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GAS CHROMATOGRAPHY WITH BACKFLUSHING. WITH LINEAR TEMPERATURE PROGRAMMING IN THE FIRST DIRECTION AND A PROGRAMMED LONGITUDINAL POSITIVE TEMPERATURE GRADIENT DURING THE OPPOSITE DIRECTION OF GAS FLOW

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SUMMARY

A new application of gas chromatography with backflushing is proposed: it may be defined as a two-stage operation. In the first stage the carrier-gas flow is in the usual direction and the temperature of the column is programmed at constant rate. In the second stage, the temperature programming is stopped, the gas flow is reversed and the column is heated by a positive longitudinal temperature gradient, the growth rate of which is constant. The column inlet is maintained at constant temperature. A theory of retention of solutes is proposed, and the role of the following parameters is specified: time of backflushing, rate of linear temperature programming, rate of gradient temperature programming, column temperature at time of injection. The advantages of this technique over classical backflushing gas chromatography include shorter retention times, narrower peaks and improved resolution.

INTRODUCTION

Backflushing gas chromatography has been known for many years^{1,2}. With this method, volatile solutes are conventionally eluted during the first direction of carrier-gas flow; at backflushing time (t_{bf}), the gas flow is reversed and the less volatile solutes that are still in the column are eluted as broadened and poorly separated peaks. The main advantage of this method is that complete analysis of poorly volatile solutes in a mixture may be carried out at a lower temperature (and with shorter retention times) than in isothermal gas chromatography, but these solutes are not well separated and cannot be determined individually.

We have already used^{3,4} backflushing gas chromatography under isothermal conditions in the first direction of gas flow and with a positive longitudinal temperature gradient during the reverse direction of carrier gas. This method provides considerably narrower peaks for the solutes that have been "reversed" and permits their partial separation.

Development along this line of research has led to a more sophisticated meth-

od, with better performance; this is a variant of backflushing gas chromatography in which, during the forward direction of the carrier gas, the volatile solutes are eluted (with linear temperature programming). During backflushing the carrier-gas direction is reversed, temperature programming is stopped and programming of the longitudinal temperature gradient is started simultaneously. Thus, the poorly volatile solutes that have been "reversed" are separated into narrow and closely spaced peaks.

THEORY OF MIGRATION OF SOLUTES

In this section, the following assumptions are made:

- (1) The carrier gas and the solute vapours behave as ideal gases.
- (2) The linear gas velocity in the forward direction varies according to Darcy's law, but is almost constant during the reverse direction; it varies little with temperature.
- (3) Temperature programming involves a constant heating-rate; it starts at injection and stops at the backflushing time, without thermal inertia.
- (4) The positive longitudinal temperature gradient programming starts at the backflushing time; its heating-rate is constant.
- (5) The solute-solvent system is in thermodynamic equilibrium.
- (6) The standard vaporisation enthalpy of the solute in solution does not vary with temperature.

At temperature T and abscissa value x (see Fig. 1), the solute-migration speed is equal to the product of the retention coefficient R_{ft} and the linear carrier-gas velocity U_x , thus

$$\frac{dx}{dt} = U_x \cdot R_{ft} \quad (1)$$

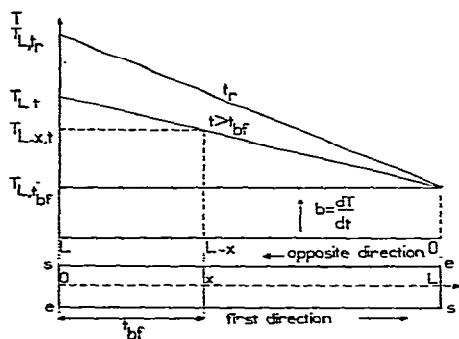


Fig. 1. Scheme representing column and principle of method.

