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## Gas Chromatography with Backflushing: Isothermal during the First Step, Programming of Longitudinal Temperature Gradient during the Second Step

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### Abstract

A new method derived from gas chromatography with backflushing is described. It is a two-step method: isothermal during the first direction of gas flow and then, at backflushing time, the gas flow is reversed and simultaneously a program of longitudinal temperature gradient is started. Volatile solutes are eluted during the forward direction of the carrier gas in the usual way while poorly volatile ones are reversed and separated into narrow and closely spaced peaks. For this method the retention times of poorly volatile solutes are shorter and the column temperature is lower than for classical ones. The results of the retention theory are easy to use with the help of a nomogram. Hence any analyst is able to find the best parameter values in order to solve his own problem in less than 1 min.

### INTRODUCTION

The application of GC to the analysis of a mixture is not easy when its components have very different volatilities and are sensitive to temperature. It is well known that chromatography with backflush is often the best method to solve those difficult problems. Isothermal chromatography with backflush has been used for many years (1-3). By using this method, volatile solutes are conventionally eluted during the first direction of gas flow. At backflushing time, the gas flow is reversed and the poorly volatile solutes appear on the chromatogram as broad and poorly separated peaks (Fig. 1). However, the main advantages of this method over the other classical ones are a lower column temperature and a shorter retention time.

Development of backflushing methods has led to a more sophisticated method and also to better performance (4,5). However, the commercial

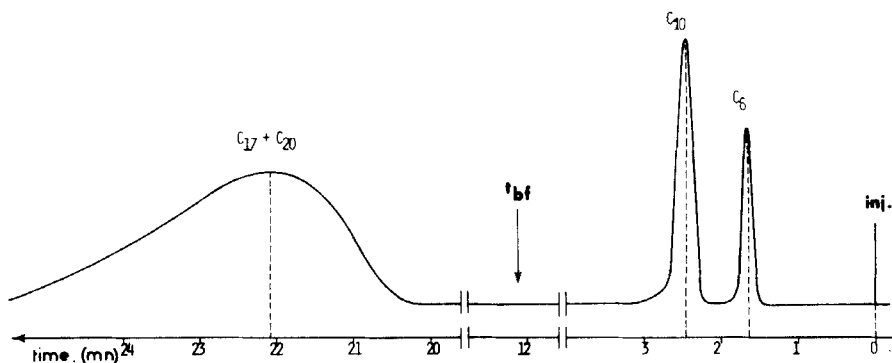


FIG. 1. Chromatogram with isothermal backflush.  $C_6$ : hexane.  $C_{10}$ : decane.  $C_{17}$ : heptadecane.  $C_{20}$ : eicosane.  $t_{bf} = 727$  s.  $T_0 = 423$  K. 2% OV 17.

backflush tap caused poorly volatile solutes to be trapped and this fact largely reduced interest in this work.

In this paper we have overcome this fact by using our own backflush tap. Moreover, in previous papers (4, 5) another problem was noticed. This concerned the difficulty of calculating the retention time of solutes by using the transcendental equation. Therefore we show in this paper a nomogram permitting both the retention time of any solute and the best operational conditions to be found.

## THEORETICAL PART

Classical assumptions were made:

- (1) The linear gas velocity did not vary greatly along the column, and it varied little with temperature.
- (2) Programming of a longitudinal temperature gradient started at back-flushing time with a constant heating rate.
- (3) The temperature gradient was such that the temperature was kept constant at the column inlet, while a linear temperature program took place at the column outlet.

In isothermal conditions, the speed of a solute was

$$dx/dt = L/trT \quad (1)$$

where  $L$  is the column length and  $trT$  is the retention time of the solute at temperature  $T$ . At backflushing time,  $t_{bf}$ , the solute abscissa was  $x$ :

$$x = tbf \frac{L}{trT} \tag{2}$$

During the reverse direction of gas, this solute went back into the column and the column temperature was a function of abscissa and time:

$$dT = V_0 \frac{t}{L} dx + V_0 \frac{x}{L} dt \tag{3}$$

where  $V_0$  is the rate of the temperature program at the column outlet.  
The combination of these equations gave a transcendental equation:

