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## MASS FLOW CONTROL AND TEMPERATURE PROGRAMMING IN GAS CHROMATOGRAPHY

### II\*. FLOW CONTINUITY EQUATION AND ITS CONSEQUENCES IN PROGRAMMED-TEMPERATURE GAS CHROMATOGRAPHY

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#### SUMMARY

The role of the column void volume and of the associated external volumes on the column outlet mass flow-rate changes during temperature programming was studied. At a constant column inlet mass flow-rate, a decrease in the column outlet mass flow-rate is displayed, the relative magnitude of which depends on a dimensionless number consisting of the rate of the temperature programme, the viscosity of the carrier gas, the permeability of the column and both the internal and external volumes associated with the column.

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#### INTRODUCTION

Two types of pneumatic controller are used in gas chromatography (GC): inlet pressure and mass flow controllers; most GC instruments are equipped with the latter. One of the obvious reasons for this is the wide use of the programmed-temperature GC (PTGC) technique. Under constant mass flow conditions in the column, the determination of retention temperatures is straightforward, and correct quantitation, even with concentration-sensitive detectors, becomes possible.

Earlier studies, summarized by Harris and Habgood<sup>1</sup>, did not take account of the dynamic character of the changes that take place in the column during a linear increase in the oven temperature. It is obvious that the column is unable to follow exactly the temperature of the air in the oven. Bártů<sup>2</sup> and Bártů and Wičar<sup>3</sup>, for example, based their estimation of the column temperature in PTGC on an assumption that the rate of increase of column temperature is proportional to the actual difference between the oven and column temperatures:

$$\frac{dT^{\text{col}}}{dt} = k(T^{\text{ov}} - T^{\text{col}})$$
$$T^{\text{ov}} = at + T_0^{\text{ov}} \quad (1)$$

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\* For Part I, see *J. Chromatogr.*, 295 (1984) 395.

where  $T^{\text{col}}$  and  $T^{\text{ov}}$  are the column and oven temperatures, respectively.

Guiochon<sup>4</sup> recognized the transient character of the carrier gas flow in the column during PTGC and found different courses of the column inlet pressure at various temperature programming rates. Guiochon attributed the observed differences to the invalidity of the Darcy law equation under dynamic conditions and tried to estimate the influence of this effect by semi-empirical means. He concluded that the rate of gas mass hold-up of the column relative to the gas mass flow-rate is equal to the dead retention time.

A simplified approach is presented in this paper, and the use of a precise computer-controlled GC apparatus, described in Part I, for experimental measurements will be reported in Part III.

#### ROLE OF THE COLUMN VOID VOLUME

The flow of a fluid in any particular system is determined by two vectorial equations, *viz.*, the Navier-Stokes and flow continuity equations. The former expresses the balance between external (pressure), drag (viscosity) and inertial forces acting on a volume element of the flowing fluid. The Poisseuille equation, for example, presents a simplified one-dimensional solution to the Navier-Stokes equation for laminar and stationary flow of a fluid through a capillary.

The flow continuity equation:

$$\frac{\partial \rho}{\partial t} + \text{div}(\rho \bar{v}) = 0 \quad (2)$$

where  $\rho$  and  $\bar{v}$  are the local density and velocity of the fluid, respectively, constitutes an application of the conservation principle to the flow of a fluid and expresses the fact that the difference between the mass flow into and out of any arbitrary volume element in the fluid manifests itself in a change of the fluid density within that element.

An exact solution of the Navier-Stokes and flow continuity equation applied to a chromatographic column is, of course, impossible; we are able merely to apply the mass conservation principle to the carrier gas flow in a column during a linear temperature programme.

Let us consider a simplified dynamic model of a packed column consisting of a piece of void tube and a capillary in series (Fig. 1a). The void volume of the packed column is simulated by the tube volume,  $V_c$ , the pneumatic resistance of the column being represented by the capillary. The mass flow controller supplies into the system a constant column inlet mass flow,  $F$ . At a constant column temperature  $T_0$ , the mass flow-rate at the column outlet,  $F_0$ , is given by

$$F = F_0 = \frac{K}{RT_0\eta(T_0)} [P^2(T_0) - P_0^2] \quad (3)$$

where  $K = \pi r^4/16L$  provided steady-state conditions are established;  $r$  and  $L$  are the capillary radius and length, respectively, and  $R$ ,  $T_0$ ,  $\eta$ ,  $P(T_0)$  and  $P_0$  are the gas constant, absolute column temperature, gas viscosity and column inlet and outlet pressures, respectively.

