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# EXPONENTIAL FLOW PROGRAMMING IN GAS CHROMATOGRAPHY

SÖREN NYGREN
*The National Food Administration, Food Research Department, Box 622, S 751 26 Uppsala (Sweden)*

## SUMMARY

The flow-rate of the carrier gas in gas chromatography can be programmed by a technique developed for use with capillary columns. Provided that the flow-rate is an exponential function of time, the chromatograms obtained are very similar to those obtained with linear temperature programming. Two types of flow programmers have been constructed, both of which are continuously operating mechanical systems controlled by digital electronic units. The effect of flow programming compared with temperature programming is illustrated by a few chromatograms.

## INTRODUCTION

In the chromatographic separation of multi-component samples, one often encounters great differences in the capacity factors, $k'$. This situation, which is sometimes called "the general elution problem", results in the poor separation of components with small $k'$ values, and long retention times and broad bands of compounds with large $k'$ values. The gas chromatographer usually solves these problems by using temperature programming. As $k'$ is dependent on temperature, this is a convenient means of changing the separation conditions. In some instances, however, the substances decompose or the stationary phase starts to bleed at higher temperatures.

Another interesting parameter that might be manipulated in order to improve the analysis is the flow-rate of the mobile phase. The $k'$ value will not alter during a change of carrier gas if the band positions and the band broadening are plotted against the retention volumes. As, under isothermal conditions, the volume of gas needed to elute a certain compound is constant, the retention time of that component will decrease when the flow-rate in the column is increased.

The elution times and the band widths of the sample components obtained with flow programming are very similar to those obtained with temperature programming when a detector such as a flame-ionization or an electron-capture detector is used. These detectors respond not to the concentration but rather to the total amount of the compound per unit time. Flow programming is also called pressure programming, as the change of flow is achieved by changing the inlet gas pressure.

The gas chromatographic run can be programmed at relatively low temperatures and the programming range is large enough for most analyses.

In 1959, Lipsky *et al.*[1] reported probably the first flow programme. A capillary

column was used and the flow-rate of the carrier gas was programmed in three pressure steps to speed up the analysis of fatty acid esters. Many chromatographers have since worked with this technique and the development of flow programming has been described in many papers[2–7] and was summarized by Ettre *et al.*[8].

During a flow programme, the flow is changed either stepwise or continuously. Step programming can be effected simply by changing the inlet pressure with a pressure regulator or, in a more sophisticated way, with a multi-port valve and restrictors which have different permeabilities. The most common means of achieving continuous programming is with a pneumatic system whereby a combination of pressure and flow controllers is used. One can also use combined buffer vessels and valves to produce both linear and non-linear flow programmes. With such equipment, the flow-rate will change automatically during a programme.

A mechanical system for continuous programming needs some device to regulate the gas flow[9], for example a motor which opens a valve and which is controlled by a mechanical or electronic unit.

## EXPERIMENTAL

### *Apparatus*

The gas chromatograph used was a Varian 1400 (Palo Alto, Calif., U.S.A.) modified for capillary columns[10] and equipped with tritium-source electron-capture and flame-ionization detectors. We have devised a mechanical system for continuously varying the flow-rate of the carrier gas and have constructed two types of flow programming apparatus. Flow programmer No. 1 consists either of a needle valve or a flow or pressure regulator driven by a stepper motor. In flow programmer No. 2, the gas pressure is regulated with a solenoid valve operating at a constant frequency and with a variable band width. The electronic units that control the mechanical systems are digital and are built up of CMOS circuits. To store the programme functions we utilize a cassette tape with a standard tape recorder.

### *Use and function of apparatus*

In our early work with flow programming we increased the column gas flow in an indirect way by decreasing the flow through the splitter line with a micrometering valve[9]. This kind of inverse programme was possible when there was no pressure regulator in the gas inlet. The setting was done by hand.

Later we used the flow programmer (No. 1) with the stepper motor, whereby the valve position was programmed stepwise in small increments of about 400 steps per revolution (Fig. 1). One step of the stepper motor corresponds to one pulse from the digital electronic unit. The pulses cause the valve to open or to close, depending on the frequency of the signal.

Programmer No. 2 gives an intermittent gas flow with a constant frequency produced by another electronic unit, also digital, as shown in Figs. 2 and 3. The fluctuations at the inlet are completely smoothed out at the end of the column. The duration of the signal to the solenoid can be varied so as to provide a modulated band-width signal. The gas flow from the valve can be increased by increasing the percentage of open time. Here, we also use a cassette tape recorder as the memory unit for storing the flow programme signals.

