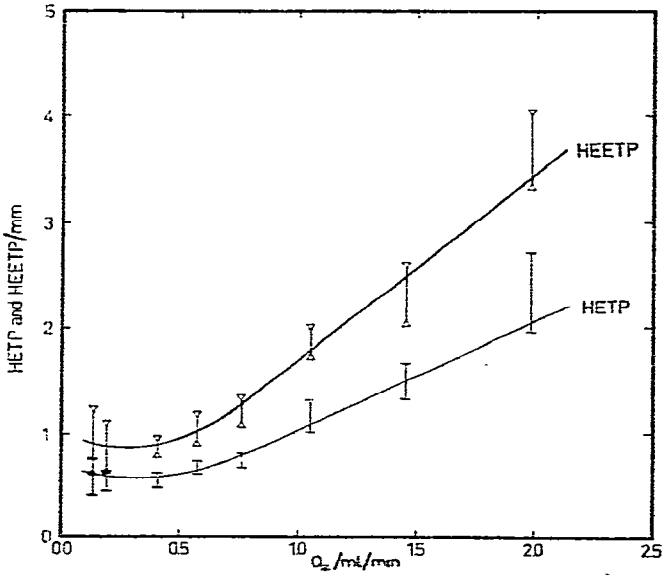

Fig. 5. Variation of the column efficiency with flow-rate according to the Golay equation.

The flow programming used in our experiments allows us to choose different forms of flow programme functions (constant, logarithmic, linear, exponential or combinations of these). With exponential programming, the half-widths of the peaks are relatively constant over the whole chromatogram and the interpretation of the chromatograms is simplified, particularly when an integrator is used. The method can be used with an electron capture detector, in spite of its flow sensitivity, because the total column flow increase during the run is only a few per cent of the make-up gas flow.

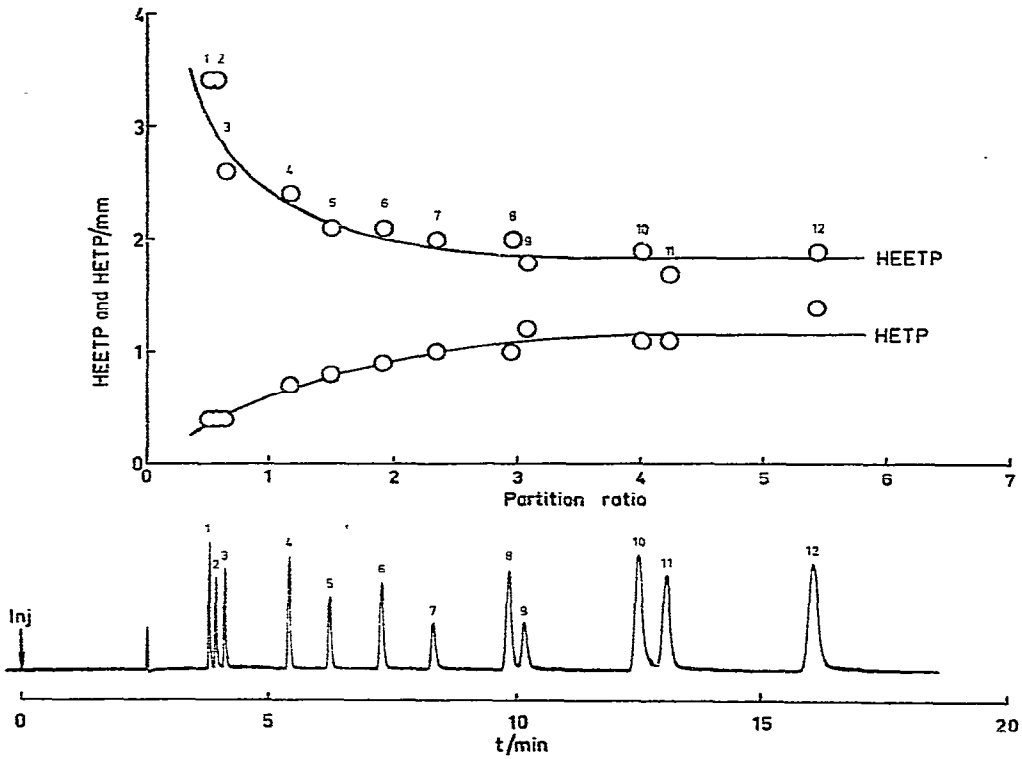

Fig. 6. Illustration of the change of the heights equivalent to a theoretical plate at different partition ratios. The experimental variations in the equivalent heights, for compounds that have partition ratios greater than 3, were used as error limits (standard deviations) for the heights in Fig. 5. Peaks: 1 = α-BHC; 2 = β-BHC; 3 = lindane; 4 = heptachlor; 5 = aldrin; 6 = heptachlor epoxide; 7 = *p,p*-DDMU; 8 = dieldrin; 9 = *p,p*-DDE; 10 = *p,p*-DDD; 11 = *o,p*-DDT; 12 = *p,p*-DDT.

So far, the splitter has been operated manually, but the system needs a mechanical unit to operate the valve. An apparatus containing a valve and a stepper motor controlled by an electronic programming unit, which will vary the flow automatically during the run, is under construction. We also intend to use this apparatus to control an automatic sampler and to operate cooling traps[11,12] and an automatic splitless injection device[13–15].

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