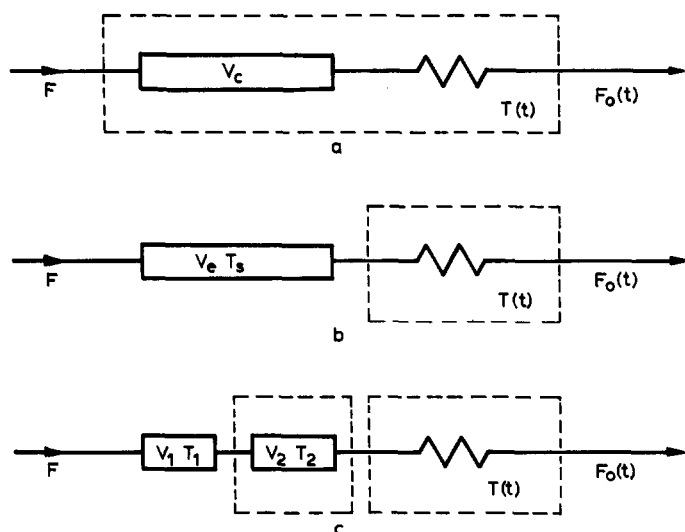


Fig. 1. Hydrodynamic model of a chromatographic column in PTGC. (a) Column without external volumes; (b) zero-volume column with external volumes; (c) zero-volume column with external volumes, different external volumes kept at different constant temperatures  $T_1$  and  $T_2$ .

In order to keep the problem linear, we reduce the hydrodynamic resistance of the capillary so as to make the pressure difference  $P(T) - P_0$  substantially smaller than  $P_0$ ; then

$$F_0 = \frac{2KP_0}{RT_0\eta(T_0)}[P(T_0) - P_0] \quad (3a)$$

At time  $t = 0$ , we start a linear temperature programme:

$$T = at + T_0 \quad (4)$$

In contrast to Guiochon's considerations, we suppose that the accommodation of forces to new conditions within the capillary proceeds much faster than the capillary temperature change for any reasonable temperature programme. As a consequence of this postulate, eqn. 3a remains valid even during the course of the temperature programme.

The mass conservation principle for the carrier gas flowing through the model system is expressed by

$$F = \frac{d\rho}{dt} + F_0(t) = \frac{V_c}{RT} \cdot \frac{dP}{dt} + \frac{2KP_0}{RT\eta(T)}(P - P_0) \quad (5)$$

For the sake of simplicity, the temperature dependence of the gas viscosity will be approximated by the linear relationship

$$\eta(T) = \mu_0 T \quad (6)$$

and, according to eqn. 4,

$$\frac{dP}{dt} = a \cdot \frac{dP}{dT}$$

The final form of the mass balance equation (eqn. 5) is

$$F = \frac{aV_c}{RT} \cdot \frac{dP}{dT} + \frac{2KP_0}{R\mu_0 T^2} (P - P_0) \quad (7)$$

For the initial conditions (see eqns. 3a, 4 and 6

$$T = T_0; P(T_0) = P_0 + \frac{FR\mu_0 T_0^2}{2KP_0} \quad (8)$$

we obtain the solution

$$P(T) = P_0 + \frac{FR}{aV_c(\beta_c + 2)} \left[ T^2 + \frac{2}{\beta_c} \cdot T_0^2 \left( \frac{T_0}{T} \right)^{\beta_c} \right] \quad (9)$$

where

$$\beta_c = \frac{2KP_0}{aV_c\mu_0}$$

From eqns. 5 and 9 there holds for the column outlet mass flow

$$\frac{F_0(T)}{F} = \frac{\beta_c}{\beta_c + 2} + \frac{2}{\beta_c + 2} \left( \frac{T_0}{T} \right)^{2+\beta_c} \quad (10)$$

As the dimensionless quantity  $\beta_c$  reaches relatively high values on packed columns (tens to hundreds), the interpretation of eqn. 10 is simple: the outlet mass flow  $F_0$ , originally equal to the inlet mass flow  $F$ , decreases rapidly during the initial stage of linear temperature programme, reaching a constant value

$$\frac{F_0}{F} = \frac{\beta_c}{\beta_c + 2} \quad (11)$$

which is determined by the temperature programming rate and by the carrier gas viscosity in a given column. As the pressure in the void volume of the simulated column increases in the course of temperature programming, a part of the gas mass supply is consumed to increase the pressure and the rest leaves the column. The constant  $F_0/F$  value, determined by eqn. 11, characterizes the situation when the thermal expansion of the carrier gas in the column, complemented by a constant fraction of the inlet flow, is able to guarantee a constant outlet flow regardless of the continuing column temperature increase.

