CARRIER GAS PROGRAMMING IN GAS CHROMATOGRAPHY BY MEANS OF ALTERNATELY CONNECTED COLUMNS UNDER ISOTHERMAL CONDITIONS

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Gas chromatography is one of the most rapidly developed branches of instrumental analysis. It is especially important in organic analysis because of its high sensitivity and the good separation that can be attained. On a suitably prepared column the components of even a complicated system can be obtained separately. The efficiency of analysis can be improved by changing the temperature of column and inlet pressure (flow rate) of carrier gas during the analysis. Sometimes these operations are inevitable since some components may be bound to the column so strongly that the analysis lasts very long. The time of residence of the single components in the column can be changed at will by increasing or reducing the flow rate of carrier gas according to a program.

Some authors have suggested the method of programmed flow as soon as in 1959—1960 [1—3]. Although the research work done in the field has brought important practical and theoretical results [4—8], the results made possible the evolution and quick development of the new technique only after 1964 [9—15].

Carrier gas programming can be realized in continuous and combined form. Carrier gas programming is stepwise, if the program prescribes one or more sudden changes of the inlet pressure (flow rate) during the analysis. Stepwise carrier gas programming can be realized in three different ways:

1. By the stepwise, discontinuous variation of the inlet pressure of the carrier gas [16—17].
2. By back-flush [18—19].
3. By means of alternately connected columns.

In our present paper the stepwise, discontinuous programming by means of alternately connected columns is dealt with under isothermal conditions. This carrier gas programming may be

1. accelerating
2. retarding and
3. mixed (accelerating — retarding).

Carrier gas programming may be called accelerating if the following relationships hold for an analysis:

$$F_1 < F_2 < F_3 < \ldots < F_k . \tag{1}$$

Carrier gas programming is retarding if the below relationships hold for an analysis:

$$F_1 > F_2 > F_3 > \ldots > F_k . \tag{2}$$

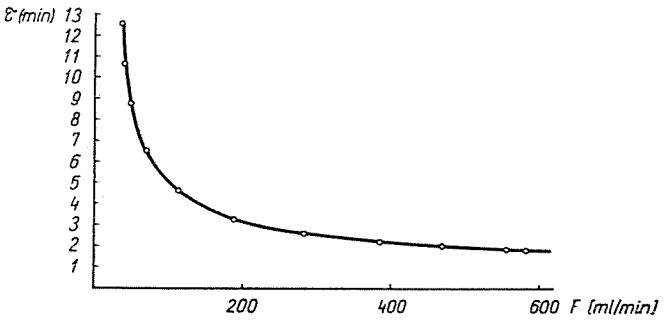

Fig. 1

The programming is mixed if

$$F_1 > F_2 > F_3 < F_4 > F_5 \ldots \tag{3}$$

or

$$F_1 < F_2 < F_3 > F_4 < F_5 \ldots \tag{4}$$

i.e. the program consists of accelerating and retarding sections. Accelerating program means short analysis time, but it sometimes does not result in the appropriate resolution of the bands. As proved by experience, the increase of the flow rate of carrier gas above a certain limit does not result in a remarkable reduction in analysis time, as shown in Fig. 1.

Carrier gas programming by alternately connected columns seemed to eliminate the difficulties mentioned above, since this technique was likely to combine short analysis time with good resolution of peaks. The results of experiments have proved the above assumptions.

The chromatogram shown in Fig. 2 was produced by a Carlo Erba Fractovap Model C type instrument under the following experimental conditions:

Detector: thermistor
Bridge current: 20,0 mA
Sensitivity: 1/4
Columns:

Column A: 0.3 m in length, 4 mm in internal diameter, U-shaped, high speed column (Fig. 3).

Column B: 2.5 m long, 5 mm internal diameter spiral copper tube.

Column fillings:

Column A: 0.5 per cent by weight of silicone oil 550 on 100/120 mesh glass bead support.

Column B: 20.0 per cent by weight of silicone oil 550 on 60/80 mesh Celite 545 support.

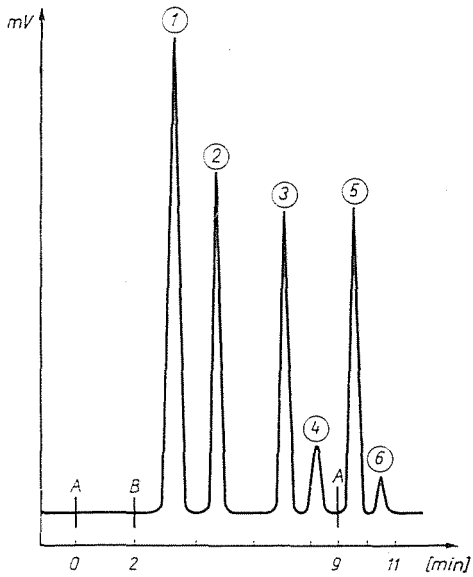

Fig. 2. Chromatogram of a model mixture obtained with programming by alternately connected columns. Components of the mixture in the order of peaks: 1. benzene; 2. toluene; 3. m- and p-xylene; 4. o-xylene; 5. methyl salicylate; 6. methyl phthalate

