

# PROGRAMMED FLOW GAS CHROMATOGRAPHY

## PART I

C. COSTA NETO, J. T. KÖFFER AND J. W. DE ALENCAR\*

*Instituto de Química da Universidade do Brasil, Rio de Janeiro (Brazil)*

(Received September 3rd, 1963)

The objective of research in gas chromatography in recent years has been the resolution of more complex mixtures. One of the many ways devised to solve this problem is the programmed temperature technique. By means of this technique it is possible to separate not only groups of substances with wide boiling point ranges but also the constituents of each group.

This paper describes the utilization of a programmed flow of the mobile phase<sup>1</sup> in isothermic or temperature programmed runs, in order to obtain the separation of complex mixtures.

In his recent book PURNELL<sup>2</sup> also suggested the possibility of a programmed flow technique; more recently SCOTT<sup>3</sup> proposed the use of programmed flow in preparative scale chromatography with analytical columns.

### RELATIONSHIP BETWEEN CHROMATOGRAM PARAMETERS AND THE MOBILE PHASE FLOW RATE IN ISORHEIC\*\* RUNS

The effect will be discussed of the gas flow rate on the parameters that can be directly taken from the chromatogram, *i.e.*, retention time, peak width, peak area and peak height. The system chosen to study these effects consisted of Nujol (as the stationary phase) and various alkanes, in order to minimize secondary effects in the partition process\*\*\*.

#### (1) *Peak migration and flow rate*

Peak migration can be related to flow rate by means of the equation:

$$t_N = KV_L/F_c \quad (1)$$

The validity of this equation for the system used in this paper is shown in Figs. 1, 2 and 3.

In programmed flow chromatography  $V_N$  rather than  $t_N$  should be used as the

\* Instituto de Química da Universidade do Ceará, Fortaleza, Brazil.

\*\* An isorheic process is defined as a process that occurs at a constant flow rate (from the Greek, *iso* = same and *rheo* = flow).

\*\*\* It should be emphasized here that all the results given and discussed in this paper refer to experimental procedures, equipment and phase systems described in the experimental part. It is not our intention to say that the results presented are general relationships nor that they are particular cases of a more general theory. Further work is in progress to verify this.

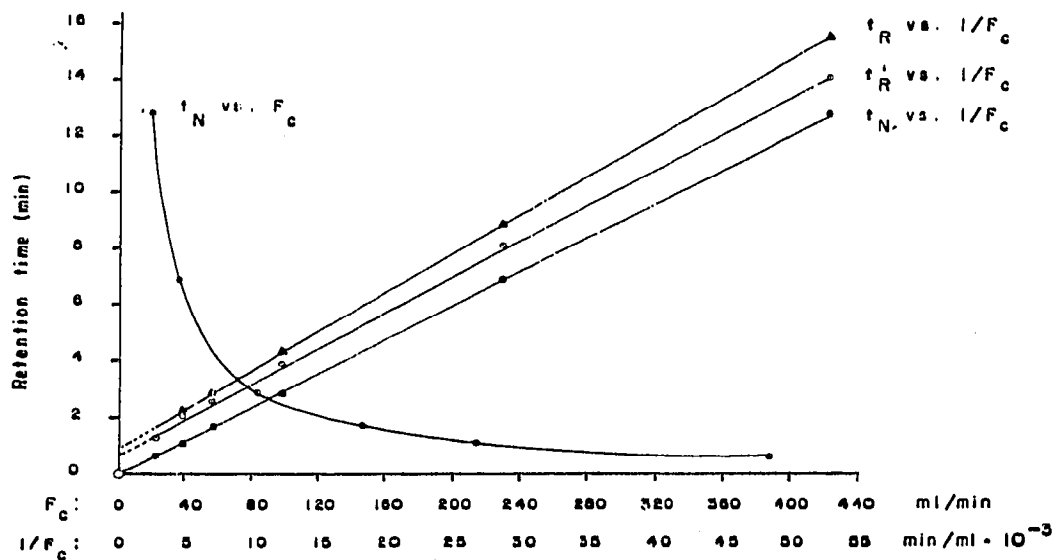


Fig. 1. Plot of retention ( $t_R$ ) time (min), corrected retention time ( $t'_R$ ) (min) and net retention time ( $t_N = jt'_R$ ) (min) vs.  $1/F_c$  (min/ml) for 2,3-dimethylpentane; stationary phase: Nujol 20% on CG-SORB TB.