$$\frac{dT}{dx} = V_0 trT \frac{L - x}{L^2} - \frac{T - T_0}{L - x} \tag{4}$$

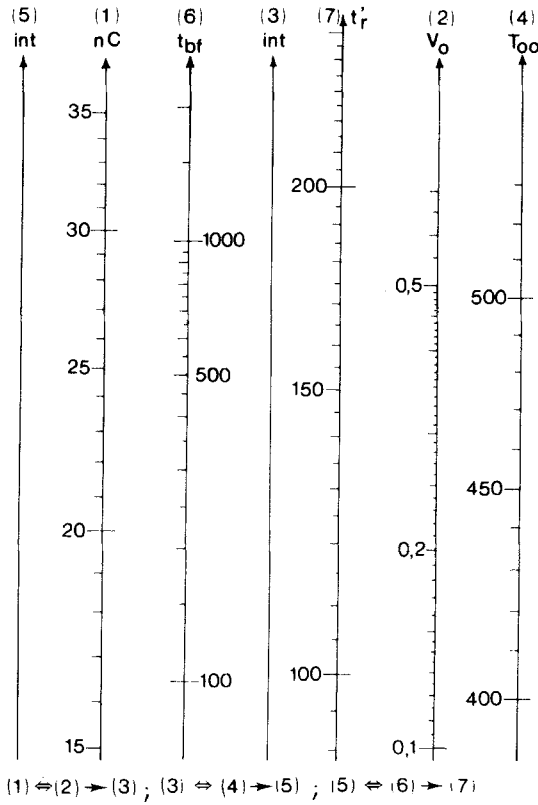


FIG. 2. Nomogram with logarithmic scales.

in which the retention time of a solute in the isothermal condition depended on the temperature according to the classical relation

$$trT = tg \left[ 1 + A \exp \frac{\Delta H_v}{RT} \right] \quad (5)$$

where  $tg$  is the retention time for the carrier gas, and  $A$  and  $\Delta H_v$  are being a constant characteristic of the solute and its vaporisation enthalpy, respectively.

Equation (4) was numerically solved, step by step. A nomogram with a logarithmic scale for all the parameters is shown as Fig. 2. By using this nomogram and a ruler, it does not take more than 30 s to find the retention time for any solute. This nomogram requires the carbon number of the solute when the solute is an alkane, or its retention index ( $nC$ ) in other cases. The time taken between the instant when the gas flow was changed (at  $tbf$ ) and the retention time ( $t'r$ ). Of course, the retention time was the sum of  $tbf$  and  $t'r$ .

## RESULTS AND INFLUENCE OF PARAMETERS

Three parameters are of importance in regard to the retention time of a solute: backflushing time, initial column temperature, and gradient heating rate.

By using the method of less square roots, we found the following relation between time  $t'r$  and the values of the other parameters:

$$t'r = 19 \times 10^{-5} (tbf)^{0.5} (T_0)^{2.1} (nC)^{-0.88} (V_0)^{-0.38} \quad (6)$$

### Backflushing Time $tbf$

Because time  $t'r$  was found to be shorter than time  $tbf$ , the retention time was then smaller than  $2tbf$ . The increase in  $t'r$  was smaller than the corresponding increase in  $tbf$ , as shown in Eq. (6). Another interesting fact was that the higher the retention index of the solute, and shorter was its retention time.

### Initial Column Temperature $T_0$

Our method permitted us to work at a lower temperature than in the usual methods. The use of a higher initial temperature enabled the solute to penetrate deeper into the column and also led to a much narrower peak, and thus improved the separational process.