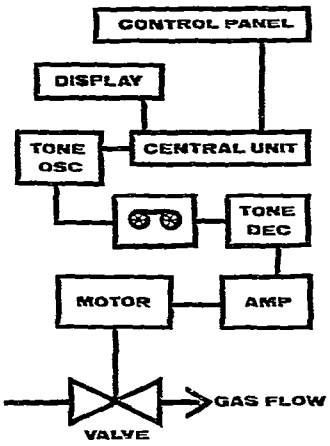


Fig. 1. Schematic layout of the flow programmer No. 1. The mechanical system consists of a stepper motor which regulates the gas flow by means of a valve, which can be a needle valve or a flow or pressure regulator. The motor function is controlled by a digital electronic unit constructed of CMOS circuits. Two tone oscillators give signals —one for opening and the other for closing the valve— which are recorded on a cassette tape with a standard tape recorder. The programming is done from the control panel. Signal pulses are programmed stepwise for opening or closing the valve. Alternatively, one can programme continuous pulses which will put the valve in a certain position. After a set of pulses, the tape recorder is automatically stopped. During the preparation or execution of a programme the current valve position and the elapsed time are shown by a display. When the recorded programme is run, tone decoders and an amplifier give signals to drive the motor. Despite the stepwise change of the valve position caused by the principle of operation of the stepper motor, the device permits an essentially continuous variation of the gas flow, as there are of the order of 1000 steps in one programme.

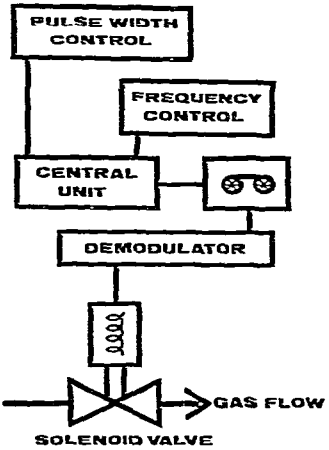


Fig. 2. Schematic layout of the flow programmer No. 2. This apparatus produces an intermittent gas flow created by a solenoid valve. A constant low-frequency signal (*ca.* 1 Hz) can be modulated in pulse width, with a duty cycle settable between 0 and 100%. Here also, the signal is recorded on a cassette tape which serves as a memory. When the programme is run, the signals are converted in a demodulator to feed the solenoid valve. This instrument is also constructed with digital electronics. The interface between the mechanical parts and the digital electronics is very simple when the mechanical system consists of a stepper motor or a solenoid valve. The pulsed flow goes from zero to the inlet pressure level (*ca.* 2 atm) during each pulse period. These rather violent pressure fluctuations are not noticed at the end of the column as it has a great buffering capacity.

## RESULTS

To show the effects of exponential flow programming, some non-programmed and temperature- and flow-programmed chromatograms of chlorinated hydrocarbons are compared (Figs. 4–8). With exponential programming, the flow-rate, $Q$, is a function of time, $t$, according to the relationship $Q = Q_0 \cdot e^{kt}$, where $Q_0$ is the initial flow-rate and $k$ the time constant or programming rate. Flow programming can be used alone to give chromatograms that are very similar to those obtained with temperature programming. The programming techniques can be used in combination to speed up the analysis, or sequentially, for example to avoid bleeding of the stationary phase. The programming range is demonstrated with two other samples. Fig. 9 shows a run with a mixture of polychlorobiphenyl (PCB) components which was