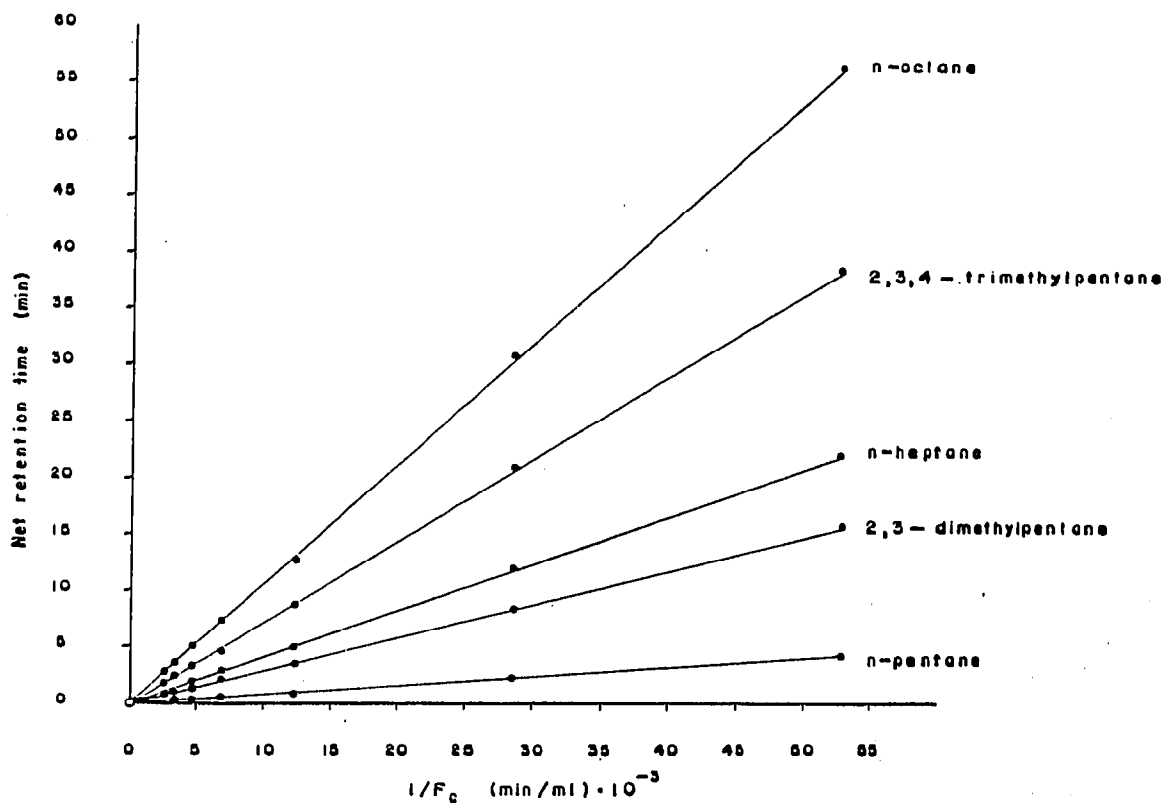


Fig. 2. Plot of net retention time (min) vs.  $1/F_c$  (min/ml) for various hydrocarbons on Nujol.

retention parameter for the characterization of the peaks since  $V_N$  is constant and independent of flow rate. An integral volume measuring device would be highly desirable to accompany any equipment using a programmed flow technique.

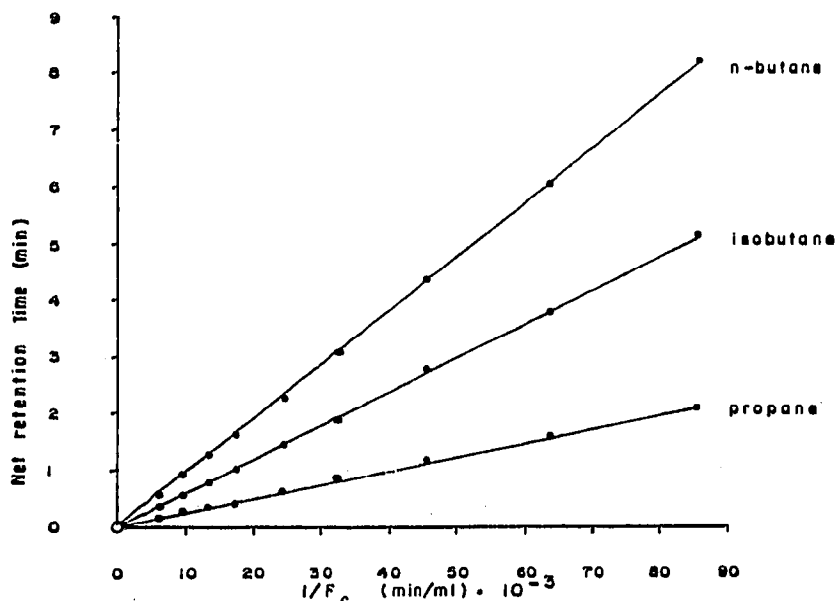


Fig. 3. Plot of net retention time (min) vs.  $1/F_c$  (min/ml) for propane, isobutane and *n*-butane

(2) Peak width ( $w$ ) and flow rate

Peak width can be related to flow rate by means of the equation:

$$w = A + B \left( \frac{1}{F_c} + \frac{C}{F_c^2} \right) \quad (2)$$

Fig. 4 shows the plot of  $w$  versus  $(1/F_c + C/F_c^2)$ .

It should be noted in the curves of Fig. 4 for propane, isobutane and *n*-butane, that all the coefficients of eqn. (2) are different (Table I). It is possible that the values

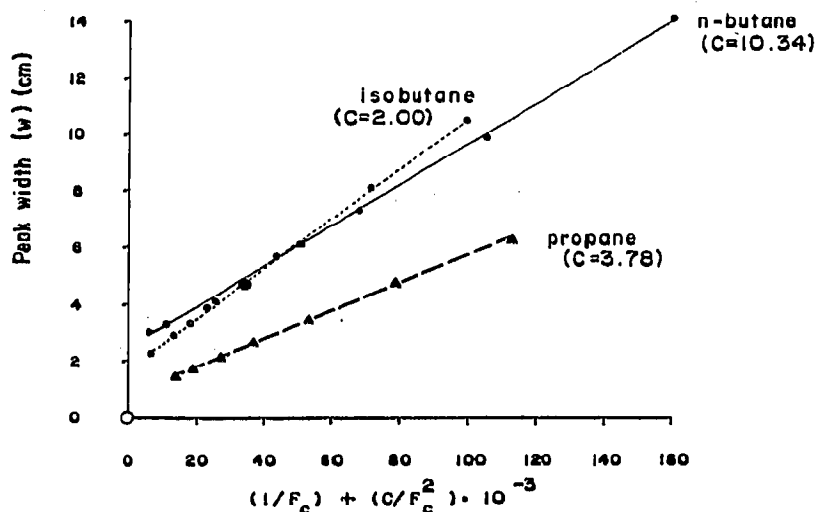


Fig. 4. Plot of peak width ( $w$ ) (cm) vs.  $(1/F_c) + (C/F_c^2)$  for propane, *n*-butane and isobutane. The values of  $C$  are shown in the corresponding curves.

TABLE I  
COEFFICIENTS OF EQUATION (2)

$$w = A + B \left( \frac{1}{F_c} + \frac{C}{F_c^2} \right)$$

$w$  in cm;  $F_c$  in ml/min

Compound	% in the mixture	A	B	C
Propane	59.2	0.8	50	3.78
Isobutane	23.9	1.8	88	2.00
<i>n</i> -Butane	16.9	2.4	72	10.34

of these coefficients depend on the amount and the nature of the substance, but it is not likely that the detector-response dependence on flow rate makes any significant contribution. Further work is in process to clarify this.

The peak width is a basic parameter for the calculation of the efficiency of the column and resolution of peaks. The results using eqn. (2) for these calculations are shown in the next section.