By using Darcy's and Boyle-Mariotte's laws, the pressure (P_x) is obtained as a function of the column length, L :

$$P_x = \left[P_e^2 - \frac{x}{L} (P_e^2 - P_s^2) \right]^{\frac{1}{2}} \quad (2)$$

where P_s and P_e are the pressures at the column outlet and inlet, respectively.

The retention coefficient of a solute at a temperature T is related to the standard vaporisation enthalpy of this solute in solution by the expression

$$R_{ft} = \left[1 + \exp \frac{-\overline{\Delta S}_v^0}{R} \cdot \exp \frac{\overline{\Delta H}_v^0}{RT} \right]^{-1} \quad (3)$$

where R is the ideal-gas constant and $\overline{\Delta S}_v^0$ is the standard vaporisation entropy of the solute in solution (unrelated to the temperature) and $\overline{\Delta H}_v^0$ is the standard enthalpy of vaporisation of the solute in solution on the column.

Solute migration in the first direction of carrier-gas flow, with temperature programming during the backflushing time (t_{bf})

At zero time and temperature T_0 , the solute is injected and temperature programming starts simultaneously. Solute migration takes place until the backflushing time, t_{bf} , during the forward direction of carrier-gas flow. At time t_{bf} , the solute has travelled a distance x and the column temperature is T_{bf} . The heating-rate, b , is given by the relationship

$$b = \frac{dT}{dt} \quad (4)$$

Combination of eqns. 1, 2 and 4 gives the fundamental differential equation

$$\frac{dx}{U_x} = \frac{1}{b} \cdot R_f \cdot dT \quad (5)$$

Integration of this equation between zero and x for the first member and between T_0 and T_{bf} for the second member gives the distance x where the solute is found at time t_{bf} , by rewriting eqn. 3 as follows

$$t_{gv} \cdot \frac{P_e^3 - P_x^3}{P_e^3 - P_s^3} = \frac{1}{b} \int_{T_0}^{T_{bf}} R_f \cdot dT \quad (6)$$

where

$$t_{gv} = \frac{2L}{3V_s \cdot P_s} \cdot \frac{P_e^3 - P_s^3}{P_e^2 - P_s^2}$$

The integral in the second member of eqn. 6 is transcendental and can be resolved numerically by means of the trapezoid rule.

Solute migration in the opposite direction of carrier-gas flow, with positive longitudinal temperature gradient programming

At time t_{bf} , the following three operations are carried out simultaneously: backflushing of the carrier gas, stopping of the temperature programming, and starting of the positive longitudinal temperature gradient programming at constant rate.

With the positive longitudinal temperature gradient, the outlet temperature of the column during backflushing increases linearly and the inlet temperature remains constant (see Fig. 1).

During backflushing, the column temperature is a function of the distance x and time t :

$$dT = \left(\frac{\delta T}{\delta x}\right)_t \cdot dx + \left(\frac{\delta T}{\delta t}\right)_x \cdot dt \quad (7)$$

At distance $(L - x)$ and time t , this temperature T is given by (see Fig. 1):

$$T_{L-x,t} = V_L \cdot t \cdot \frac{L-x}{L} + T_{L,t_{bf}} \quad (8)$$

where V_L ($^{\circ}\text{C}/\text{sec}$) is the gradient heating rate at the column outlet during backflushing.

The theory of solute retention in the reverse direction has been derived⁴, so that we know the fundamental differential relation to be given by

$$\frac{dT}{dx} = V_L \cdot \frac{L-x}{L^2} \cdot t_{rT} - \frac{T_{L-x,t} - T_{L,t_{bf}}}{L-x} \quad (9)$$

This equation cannot be integrated and it has been numerically solved by using a computer. For the value L of distance x , we obtain the solute retention temperature T_{L,t_r} .