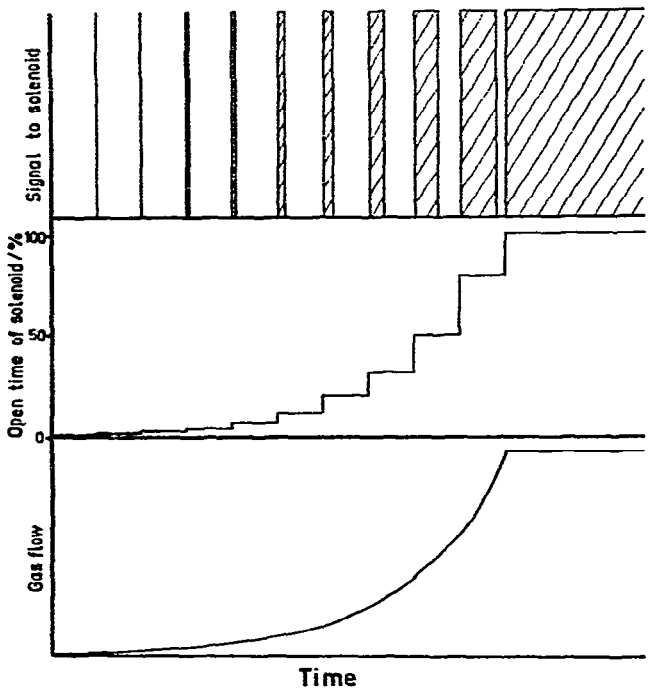


Fig. 3. Relationship between the controlling signal of the solenoid valve and the gas flow passing through it. At the beginning of the programme, the signal from one pulse is very short (*ca.* 20 msec) and increases in duration as the programme proceeds. If the increase in signal duration with time is exponential there will be an exponential increase in percentage open time of the valve. When a gas is allowed to pass through, the flow-rate thus changes according to the same exponential function.

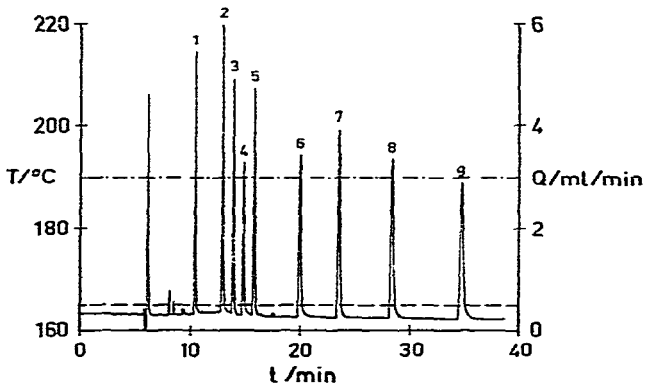


Fig. 4. Separation of a mixture of chlorinated hydrocarbons. Peaks: 1 = pentachlorobenzene (3.0 ng/$\mu$l); 2 = technazene (1.5 ng/$\mu$l); 3 = $\alpha$-HCH (2.0 ng/$\mu$l); 4 = $\beta$-HCH (4.0 ng/$\mu$l); 5 = $\gamma$-HCH (lindane) (2.5 ng/$\mu$l); 6 = pyrazon (2.0 ng/$\mu$l); 7 = heptachlor (2.0 ng/$\mu$l); 8 = aldrin (2.0 ng/$\mu$l); 9 = heptachlorepoxide (2.0 ng/$\mu$l). Splitter ratio: 1:100. Injection: 5 $\mu$l. Capillary column: 25 m, SE-30. Carrier gas: nitrogen. Electron-capture detector. Temperature: isothermal at 190°. Flow-rate: isorheic at 0.5 ml/min. —·—, Temperature curve. — — —, Flow-rate curve. Under these conditions, the analysis takes approximately 35 min. In Figs. 5–8, the separations were run with the same sample and under the same conditions apart from the temperature and flow-rate.

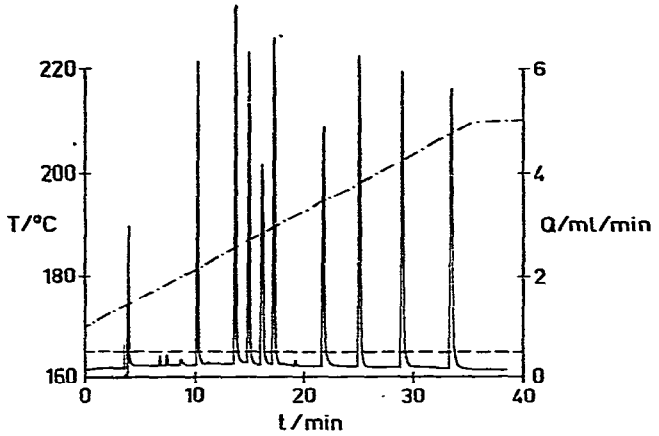


Fig. 5. As Fig. 4: isorheic at 0.5 ml/min. Temperature programming from 170 to 210° at a low programming rate (*ca.* 1°/min). The analysis time is unchanged (35 min). When programming in this manner, the separation is better in the first part of the chromatogram.