The plot of Fig. 4 shows the total peak width. A peak width asymmetry based on the ratio of the front half-peak width to the total peak width was fairly constant, at  $0.43 \pm 0.03$ , for all the flow rates.

### (3) Peak area and flow rate

The peak area is a major characteristic in quantitative analysis and a knowledge of the behaviour of the peak area with the flow rate is of fundamental importance when using a programmed flow technique for quantitative purposes. The literature contains some references<sup>2, 4</sup> to the behaviour of the area with flow rate.

The peak area is certainly dependent on the detector response, which, in the case of the thermoconductivity detectors is not simply a function of the gas flow rate. Nevertheless we found that the peak area behaved as a linear function of  $1/F_c$  in our experimental system (as can be seen in Fig. 5) as indicated by eqn. (3),

$$A_{i,F_c} = q_i \cdot \frac{1}{F_c} \quad (3)$$

where  $q_i$ , the slope of the line, is dependent on the amount of substance (%  $i$ ) and probably on its nature ( $i$ ). The absolute value of  $q$  depends also on the nature of the detector response ( $Y$ ).

As can be seen in Fig. 5, the ratio of the areas is constant at any flow rate.

It is certain that our data depend somewhat on the equipment used in our experiments, but if these results can be generalized, at least for the particular type of detector used, it would be an important feature for quantitative analysis in a programmed flow process.

To a first approximation, valid for very similar substances, the influence of the nature of the substance on the slope could be neglected, and for the same equipment, relative values of  $q$  are all that are needed. In this way,  $q$  can be directly related to the relative amounts of the constituents and the following equation can be derived to

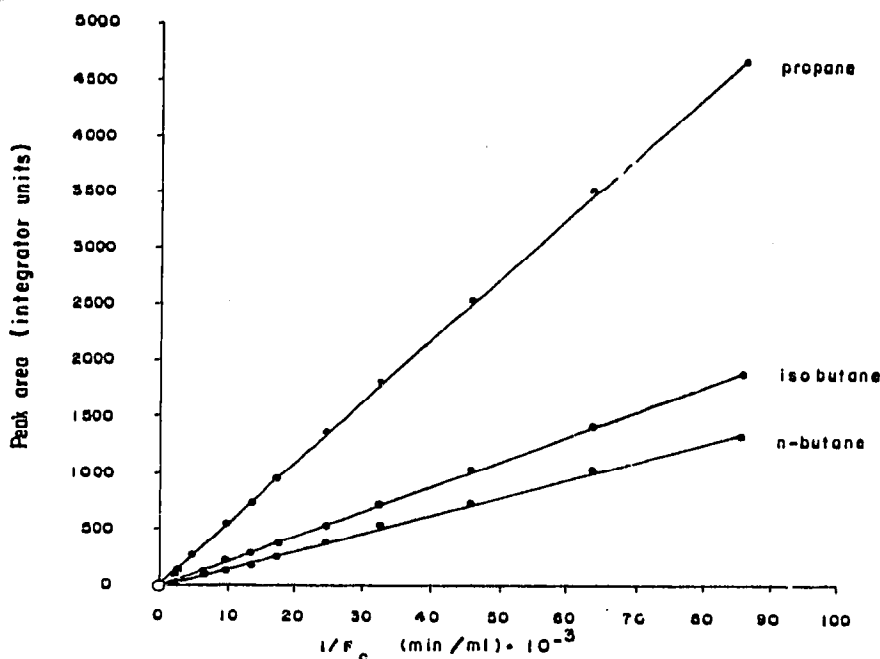


Fig. 5. Plot of peak area vs.  $1/F_c$  (min/ml) for propane, isobutane and *n*-butane; stationary phase: Nujol 20% on CG-SORB TB 80-100 mesh.

calculate the relative amount of the constituents of a mixture submitted to a programmed flow run.

In order to calculate the amount of any substance by internal normalization, all the areas in the same flow must be related, so that

$$\% i = A_{i, F_c} / \sum_I^m A_{m, F_{c_i}} \quad (4)$$

The area of any component *i* at a flow rate  $F_{cn}$  can be related to the area at a flow rate  $F_{c_i}$  by means of eqn. (3).

Eqn. (4) can be written as

$$\% i = A_{i, F_{cn}} \cdot F_{cn} / \sum_I^m A_{m, F_{cn}} \cdot F_{cn} \quad (5)$$

From this equation the various components in a step-programmed flow analysis can be determined. As the amount of substance is constant for all points on the same line (Fig. 5), the slope of the line reflects the influence of the flow rate on the detector response. Thus, in order to calculate a certain area it is necessary to know at what flow rate the area is being measured and in a programmed flow chromatogram eqn. (5) may be used to calculate the amount of substances, provided that the whole peak area is measured at the same flow rate.

#### (4) Peak height (*h*) and flow rate

The peak height is also a suitable parameter for quantitative analysis because it is dependent on the amount of substance. Nevertheless it is also very much dependent on the detector response *Y*. In thermal conductivity detectors, *Y* is very critical, especially in its dependence on the flow rate.