The integration of eqn. 4 between $T_{L,t_{bf}}$ and T_{L,t_r} for temperature gives the time (t'_r) taken by the solute to leave the column when the carrier gas is flowing in the reverse direction, so that

$$t'_r = \frac{T_{L,t_r} - T_{L,t_{bf}}}{V_L} \quad (10)$$

APPARATUS AND EXPERIMENTAL CONDITIONS

An F7 gas chromatograph (Perkin-Elmer) equipped for temperature programming and backflushing and fitted with a stainless-steel column (2 m long; 4 mm I.D.; 6 mm O.D.). The stationary phase was SE-30 silicone rubber (20%) supported on Gas-Chrom R (60–80 mesh), and the carrier gas was hydrogen ($P_e = 1.81$ atm; $P_s = 1.38$ atm; flow-rate 53.5 ml/min) (Air Liquide, Paris, France).

The longitudinal temperature gradient was achieved by means of insulated resistance wire (12.5 Ω/m) wound round the column (the length of wire per unit of column length varied along the column according to an arithmetical progression). Linear longitudinal temperature gradient programming was attained by applying a variable voltage and was continuously recorded.

The test solutes were n -alkanes for which the values of $\overline{\Delta H}_v^0$ and A ($= \overline{\Delta S}_v^0/R$) had been calculated (see Table I).

TABLE I

VALUES OF STANDARD ENTHALPY OF VAPORISATION OF SOLUTE IN SOLUTION ($\overline{\Delta H}_v^0$) AND OF THE CONSTANT A

Values of $\overline{\Delta H}_v^0$ are expressed in cal/mole.

Parameter	Solute					
	<i>n</i> -Hexane	<i>n</i> -Heptane	<i>n</i> -Octane	<i>n</i> -Nonane	<i>n</i> -Decane	<i>n</i> -Undecane
$\overline{\Delta H}_v^0$	5914	6800	7960	8680	9260	10256
$A \times 10^3$	1.033	0.623	0.369	0.194	0.160	0.082

EXPERIMENTAL RESULTS AND EFFECTS OF PARAMETERS

Values of retention times calculated from eqns. 9 and 10 coincided well with the corresponding experimental values, the relative error being less than 10% and resulting mainly from the temperature programming during the first direction, which has an inertia when starting and stopping.

We shall now consider the influence of the following parameters of our method on retention time and solute-separation efficiency: backflushing time, t_{bf} ; temperature heating-rate, b ; longitudinal gradient heating-rate, V_L ; and column temperature at injection, T_0 .

Influence of backflushing time

The influence of the backflushing time was studied by keeping T_0 at 76° , V_L at $9^\circ\text{C}/\text{m}\cdot\text{min}$ and b at $10^\circ\text{C}/\text{min}$ and varying t_{bf} successively. We illustrate the effect by considering t_{bf} values of 300 and 480 sec.

Figs. 2 and 3 show chromatograms obtained by our method. In Fig. 2 ($t_{bf} = 300$ sec), hexane is eluted in the first direction, and the pair heptane–octane are eluted in the opposite direction. In Fig. 3 ($t_{bf} = 480$ sec), hexane and heptane are eluted in the first direction, and octane–nonane in the opposite direction. The peaks of the solutes eluted in our method are much narrower than in conventional backflushing gas chromatography, and separation is attained.

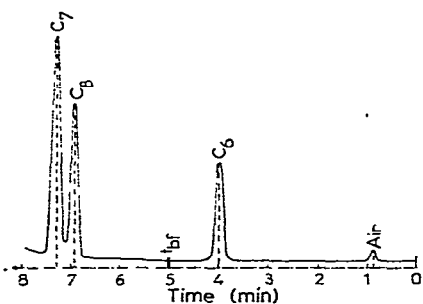


Fig. 2. Chromatogram of hexane (in first direction), heptane and octane: $t_{bf} = 300$ sec. $T_0 = 76^\circ\text{C}$, $b = 10^\circ\text{C}/\text{min}$, and $V_L = 9^\circ\text{C}/\text{m}\cdot\text{min}$.