## ROLE OF EXTRA-COLUMN VOLUMES

An important feature of our simplified dynamic column model is a separated column void volume heated simultaneously with a capillary. A slight modification of the basic model, consisting in removing the separated volume out of the heated zone of the column oven, will be used to study the dynamic role of extra-column volumes, such as the controller body volume, inlet tubing volumes and injection port volume. The new model is shown schematically in Fig. 1b.

The mass balance equation is now

$$F = \frac{aV_e}{RT_s} \cdot \frac{dP}{dT} + \frac{2KP_0}{R\mu_0 T^2} (P - P_0) \quad (12)$$

where  $T_s$  is the constant ambient temperature. The solution of eqns. 12 and 8 is

$$P(T) = P_0 + \frac{FR}{aV_e} \left\{ \frac{T_0}{\beta_e} \cdot e^{-z} + T_s \int_{T_0}^T \exp \left[ -\frac{\beta_e T_s (T-x)}{Tx} \right] dx \right\} \quad (13)$$

and, for the outlet mass flow-rate, by combining eqns. 5 and 13:

$$\frac{F_0(T)}{F} = \left( \frac{T_0}{T} \right)^2 e^{-z} + \frac{\beta_e T_s}{T^2} \int_{T_0}^T \exp \left[ -\frac{\beta_e T_s (T-x)}{Tx} \right] dx \quad (14)$$

where

$$z = \frac{\beta_e T_s (T - T_0)}{TT_0}$$

and

$$\beta_e = \frac{2KP_0}{aV_e \mu_0}$$

If the extra-column volumes are kept at different, but constant, temperatures (see Fig. 1c), then solution 14 remains valid after the substitution

$$\beta_e T_s = \frac{2KP_0 T_1 T_2}{a\mu_0 (V_1 T_2 + V_2 T_1)} \quad (15)$$

This is the case in which the volume  $V_1$  of the flow controller and associated tubing are kept at the ambient temperature  $T_1$  while the volume of the injection port,  $V_2$ , is kept at a constant temperature  $T_2$ .

The first term on the right-hand side of eqn. 14 guarantees the fulfillment of

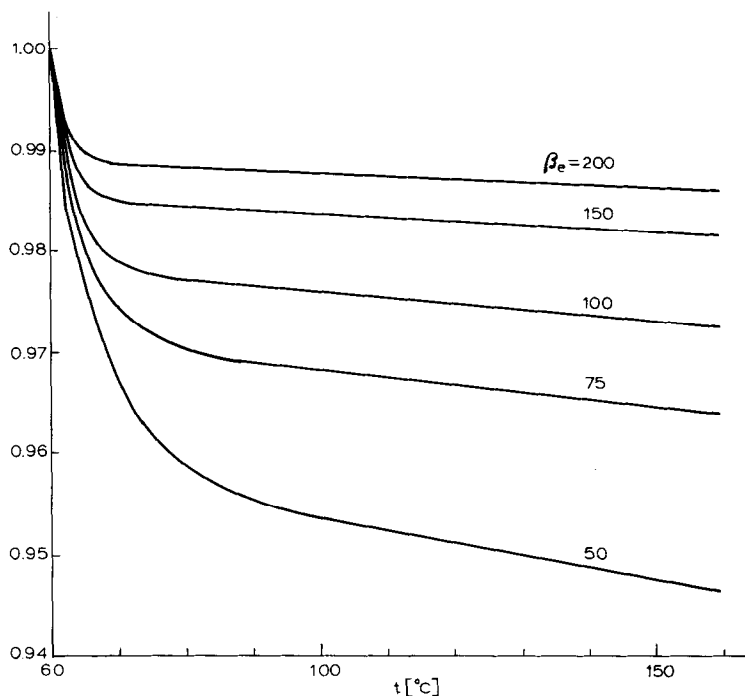


Fig. 2. Relative decrease in the column outlet carrier gas flow-rate due to external volumes.

the initial condition  $F_0(T_0) = F$ , and it decreases rapidly as the temperature increases. The second term can be evaluated numerically; Fig. 2 shows a graph of  $F_0/F$  vs.  $T$  for some  $\beta_e$  values.