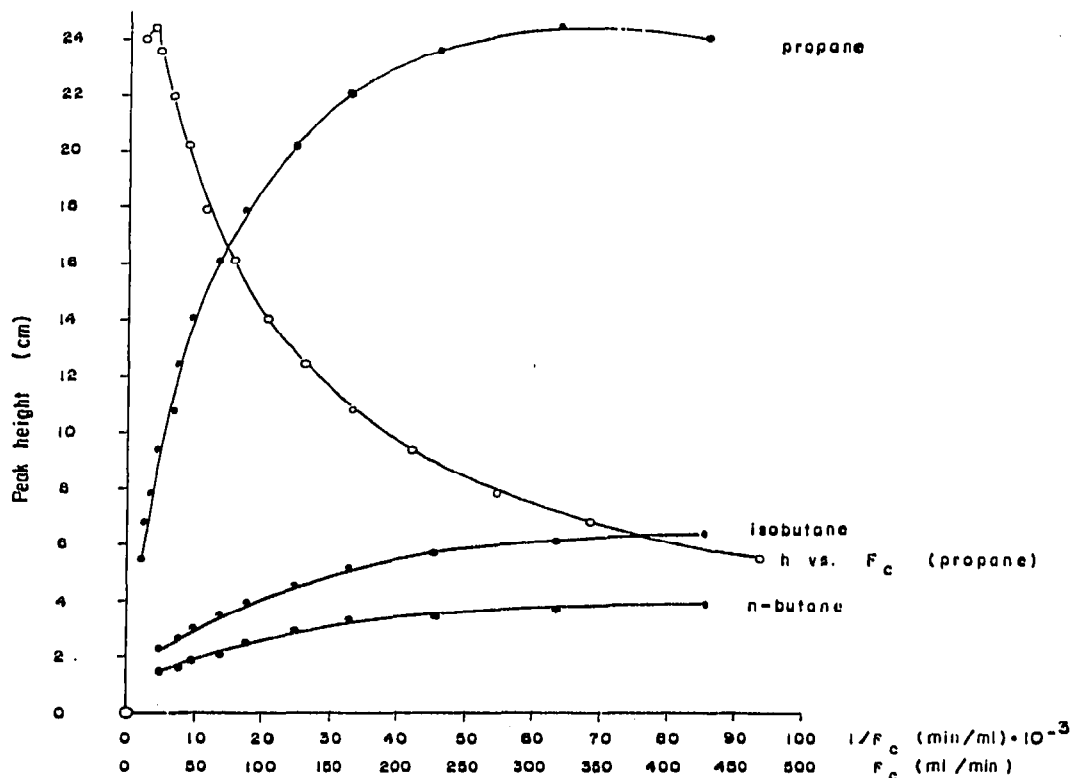


Fig. 6. Plot of peak height (cm) vs.  $1/F_c$  (min/ml) and  $F_c$  (ml/min) for propane, isobutane and butane.

Fig. 6 shows the behaviour of peak height with flow rate for the systems studied. No general function could be obtained to correlate the peak height with flow rate in the detector used.

#### EFFICIENCY AND FLOW RATE

The efficiency of a chromatographic column can be given as the number of theoretical plates ( $n$ ) it has, or the height equivalent to a theoretical plate ( $H$ ). The latter can be expressed as a function of flow by means of the well-known Van Deemter equation.

The number of theoretical plates of a column can be calculated by means of the expression:  $n = 16 (t/w)^2$ .

Combining this expression with eqns. (1) and (2) we may write

$$n = \left( \frac{4 KV_L}{AF_c + B + \frac{BC}{F_c}} \right)^2 \quad (6)$$

and

$$\sqrt{H^*} = \frac{L^{1/2}}{4 KV_L} \left( B + \frac{BC}{F_c} + AF_c \right) \quad (7)$$

This equation is similar to that of Van Deemter in its dependence on flow rate.

Eqn. (7) can be written as

$$H^* = a + \frac{b}{F_c} + cF_c + \frac{d}{F_c^2} + eF_c^2 \quad (8)$$

as compared with  $H = a' + b'/F_c + c'F_c$  in Van Deemter's equation.

Again we must emphasize that the validity of eqn. (7) depends on eqn. (2) and this has not yet been shown to be generally applicable. The experimental evidence of this relationship involves a knowledge of the coefficients which can be easily calculated from the experimental parameters of eqn. (2).

Fig. 7 shows the plot of  $H^*$ ,  $\sqrt{H^*}$  and  $H$  versus  $F_c$ .

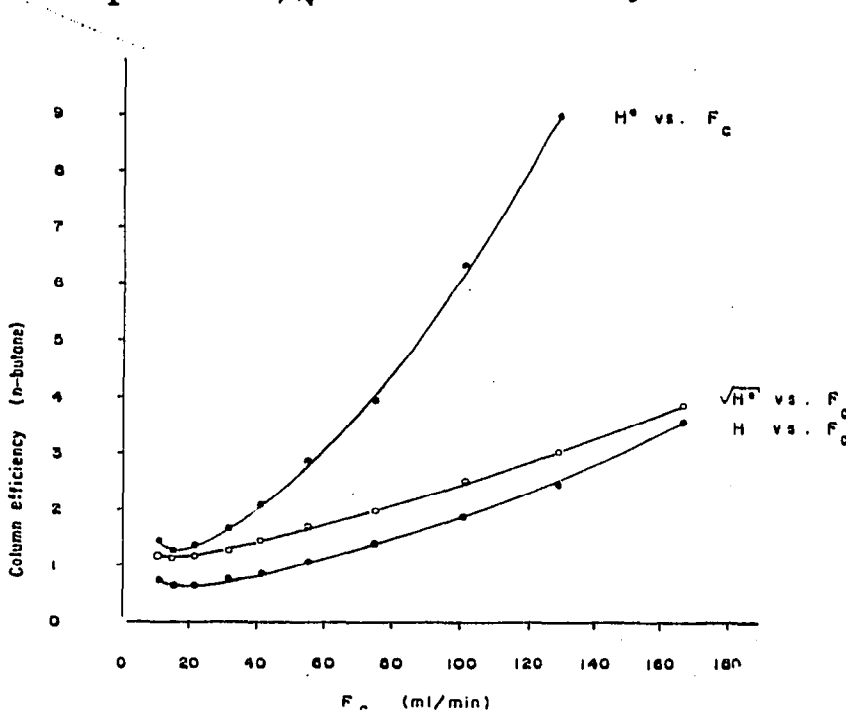


Fig. 7. Plot of column efficiency for *n*-butane as a function of  $F_c$  (ml/min).  $H^*$  is calculated with net retention parameters. Stationary phase: Nujol 20% on CG-SORB TB, 80-100 mesh.

#### RESOLUTION AND FLOW RATE

Resolution between two peaks, defined as  $R^* = 2 t_N/W$ , may be written as

$$R^* = 2 V_L \Delta K F_c / \left( \sum_i B_i C_i + \sum_i B_i F_c + \sum_i A_i F_c^2 \right) \quad (9)$$

or in a simplified way:

$$R^* = F_c / (a'' + b'' F_c + c'' F_c^2) \quad (10)$$

This function has a maximum ( $R_{\max}$ ) at  $F_c = (a''/(2c''-1))^{1/2}$  and  $R = 0$  both at  $F_c = 0$  or  $F_c = \infty$ .

In Fig. 8 the resolution of butane-isobutane peaks is presented as a function of the flow rate, in accordance with eqn. (10).