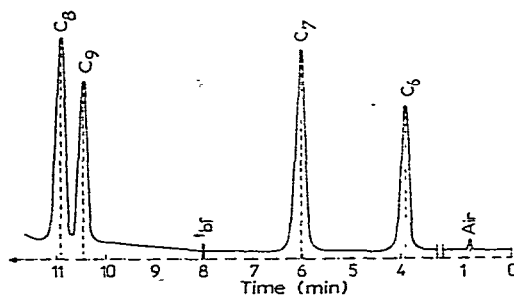


Fig. 3. Chromatogram of hexane, heptane (in first direction) and octane–nonane: $t_{bf} = 480$ sec; T_0 , b and V_L as in Fig. 2.

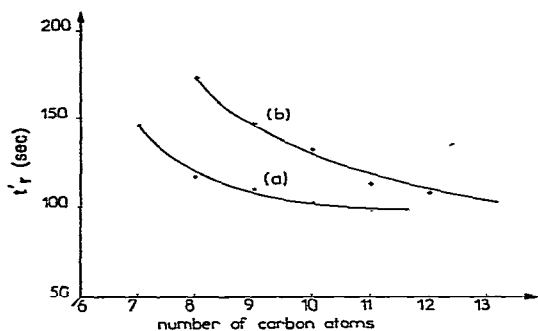


Fig. 4. Variation of time t'_r with carbon number of alkanes: (a) $t_{bf} = 300$ sec; (b) $t_{bf} = 480$ sec. Other parameters as in Fig. 2.

We found it of interest to express the variation in retention times of n -alkanes eluted by our method as a function of their carbon numbers; the results are plotted in Fig. 4, from which we can derive the limit of separation of our method.

Influence of heating rate

Temperature programming intervenes during the first direction of chromatography, and its influence appears in the solute position (x) at time t_{bf} . The influence of the heating rate (b) was established by operating with $b = 10$ °C/min and 15 °C/min, keeping T_0 at 76 °C, t_{bf} at 300 sec and V_L at 9 °C/m·min.

The values of the retention times are shown in Table II ($b = 15$ °C/min), together with the positions (x) of the solutes at time t_{bf} and the values of the resolution factor and the fraction $\Delta t_r/t_r$, where Δt_r is the peak width at the base.

From this study, we conclude that the retention time of hexane eluted in the first direction is shorter when b has its highest value; similarly, the other solutes penetrated further into the column when b was 15 °C/min.

We also conclude that the time t'_r is very slightly increased when b is varied from 10 to 15 °C/min, this increase being greater with nonane than with heptane. Also, the peaks are narrower when b is at its highest value, and finally, the resolution factor is improved when a high value is selected for b . Thus, for the pair heptane-nonane, this factor varies from 1.75 when b is 10 °C/min to 1.86 when b is 15 °C/min.

Influence of gradient heating rate

We studied the influence of the gradient heating rate (V_L) by operating at three values of V_L , keeping t_{bf} at 300 sec, b at 10 °C/min and T_0 at 76 °C; the values chosen

TABLE II
EFFECT OF HEATING RATE ($b = 15$ °C/min.)

Backflushing time (t_{bf}) = 300 sec.

Solute	t_r , sec	x , cm	t'_r	$\Delta t_r/t_r$
Hexane	212	—	—	0.081
Heptane	—	191	143	0.04
Nonane	—	54	107	0.05

Resolution factor: $C_7-C_9 = 1.86$.

TABLE III
EFFECT OF GRADIENT HEATING RATE (V_L)

Backflushing time (t_{bf}) = 300 sec.

