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LINEAR VELOCITY CONTROL IN CAPILLARY SUPERCRITICAL FLUID CHROMATOGRAPHY BY RESTRICTOR TEMPERATURE PROGRAMMING

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SUMMARY

Increasing restrictor temperature decreases mass flow through capillary columns in a predictable way. Changes in mass flow can be related to changes in column linear velocity. Restrictor temperature programming, therefore, offers the potential for independent control of column efficiency while pump pressure, at constant oven temperature, controls fluid density. Experimental measurements of mass flow through restrictors at various temperatures and pressures confirm model predictions.

INTRODUCTION

The need to control the mobile phase linear velocity through the column is one of the most fundamental concepts of chromatography, but surprisingly little attention has been paid to linear velocity control in capillary supercritical fluid chromatography (SFC). This lack of attention may have arisen, in part, because there has not been, until recently[1], any accurate mathematical model for predicting mass flow through the system. In addition, no devices exist which can accurately adjust the extremely small mass flow-rates necessary for capillary SFC.

Capillary SFC almost invariably involves pressure programming from low to higher densities to consecutively solvate and elute a range of solutes in a single run[2-4]. Most capillary SFC systems use a syringe pump which is run in a pressure-control mode. Fixed restrictors are used as mass-flow controllers at system pressures dictated by the pump. All fixed restrictors produce increasing mass flow with pressure. This increased mass flow can result in an increase in mobile phase linear velocity in the column, by as much as 10–15 times during a pressure-programmed run[5-7].

Changes in the geometry of restrictors can make the flow through them either laminar or tubulent[1]. As pressure increases, laminar-flow restrictors produce more exaggerated increases in linear velocity than turbulent-flow devices. The worst case is a very-laminar-flow restrictor operated at a high temperature with moderate (*i.e.*, 40–60°C) column temperatures. Under these conditions column linear velocity can increase more than 10 times during a pressure-programmed run (from 80 to 400 atm).

Chromatographic efficiency is dictated by the ratio of the solute binary diffusion coefficient (D_{12}) in the mobile phase, to the linear velocity (u) of the mobile phase

through the column. Diffusion coefficients decrease in rough proportion to increasing density[8,9] and viscosity[10,11] of the mobile phase and with the square root of molecular weight[12] of the solute. To maintain constant efficiency and resolution, linear velocity should decrease 2–5 times during a pressure-programmed run to compensate for increasing density and viscosity. However, since late eluters are typically heavier (higher molecular weight), linear velocity should decrease more than to just offset the effects of density and viscosity. A further decrease of around 3.2 times would be needed to compensate for an order of magnitude increase in molecular weight. The combination of increasing density, viscosity and molecular weight suggests column linear velocity may need to drop as much as 15 times during a pressure-programmed run if constant column efficiency is to be maintained. It was pointed out above that most capillary chromatographs produce increasing column linear velocity during pressure-programmed runs, instead of the substantial decreases required.

No variable restrictors capable of controlling the very small mass flows of interest in capillary SFC have been reported. Many workers[13–15] program oven temperature along with system pressure to change column density. In the extreme (*i.e.*, constant pressure) this isolates linear velocity changes from restrictor performance since mass flow out of the restrictor will remain constant if both the inlet pressure and temperature are fixed. Increasing column density while maintaining constant system mass flow will result in decreasing column linear velocity[13,16] (provided the program rate is low enough to prevent significant contributions from charging effects[7,17]). This, however, is not as complete a solution as it appears to be. Diffusion coefficients change more dramatically with temperature than with density. Diffusion coefficients are proportional to temperature to the 1.5 1.75 power[12], but are more nearly inversely proportional to density. Therefore, during inverse-temperature programs, diffusion coefficients drop faster than linear velocity. Inverse-temperature programming will lower the absolute value of linear velocity but it will not maintain constant reduced velocity of the mobile phase through the column or maintain constant column efficiency and resolution. In addition, chromatographic retention is a complex function of both fluid density and temperature. Semonian and Rogers[18] point out that chromatograms obtained at the same density but different temperatures, or through inverse-temperature programming compared to increasing-pressure programming, will probably be different.

While inverse-temperature programming of the column has some advantages over pressure programming at fixed oven temperatures, it is preferable to have independent control over both column density and mobile phase linear velocity. The present work proposes the use of restrictor temperature programming to control mass flow and column linear velocity semi-independent of column density. The temperature programs required can be predicted mathematically for most types of commonly used restrictors. The approach is to program the restrictor temperature, not to change its internal diameter, but to vary the physical properties of the mobile phase.

THEORY

A previous report[7] showed that restrictors can be modeled accurately, and that restrictors useful for capillary SFC range from those exhibiting very laminar to those with nearly turbulent flow. The degree of turbulence was shown to strongly impact

mass flow and the resulting column linear velocity *vs.* pressure profiles. The more laminar the device, the worse is the increase in linear velocity with pressure, corresponding to the worse loss in chromatographic resolution from start to finish of a pressure-programmed run. Two models are required to completely describe both very laminar and turbulent restrictors.