#### AN EXAMPLE OF PROGRAMMED FLOW

As an example of the use of the programmed flow technique, a mixture of 13 aliphatic hydrocarbons and benzene was studied.

The first four chromatograms are isorheic (and isothermic) runs in order to show the various resolutions among the peaks.

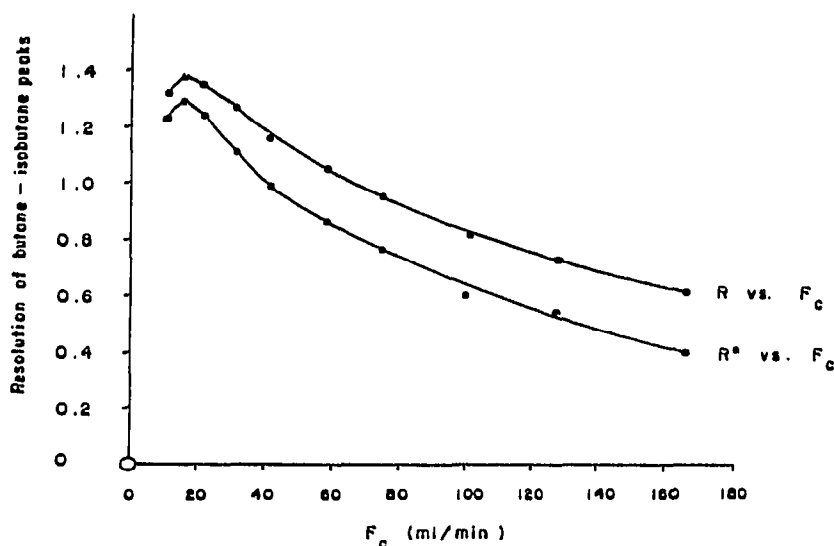


Fig. 8. Plot of the resolution of the mixture *n*-butane-isobutane vs.  $F_c$  (ml/min).  $R^*$  involves net retention parameters.

In chromatogram No. 1 (Fig. 9) at 35 ml/min all the peaks are resolved, except those of isooctane and *n*-heptane (peaks 11 and 12).

The retention times of the last constituents, the octanes, are very large and the peaks are well separated. At the highest flow rate these last peaks are still resolved, and are eluted in 6 min. Nevertheless a very great number of constituents could not be resolved. The other chromatograms (Figs. 10-13), with intermediate flow rates, show intermediate situations.

Chromatogram No. 5 (Fig. 13) shows the results of a programmed flow (discontinuous) run. The resolution obtained at the lowest flow rate is still present although less than half the time was needed for this chromatogram.

It is interesting to note that in a normal chromatographic process an inherent continuous programmed flow process takes place owing to the pressure gradient in the column.

#### CHARACTERISTICS OF THE PROGRAMMED FLOW PROCESS

1. Equilibrium is reached in the system almost instantaneously. Although the literature recommends times of 10-20 min in order to establish equilibrium conditions,

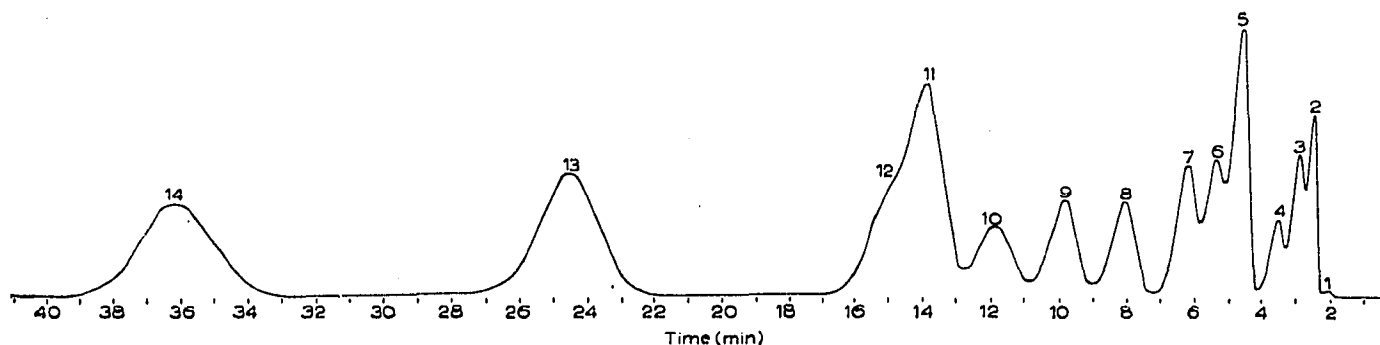


Fig. 9. Chromatogram No. 1. Helium flow rate: 35.1 ml/min. Inlet pressure: 5.0 p.s.i.g. Pressure gradient correction factor ( $j$ ): 0.85. Detector sensitivity:  $\frac{1}{4}$ .