Symbols:

F	= volumetric flow rate of the carrier gas (ml/min)
k	= serial number
t_{Rp}	= programmed retention time (min)
z	= serial number of components
w	= band width (min)
V_N	= net retention volume (ml carrier gas)
$\Delta V_{\min}$	= the minimum value of ΔV calculated from the net retention volumes of the components
x, $x+1$	= serial number of the components belonging to the $\Delta V_{\min}$ value
t	= time (min)
t_M	= retention time of air (argon, helium) (min)
A, B	= designation of the columns
j	= correction factor
t_h	= residence time in the switched off column (min)
t^*	= time passed between the switching on the column until the appearance of the component in maximal concentration (min)
p_i	= inlet pressure of carrier gas (kg/cm^2)
τ	= analysis time (min)

Temperature of columns: 140.0±0.1° C
Temperature of evaporator: 280.0±1° C
Sample: 3.0 μl introduced by a Hamilton syringe.
Recorder: Speedomax G; 2.5 mV final amplitude; 1.0 sec.
Chart speed: 1.27 cm/min.

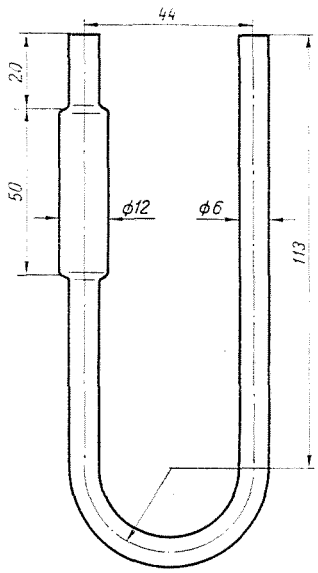

Fig. 3

In general minimum analysis time can be obtained for carrier gas programming by means of alternately connected columns if the following relationship holds for each constituent of the sample:

$$t_{Rp(z+1)} - t_{Rp(z)} = \frac{w_{(z+1)} + w_{(z)}}{2} . \tag{5}$$

In many cases the composition of the sample does not allow a carrier gas program according to equation (5). In these cases the conditions prescribed by equation (5) must be approached as near as possible so that

$$t_{Rp(z+1)} - t_{Rp(z)} > \frac{w_{(z+1)} + w_{(z)}}{2} . \tag{6}$$

Calculations concerning the carrier gas program are based on the normal chromatogram [17] and also the jF—p_i pairs measured at the temperature T

of the analysis must be known. The retention times, net retention volumes for the components and also ΔV values are calculated from the normal chromatogram, where

$$\Delta V_{z+1;z} = V_{N_{z+1}} - V_{N_z} . \tag{7}$$

With the knowledge of the retention times the point of time at which the columns must be exchanged, and the original volumetric flow rate of carrier gas F_0 must be changed to a certain F_1 value is determined without any calculation, according to the properties of sample. This point of time must be chosen so that all volatile components of the sample leave column 1 by this time. The maximum of F_1 has to be calculated by means of the following relationship:

$$j_1 F_1 = \frac{2\Delta V_{\min}}{w_x + w_{x+1}} . \tag{8}$$

All the data on the right side of equation (8) can be obtained from the normal chromatogram so that $j_1 F_1$ can be calculated.

With accelerating program care must be taken that the flow rate of carrier gas must not be higher than the calculated value because this may result in the overlapping of peaks.

The calculation of the retention time and net retention volume of the components for programming with alternately connected columns has to be carried out as follows (given for components 2 and 6 in Fig. 2).

The programmed retention time of component 2:

$$t_{Rp(2)} = t_{AB} + t_B^x \tag{9}$$

and of component 6:

$$t_{Rp(6)} = t_{AB} + t_B + t_A^x . \tag{10}$$

Net retention volume for component 2:

$$V_{N(2)} = j_{AB} F_{AB} (t_{AB} - t_M) + j_B F_B t_B^x \tag{11}$$

and for component 6:

$$V_{N(6)} = j_{AB} F_{AB} (t_{AB} - t_M) + j_A F_A t_A^x . \tag{12}$$

Carrier gas programming under isothermal conditions by means of alternately connected columns gives rise to increased requirements towards the evaluation of results. The difficulties can only be overcome by means of the internal standard addition method.

The described method of carrier gas programming was successfully used for performing different analytical problems. The calculation of the program is more involved than in other cases but the results are better than those obtained with other methods.

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Summary

Carrier gas programming by means of alternately connected columns is a possibility of the analytical application of programmed flow gas chromatography. It ensures short analysis time and also good resolution of peaks at the same time, within the limits determined by the minimum ΔV and the performance of the instrument, and so makes possible the resolution of different analytical problems.

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