Parameter	<i>n</i> -Hexane	<i>n</i> -Heptane	<i>n</i> -Octane	<i>n</i> -Nonane	<i>n</i> -Decane	<i>n</i> -Undecane	<i>n</i> -Dodecane
With $V_L = 4.5^\circ\text{C}/\text{m}\cdot\text{min}$							
t_r , sec	236	—	—	—	—	—	—
t'_r , sec	—	160	132	128	115	110	—
$\Delta t_r/t_r$	0.081	0.05	0.06	0.07	0.10	0.11	—
Resolution factor: $C_7-C_8 = 0.95$; $C_7-C_9 = 1.25$; $C_7-C_{10} = 1.57$							
With $V_L = 13.5^\circ\text{C}/\text{m}\cdot\text{min}$							
t_r , sec	236	—	—	—	—	—	—
t'_r , sec	—	132	109	99	86	75	72
$\Delta t_r/t_r$	0.08	0.04	0.04	0.04	0.05	0.10	0.12
Resolution factor: $C_7-C_8 = 1.40$; $C_7-C_9 = 1.88$; $C_7-C_{10} = 2.31$; $C_7-C_{11} = 2.10$; $C_7-C_{12} = 1.79$.							

for V_L were 4.5, 9 and $13.5^\circ\text{C}/\text{m}\cdot\text{min}$. The retention times, expressed as t'_r (sec), the resolution-factor values and the values of the fraction $\Delta t_r/t_r$ are shown in Table III.

Three chromatograms for the same solutes (hexane, heptane and octane) eluted with different gradient heating rates (4.5 , 9 and $13.5^\circ\text{C}/\text{m}\cdot\text{min}$) are shown in Figs. 6, 2 and 7, respectively.

Consideration of the values in Table II and the three chromatograms shows that t'_r decreases very quickly if a high value is selected for V_L . For example, under the chosen experimental conditions, we gain 30 sec for each solute when V_L is increased from 4.5 to $13.5^\circ\text{C}/\text{m}\cdot\text{min}$. Use of a high value for V_L also leads to narrower peaks and an improved separation.

Influence of initial column temperature

To study the influence of the initial column temperature (T_0) on retention time, we kept V_L at $9^\circ\text{C}/\text{m}\cdot\text{min}$, t_{bf} at 300 sec and b at $10^\circ\text{C}/\text{min}$, and used T_0 values of 76° and 110° ; the resulting resolution times and resolution factors are shown in Table IV.

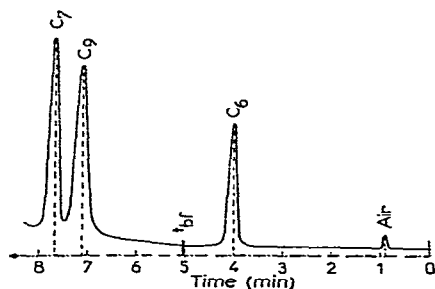


Fig. 5. Chromatogram of hexane (in first direction), heptane and nonane: $t_{bf} = 300$ sec, $T_0 = 76^\circ\text{C}$, $b = 15^\circ\text{C}/\text{min}$, and $V_L = 9^\circ\text{C}/\text{m}\cdot\text{min}$.

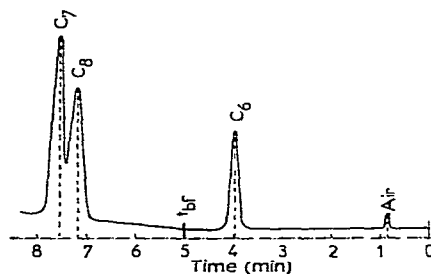


Fig. 6. Chromatogram of hexane (first direction), heptane and octane: $t_{bf} = 300$ sec, $T_0 = 76^\circ\text{C}$, $b = 10^\circ\text{C}/\text{min}$, and $V_L = 4.5^\circ\text{C}/\text{m}\cdot\text{min}$.