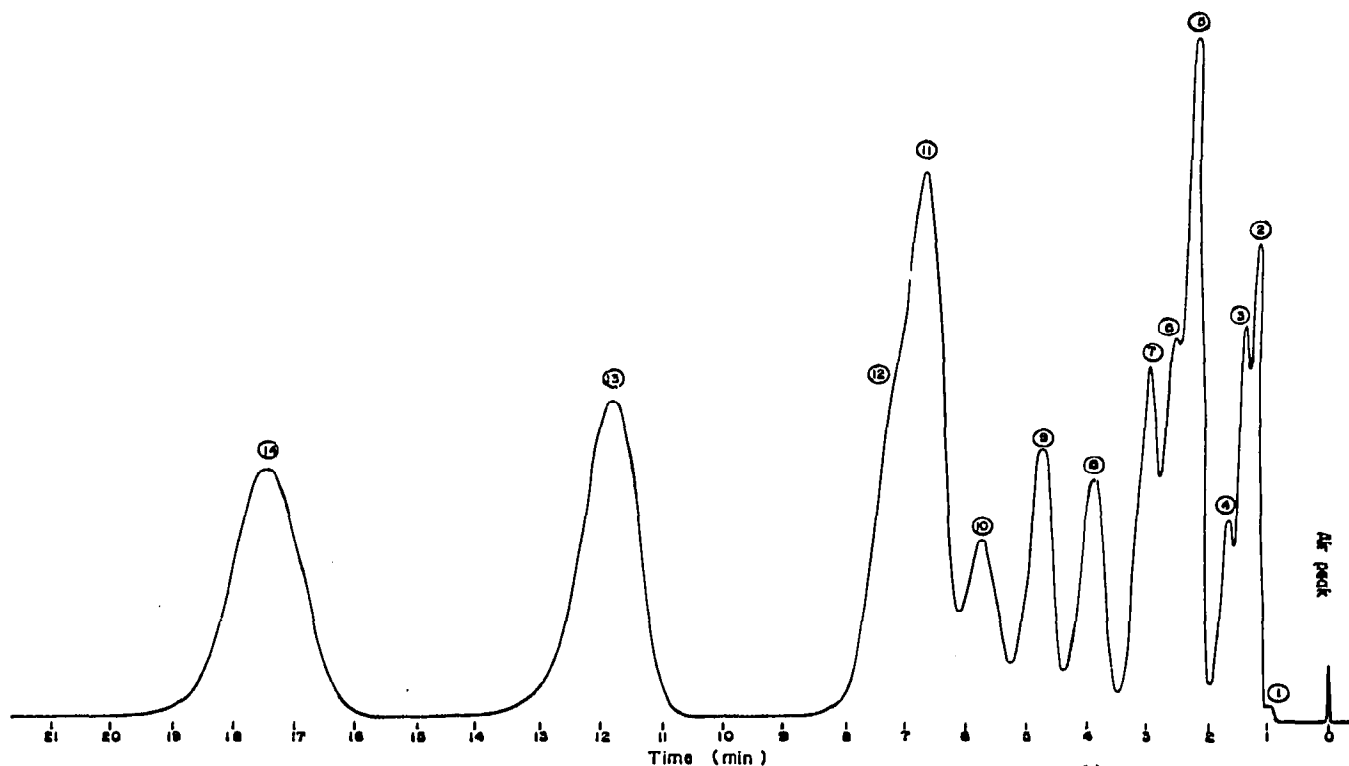


Fig. 10. Chromatogram No. 2. Helium flow rate: 82.9 ml/min. Inlet pressure: 10.0 p.s.i.g. Pressure gradient correction factor ( $j$ ): 0.73. Detector sensitivity:  $\frac{1}{4}$ .

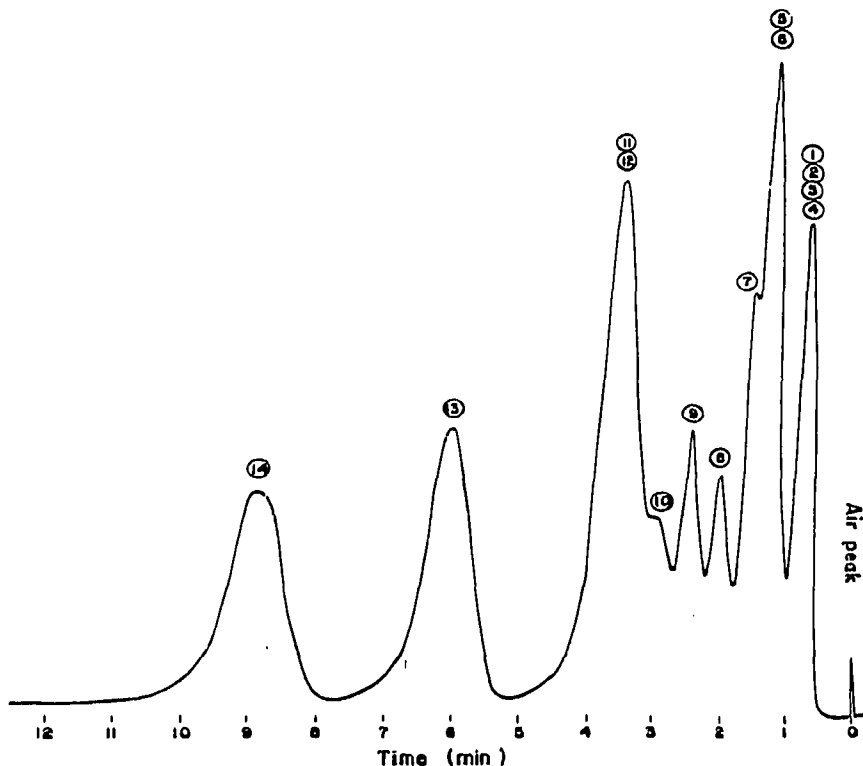


Fig. 11. Chromatogram No. 3. Helium flow rate: 212.9 ml/min. Inlet pressure: 20.0 p.s.i.g. Pressure gradient correction factor ( $j$ ): 0.55. Detector sensitivity:  $\frac{1}{8}$ .

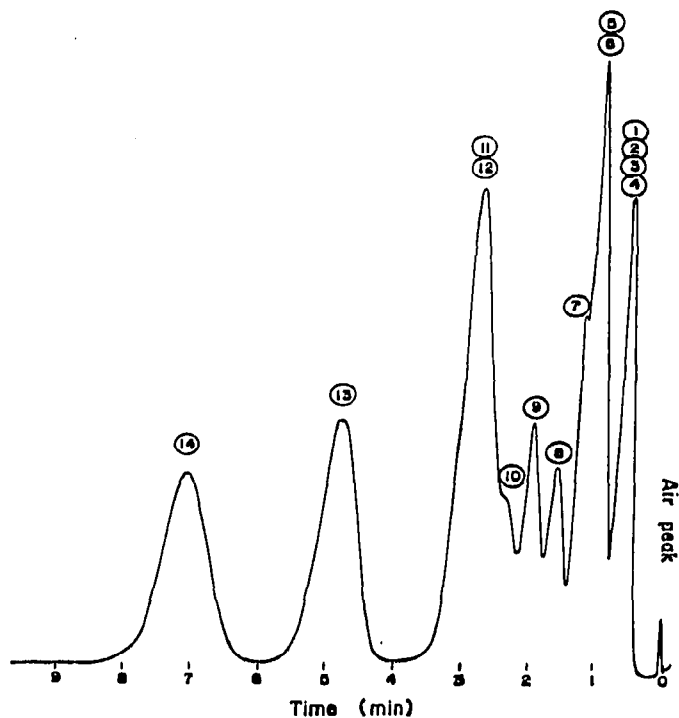


Fig. 12. Chromatogram No. 4. Helium flow rate: 293.4 ml/min. Inlet pressure: 25.0 p.s.i.g. Pressure gradient correction factor ( $j$ ): 0.50. Detector sensitivity: 1/16.