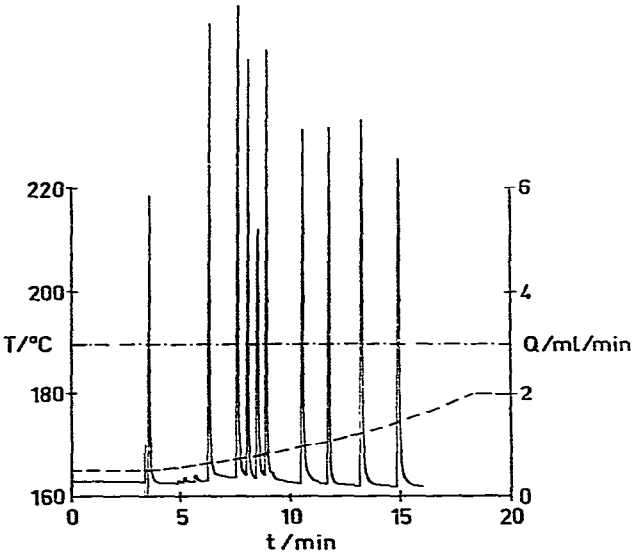


Fig. 6. As Fig. 4: isothermal at 190°. The flow programme is delayed until the solvent is eluted, then the flow-rate is increased exponentially from 0.5 to 2.0 ml/min in a 15-min programme. The analysis time is only 15 min, as the flow-rate is higher compared with the isorheic run.

exponentially programmed. The programme was not initiated until the solvent had eluted. The initial constant flow-rate is somewhat higher than the initial flow-rate of the programme; at the elevated flow-rate, the delay is shorter and the analysis is less time consuming. A commercial gasoline sample programmed in the same way as the PCB sample gave the pattern shown in Fig. 10.

In all of the programmed chromatograms, the peak widths are very narrow, and in some of the chromatograms they are almost constant during the whole run. This is possible when an exponential change of flow-rate is used.

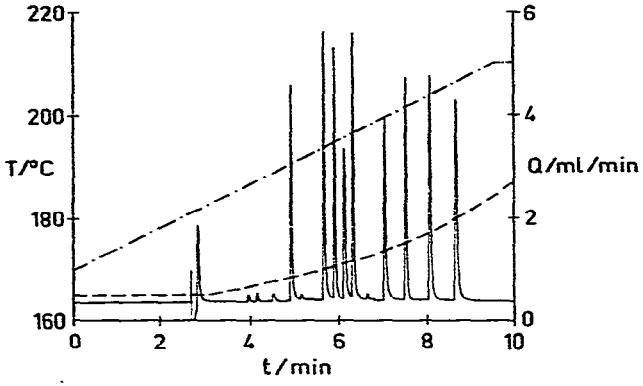


Fig. 7. As Fig. 4. A temperature programme is run from 170 to 210° at *ca.* 4°/min, at the same time as the gas flow is programmed. By double programming the analysis is accelerated, in this instance about 4-fold, and the separation is better in the first part, compared with the run shown in Fig. 4.

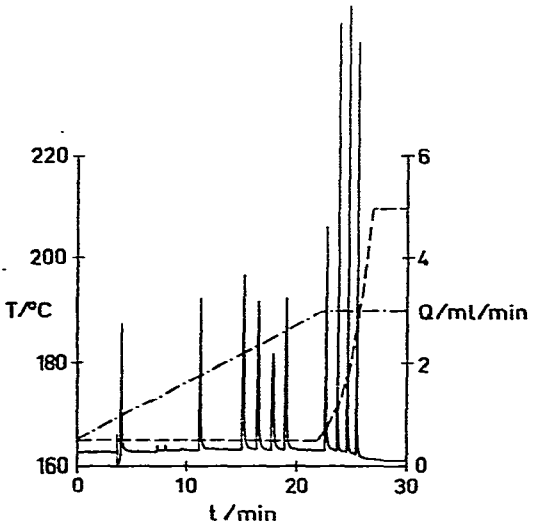


Fig. 8. As Fig. 4. This is an example of how the chromatogram can be programmed when there is a limitation at a rather low temperature. First, the run is temperature programmed from 165 to 190° at *ca.* 1°/min, followed by a very fast flow programme from 0.5 to 5.0 ml/min. The last four components are eluted about four times faster, at the same temperature, compared with the isorheic run shown in Fig. 4.

## DISCUSSION

In capillary column gas chromatography, the flow-rate of the carrier gas can be changed very quickly and the practical dynamic flow range is from about 0.1 to 10 ml/min. The volumetric flow-rate is usually measured as the ratio between the volume of the column and the retention time of a substance which is not retained. This gives an average flow-rate, which is the proper way of expressing the value of the flow-rate for programming[9,11].