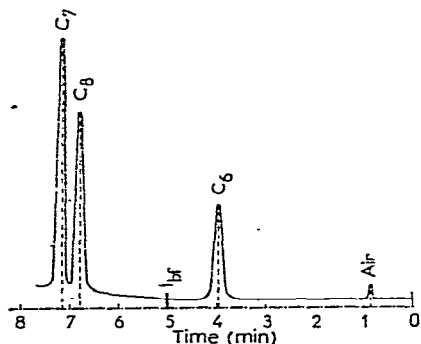


Fig. 7. Chromatogram of hexane (first direction), heptane and octane: $V_L = 13.5^\circ \text{C/m}\cdot\text{min}$; other parameters as in Fig. 6.

TABLE IV
EFFECT OF INITIAL TEMPERATURE (T_0)

Parameter	<i>n</i> -Hexane	<i>n</i> -Heptane	<i>n</i> -Octane	<i>n</i> -Nonane	<i>n</i> -Undecane
With $T_0 = 76^\circ \text{C}$					
t_r , sec	236	—	—	—	—
x , cm	—	151	78	40	22
t'_r , sec	—	141	116	100	84
$\Delta t_r/t_r$	0.08	0.04	0.05	0.06	0.10
Resolution factor: $C_9-C_{11} = 0.47$					
With $T_0 = 110^\circ \text{C}$					
t_r , sec	128	189	280	—	—
x , cm	—	—	—	145	51
t'_r , sec	—	—	—	146	122
$\Delta t_r/t_r$	0.09	0.08	0.07	0.04	0.05
Resolution factor: $C_9-C_{11} = 1.19$					

It is clear that, with the highest initial temperature, more solutes are eluted during the forward direction of the carrier gas (hexane when $T_0 = 76^\circ$; hexane, heptane and octane when $T_0 = 110^\circ$).

In Fig. 8, we show the chromatogram of the five alkanes eluted by our method, with an initial temperature of 110° .

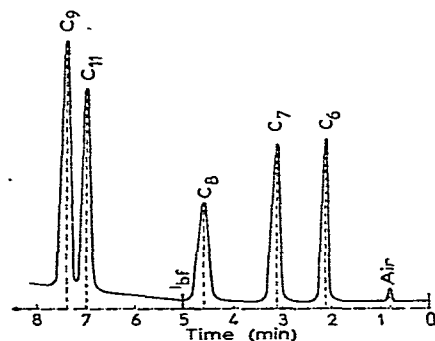


Fig. 8. Chromatogram of hexane, heptane, octane (first direction), nonane and undecane: $T_0 = 110^\circ \text{C}$, $t_{bf} = 300$ sec, $V_L = 9^\circ \text{C/m}\cdot\text{min}$, and $b = 10^\circ \text{C/min}$.

From Table IV and Fig. 8, it may be deduced that use of a higher initial temperature enables the solutes to penetrate deeper into the column (so that the emergence times of the solutes are a little longer) and also leads to much narrower peaks. Moreover, a higher T_0 value improves the separation of those solutes that have been "reversed"; thus, the resolution factor for the pair nonane–undecane is multiplied by 2.5 when T_0 is increased from 76° to 110°.

CONCLUSIONS

The method described here combines three known methods: backflushing, temperature programming during the first direction, and longitudinal temperature gradient programming during backflushing of the carrier gas.

The retention theory has been developed by using simplifying and normally accepted hypotheses; retention times calculated from the resulting equations agree with the corresponding experimental values (relative error less than 10%).

We have investigated the effects of such parameters as backflushing time, heating rate, longitudinal gradient heating rate and initial column temperature, and have re-affirmed that use of backflushing can separate, at a low temperature, solutes having very different volatilities; the most volatile is eluted in the first direction, and the least volatile leave the column during backflushing.

The present method has interesting advantages over the previous method concerning the elution of poorly volatile solutes that have undergone backflushing and the longitudinal temperature gradient —on the one hand, we gain a good deal of time; on the other, peaks are much narrower and suitable separation is attainable. These properties allow our method to be used for quantitative analyses (from the same chromatogram) of both volatile solutes and solutes of very low volatility in a mixture.

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