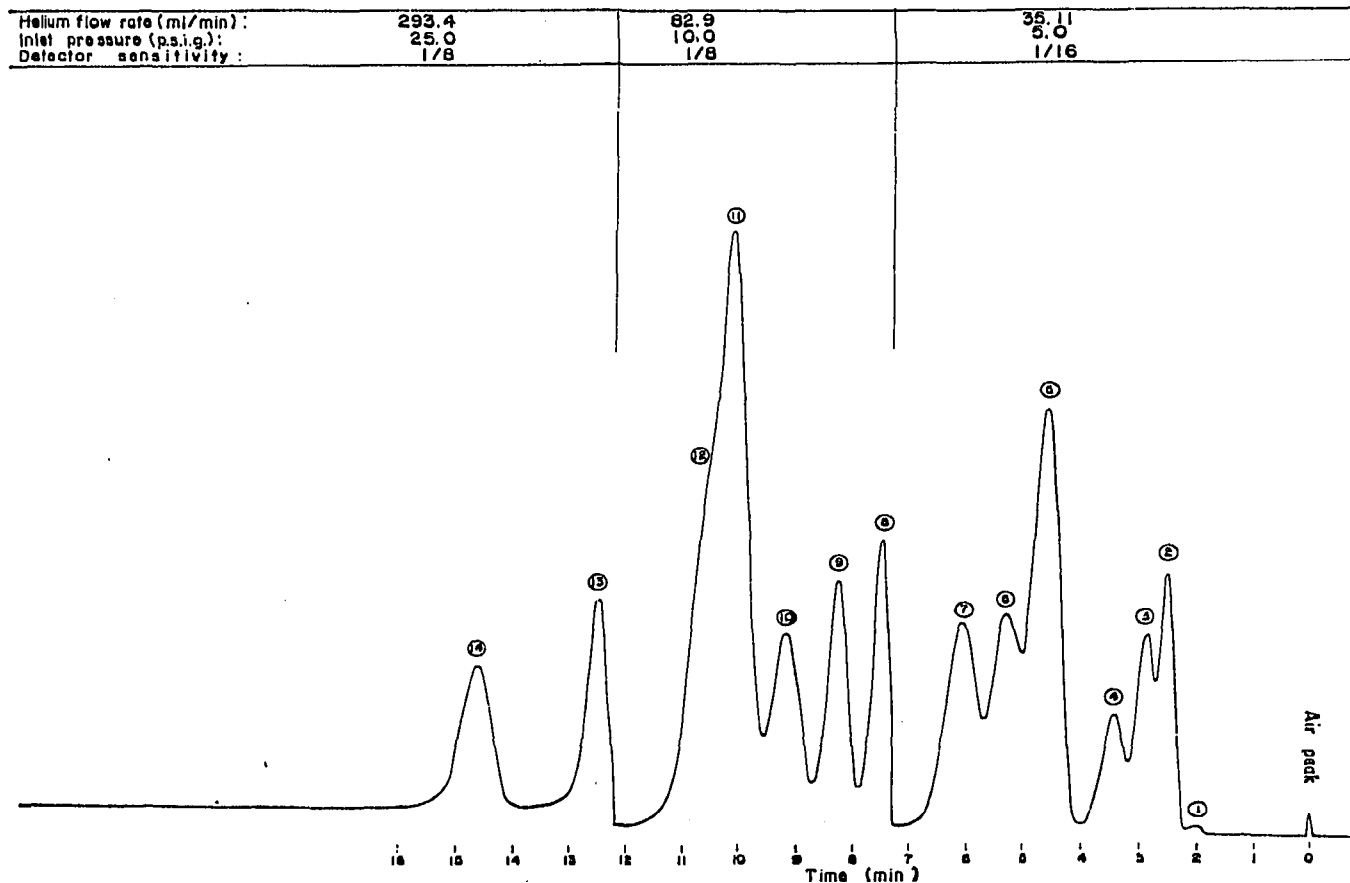


Fig. 13. Chromatogram No. 5. Programmed flow.

we found that very good reproducibility of results could be obtained almost instantly.

2. There is no increase in the volatility of the stationary phase; this allows a wider use of phases.

3. Considerable and almost instantaneous variations in the flow rates are possible, and, as we have already mentioned before, equilibrium is reached in a very short time.

We have used a discontinuous (sequence of isorheic processes) programming. This is very easy to perform manually and the cost of a step valve for the program is very small.

A continuous process could be used but it is experimentally much more complicated and did not offer any real advantage over the discontinuous process.

4. The programmed flow technique allows the resolution of complex mixtures in isothermic runs or runs with temperature programming. In addition, it has all the inherent advantages of a final temperature much lower than that of an isorheic run.

5. It improves the "quality" of the chromatogram. Sharper peaks ( $w$  decreases as  $F_c$  increases) with a great reduction in the retention time of the less volatile constituents are obtained, while complete resolution of the more volatile products is still possible.

#### EXPERIMENTAL

The chromatograms were performed under the following general conditions (the particulars are shown for each chromatogram):

(1) *Chromatograph*. Perkin-Elmer "Vapor Fractometer" model 154C with thermistor-detector (Fenwall Electronics Inc., Mass., G 112 Assembly,  $R_0$  at 25°: 6710  $\Omega$ . Bridge operated with 8 V).

(2) *Column*.  $\frac{1}{4}$  in. copper tubing, 2 m long, containing 3.21 g of Nujol ( $d_{20} = 0.88$ ) on 12.86 g of CG-SORB TB 80-100 m. Effective cross section area of the column: 0.12 cm<sup>2</sup> (determined from the slope of the straight line obtained from the plot of  $t_M^0$  vs.  $1/F_c$ , according to the expression  $t_M^0 = sl \cdot 1/F_c$  (Fig. 14).