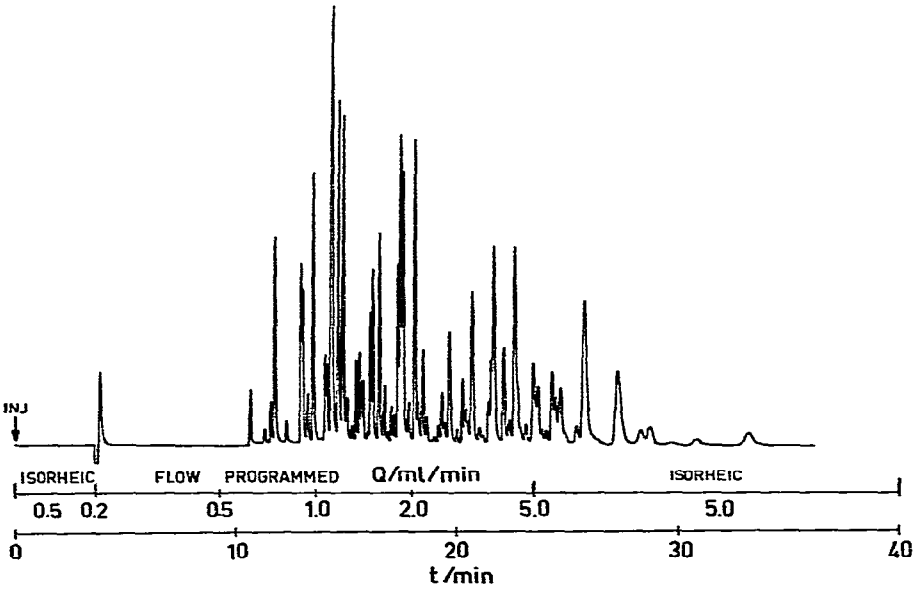


Fig. 9. Separation of a sample containing a mixture of components from the PCB Clophen A 30, 50 ng/$\mu$l. Exponential flow programme. Splitter ratio: 1:100. Injection: 5 $\mu$l. Capillary column: 25 m, SE-30. Carrier gas: nitrogen. Electron-capture detector. Isothermal at 200°.

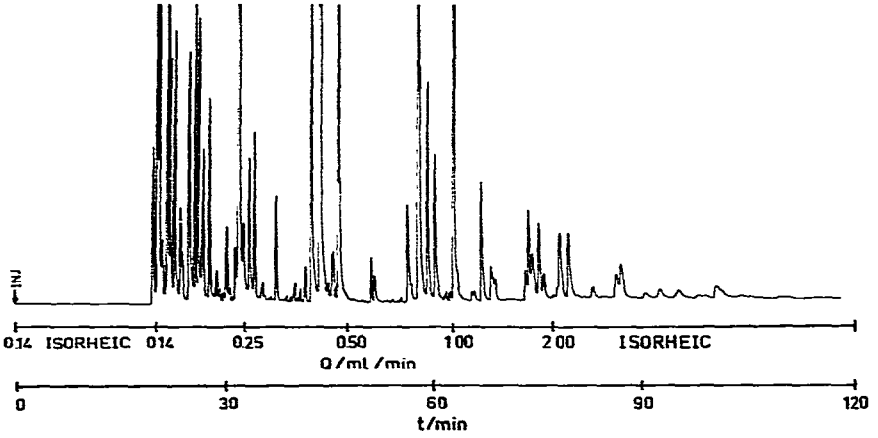


Fig. 10. Separation of a commercial gasoline sample. Exponential flow programme. Splitter ratio: 1:100. Injection: 5 $\mu$l. Capillary column: 40 m, SF 96. Carrier gas: nitrogen. Flame-ionization detector. Isothermal at 25°.

Pneumatic devices permit only rather limited variations of flow functions and seldom give a pure exponential form. When a mechanical system is used together with modern electronic equipment, any desired flow function can be programmed. The limitation seems to be the working range which, compared with temperature programming, corresponds to roughly 100° of programming range. As very sudden decreases or increases in flow-rate can be programmed, the initial conditions can be restored in a very short time after a run.

As the flow-rate will change during temperature programming, flow and temperature programming can also be used together in order to maximize the separating power of a capillary column.

A drawback of flow programming is the decrease in efficiency during a programme. Usually this problem is not serious, but one has to decide where the separation power is needed most and to choose the programming parameters so as to achieve the overall optimal separation conditions. Of course, the decrease in efficiency is much less pronounced when helium or hydrogen is used as the carrier gas instead of nitrogen. In general, the separation must always be related to the analysis time.

Both of the flow programming arrangements were devised mainly for studies of the flow function parameters in relation to the separation power and the time of analysis. For routine analytical purposes, the controlling unit must be simpler to handle for the user. With a micro-processor it is possible to construct an apparatus that is as easy to work with as a commercial temperature-programming unit.

By approaching the technique in this way, flow programming can be a versatile tool in gas chromatography, used either as an alternative to or together with temperature programming.

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