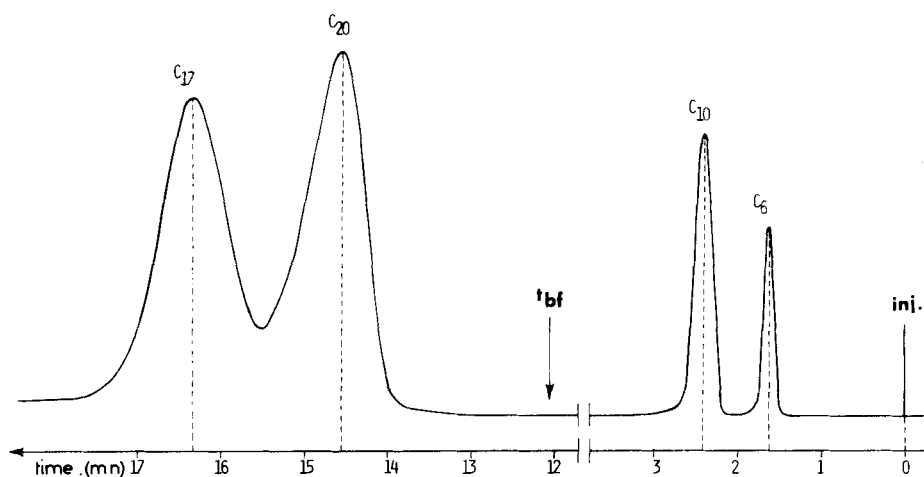


FIG. 3. Chromatogram with our method. The same solutes as in Fig. 1.  $t_{bf} = 727$  s.  $T_0 = 423$  K. 2% OV 17.  $V_0 = 0.28^\circ/\text{ms}$ .

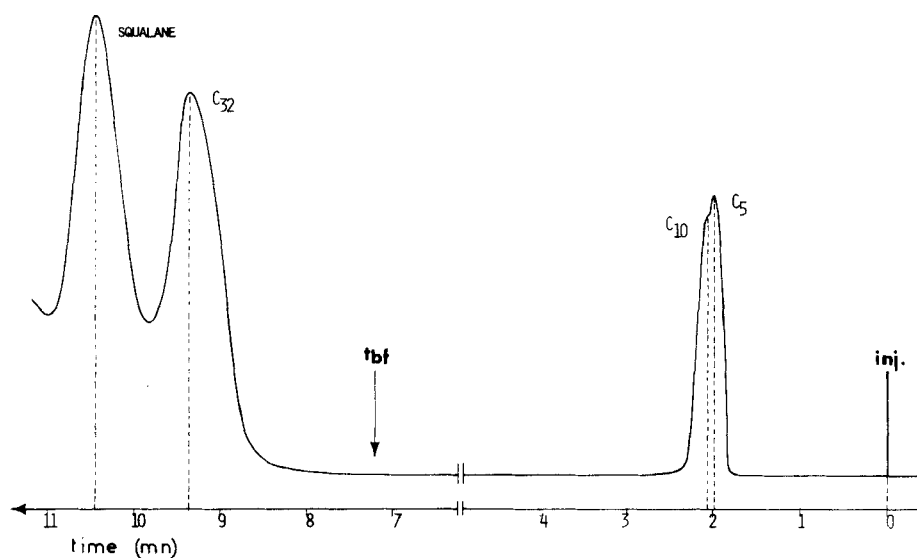


FIG. 4. Chromatogram with our method.  $t_{bf} = 432$  s.  $T_0 = 523$  K. 2% OV 17.  $V_0 = 0.50^\circ/\text{ms}$ .  
Solute: alkanes (with their carbon number) and squalane.

TABLE 1

Solutes		Calculated $t'_r$	Experimental $t'_r$
C <sub>20</sub>	} Fig. 3	165 s	160 s
C <sub>7</sub>		240 s	260 s
C <sub>32</sub>	Fig. 4	125 s	130 s

### Gradient Heating Rate $V_0$

Equation (6) shows that an increase in the gradient heating rate involves a decrease in time  $t'_r$ . This increase in the gradient heating rate also led to a narrower peak for the solute and improved separation.

### CONCLUSIONS

Two chromatograms are compared in Figs. 1 and 3. They were obtained with the same solutes (i.e., alkanes, the carbon numbers of which are noted) and under the same conditions of backflush, but in Fig. 3 a temperature gradient appeared. With our method there was a reduction in the retention time and also a complete separation of the solutes.

Another chromatogram is shown in Fig. 4 with solutes consisting of squalane and alkane with 32 carbons.

A comparison is shown in Table 1 between the experimental values of the retention time of the solutes and the corresponding calculated ones.

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