The behaviour of the alkanes in the Nujol column can be further characterized by their  $K$  value determined from eqn. (1) and the graphs of Figs. 2 and 3.

The values given in Table II were determined.

TABLE II  
K VALUES OF ALKANES  
( $V_L = 3.64$  ml Nujol)

Substance	Boiling point (°C) (1 atm)	$K$	Temperature (°C)
Propane	-42.2	6.67	26
Isobutane	-10.2	16.5	26
<i>n</i> -Butane	-0.6	26.2	26
<i>n</i> -Pentane	36.2	21.1	75
2,4-Dimethylpentane	80.5	66.6	75
2,3-Dimethylpentane	89.8	81.5	75
2,2,4-Trimethylpentane	99.3	114	75
2,3,4-Trimethylpentane	113.4	119	75
<i>n</i> -Octane	125.8	293	75

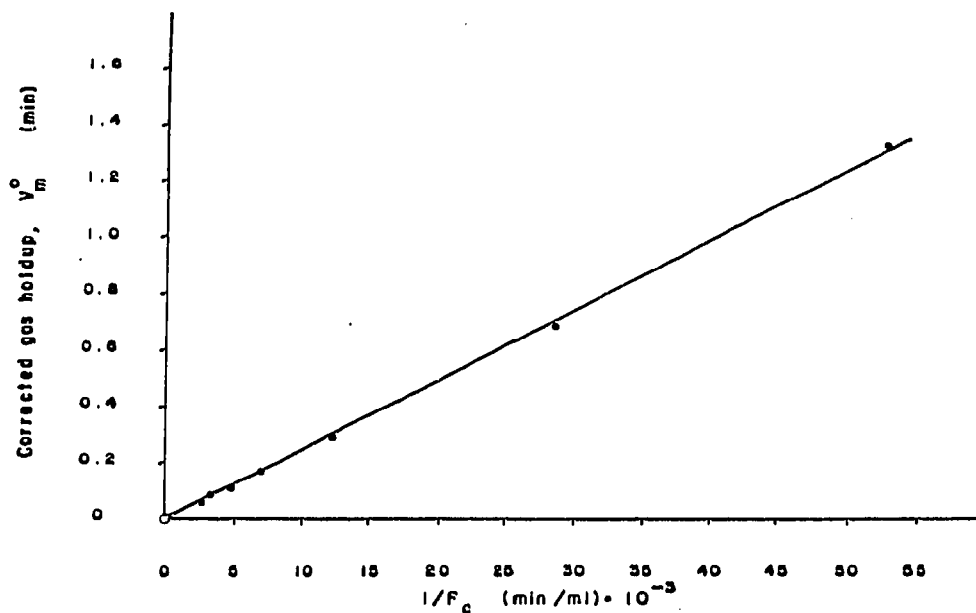


Fig. 14. Plot of corrected gas holdup  $V_M^0$  (min) vs.  $1/F_c$  (min/ml).

(3) *Recorder*. Speedomax G, Leeds & Northrup, 5 mV, equipped with a Perkin-Elmer Printing Integrator model 194. The recorder speed for the chromatograms of  $C_5-C_8$  was 1 in./min and for the chromatograms of  $C_3-C_4$  was 4 in./min.

(4) *Carrier gas*. Helium.

(5) *Temperature*. For the chromatograms of  $C_5-C_8$ :  $75^\circ$ . For the chromatograms of  $C_3-C_4$ :  $25^\circ$ .

(6) *Sample  $C_5-C_8$* . A synthetic mixture, containing the following constituents, was made:

- |                       |                            |
|-----------------------|----------------------------|
| 1. 2-Methylbutane     | 8. 2,4-Dimethylpentane     |
| 2. <i>n</i> -Pentane  | 9. 2,3-Dimethylpentane     |
| 3. 2,2-Dimethylbutane | 10. Benzene                |
| 4. 2,3-Dimethylbutane | 11. Iso-octane             |
| 5. 2-Methylpentane    | 12. <i>n</i> -Heptane      |
| 6. 3-Methylpentane    | 13. 2,3,4-Trimethylpentane |
| 7. <i>n</i> -Hexane   | 14. <i>n</i> -Octane       |

(The numbers correspond to those in the chromatograms, Figs. 9-13.)

Sample size: approximately 10  $\lambda$  were used in each injection (Hamilton syringe).

(7) *Sample  $C_3-C_4$* . Petroleum gas was used as the sample for  $C_3-C_4$  hydrocarbons and contained 59.2 % of propane, 23.9 % of isobutane and 16.9 % of *n*-butane.

Sample size: gas cell  $\frac{1}{4}$  c.c.

#### NOMENCLATURE

$A_i, F_c$  - area of peak  $i$  at flow rate  $F_c$

$F_c$  - flow rate of the mobile phase (ml/min)

$h$  - peak height

$H$  - height equivalent to a theoretical plate (calculated from uncorrected retention time)

$H^*$	- height equivalent to a theoretical plate (calculated from the net retention time)
$K$	- partition coefficient
$L$	- length of the column (cm)
$R$	- resolution of peaks (calculated from uncorrected retention time)
$R^*$	- resolution of peaks (calculated from net retention time)
$s$	- effective cross section area of the column (cm <sup>2</sup> )
$t_N$	- net retention time
$t_M^0$	- corrected retention time of air peak
$u$	- velocity of the mobile phase (cm/min)
$V_R$	- retention volume (uncorrected) (ml)
$V_R^0$	- corrected retention volume (ml)
$V_M^0$	- corrected gas hold up (ml)
$V_L$	- liquid phase volume (ml)
$V_N$	- net retention volume (ml)
$w$	- peak width

## ACKNOWLEDGEMENTS

We wish to thank Prof. RODERICK A. BARNES for reading and correcting the manuscript. This work was made possible with a grant from the Comissão Supervisora do Plano dos Institutos (MEC) to the Graduate Program of the University of Brazil and also from the Conselho de Pesquisas da UB.

## SUMMARY

The results obtained on programmed flow gas chromatography of a mixture of hydrocarbons are presented. The following relationships between various parameters and flow rate are discussed:

- (1) Peak migration and flow rate of the mobile phase.
- (2) Effect of flow rate on peak width, height and area.
- (3) Effect of flow rate on efficiency and resolution.

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