As long as the model system remains linear, the  $F_0/F$  function for combined external and internal volumes could be obtained by the superposition of eqn. 10 and 14:

$$\frac{F_0(T)}{F} = \frac{1}{\beta_e + 2} \left[ \beta_e + 2 \left( \frac{T_0}{T} \right)^{\beta_e + 2} \right] \left\{ \left( \frac{T_0}{T} \right) e^{-z} + \frac{\beta_e T_s}{T^2} \int_{T_0}^T \exp \left[ - \frac{\beta_e T_s (T - x)}{Tx} \right] dx \right\} \quad (16)$$

#### RETURN TO ISOTHERMAL CONDITIONS

At the end of a linear temperature programme, *i.e.*, at the moment when the column outlet mass flow-rate reaches its minimum value (and when the temperature begins to be constant), it is a new process that restores the originally existing equality

between the column inlet and outlet mass flow-rates in the column. The material balance equation determining the restoration process

$$F = \frac{1}{R} \sum \frac{V_i}{T_i} \cdot \frac{dP}{dt} + \frac{K}{RT\eta(T)}(P^2 - P_0^2) \quad (17)$$

and the initial condition

$$t = 0; \quad F_0(0) = \frac{K}{RT\eta(T)} \left[ P^2(0) - P_0^2 \right] \quad (18)$$

yield the solution

$$\frac{\bar{P} - P(t)}{\bar{P} + P(t)} = \frac{\bar{P} - P(0)}{\bar{P} + P(0)} \cdot \exp(-t/H) \quad (19)$$

where

$$H = \frac{1}{2KP_0\bar{P}R} \sum \frac{V_i}{T_i} \quad (20)$$

In eqns. 17 and 20,  $V_i$  and  $T_i$  stand for the external and internal volumes and temperatures, respectively, and  $\bar{P}$  is the steady-state column inlet pressure.

For the column-outlet mass flow-rate,

$$\frac{F_0(t)}{F} = \frac{\left[ \frac{1 - r(t)}{1 + r(t)} \right]^2 \bar{P}^2 - P_0^2}{\bar{P}^2 - P_0^2} \quad (21)$$

where

$$r(t) = \frac{\bar{P} - P(0)}{\bar{P} + P(0)} \cdot \exp(-t/H) \quad (22)$$

According to eqn. 21, a sharp rise in the column outlet mass flow-rate is displayed at the end of the temperature programme. By comparing the time coordinate of the moment at which  $F_0$  ceases to decrease and starts its rise with that of the temperature programme end, we could, for instance, determine the column temperature time constant.

## DISCUSSION

Eqn. 16 obviously represents merely a very simplified solution of the problem. When dealing with real columns, we are unable to separate the void volume and the hydrodynamic resistance of the column. Consequently, we should operate with the column mean pressure rather than with the inlet pressure. If the column pressure

drop remains small enough compared with the outlet pressure, at least qualitative conclusions can be drawn from eqn. 16. In a less favourable case, the problem leads to the Ricatti-type equation, and any attempt to separate the influence of the external and column void volumes (see eqns. 14 and 10), necessarily fails.

Regardless of this objection, it remains clear that the column outlet flow-rate decreases in the course of temperature programming. As the mean column pressure increases, the carrier gas hold-up of the column and of the associated external volumes increases accordingly, and as the mass flow controller is the only source of carrier gas, part of this source is used to increase the carrier gas hold-up and only the remainder leaves the column outlet.

The decrease in column outlet flow-rate typically reaches a few percent and is, therefore, of less significance with respect to the determination of retention temperatures; in quantitative analysis, its significance depends on the detector used. With concentration-sensitive detectors, such as a thermal conductivity detector, the peak areas determined are directly influenced by the carrier-gas flow changes at the column outlet, and errors amounting to a few percent are to be expected. This could be an explanation of the discrepancies in quantitation found by Novak *et al.*<sup>5,6</sup>

With mass rate-sensitive detectors, such as the flame-ionization detector, the effect of column outlet flow-rate changes is low and the changes in carrier gas flow-rate influence merely the ionization efficiency.

In order to suppress the unwanted effects of column outlet flow-rate changes in quantitative analysis, we have to reduce the external volumes, to use columns of small inner diameter and to use hydrogen in preference to helium as the carrier gas in PTGC.

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