Laminar-flow restrictors

Laminar-flow restrictors tend to perform very poorly chromatographically. The loss in efficiency with increasing pressure was discussed above. In addition, since virtually all system pressure is dissipated inside the restrictor, part of the restrictor operates at very low density where solutes can drop out of solution and be lost to the restrictor walls or agglomerates and produce detector spikes. Most workers have, therefore, abandoned laminar-flow restrictor designs. However, some frequently used restrictors still produce laminar flow.

Modified Poiseuille equation

Restrictors that can be described by the modified Poiseuille equation (eqn. 1) exhibit laminar flow, and large increases in mass flow *vs.* pressure. Typical calculations using this equation indicate that mass flow decreases with increasing temperature. This is due to the large decreases in the ratio of density to viscosity with increasing temperature[1].

$$F_{\text{rest}} = \frac{\pi r^4}{8} \frac{g_c}{L} \frac{P_{\text{in}} \rho_{\text{av}}}{\eta_{\text{av}}} \tag{1}$$

where F_{rest} = restrictor mass flow in g/s, r = radius in cm, g_c = $1.0136 \cdot 10^6$ g/cm s^2 atm, L = length in cm, P_{in} = restrictor inlet pressure in atm (assumes entire pressure drop occurs inside restrictor), and ρ_{av} and η_{av} = average density in g/cm^3 and average viscosity in g/cm s, respectively.

Column linear velocity

Column linear velocity can be related to restrictor mass flow using eqns. 2 and 3. Under steady-state conditions, mass flow through all parts of the system must be equal, so

$$F_{\text{col}} = F_{\text{rest}} \tag{2}$$

where F_{col} = column mass flow in g/s. Also

$$u_{\text{col}} = F_{\text{col}}/(\rho_{\text{col}} \times A) \tag{3}$$

where u_{col} = velocity of mobile phase in the column, ρ_{col} = fluid density in the column, and A = column cross-sectional area.

Substituting eqns. 2 and 3 into eqn. 1 produces eqn. 4 which relates flow velocity in the column to restrictor and column parameters. Constants can be grouped in one term and the variables pressure, density, and viscosity, in another.

$$u_{col} = \frac{\pi r^4}{8 \, LA} \, g_c \, \frac{P_{in} \rho_{av}}{\rho_{col} \eta_{av}} \tag{4}$$

Plotting the values of the right-hand term at different pressures and temperatures produces curves as shown in Fig. 1 showing the relative magnitude of changes in linear velocity independent of restrictor dimensions. Conditions producing constant column linear velocity independent of pressure would produce horizontal lines in Fig. 1. These results indicate that increasing restrictor temperature can be used to offset the normal increase in column linear velocity caused by increasing head pressure.

Temperature program rates

The restrictor temperature ramp rate required, to just offset increasing linear velocity caused by pressure ramps, can be predicted, as shown in Fig. 2. For the listed conditions, a temperature increase of 2°C is required to offset a pressure increase of 1 atm, and approximately linear temperature ramps compensate for linear pressure ramps. Constant linear velocity *vs.* pressure, however, was shown to be not enough to produce constant column efficiency over a run. Examining Fig. 1 shows that at least over narrow ranges of pressure, lines with negative slopes can be drawn. allowing some decrease in linear velocity with increasing pressure.
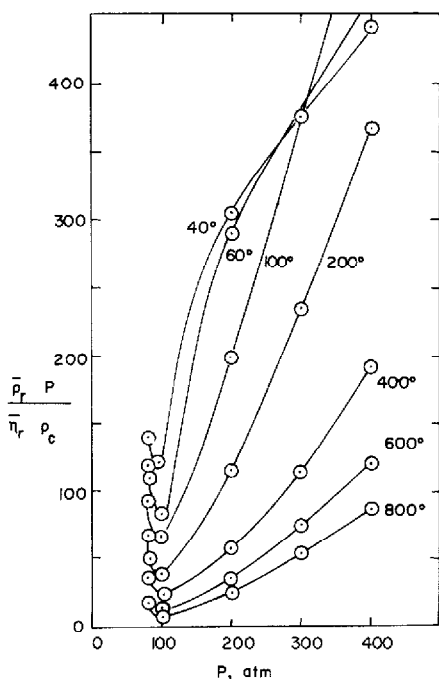

Fig. 1. Predictions of column linear velocity using the modifier Poiseuille equation. Term on left axis is nproportional to column linear velocity. Numbers next to curves indicate restrictor temperature. Column temperature assumed to be 40°C. $\bar{\rho}_r$ and $\bar{\eta}_r$ are average density and viscosity in the restrictor, ρ_c is column density and P is restrictor inlet pressure.
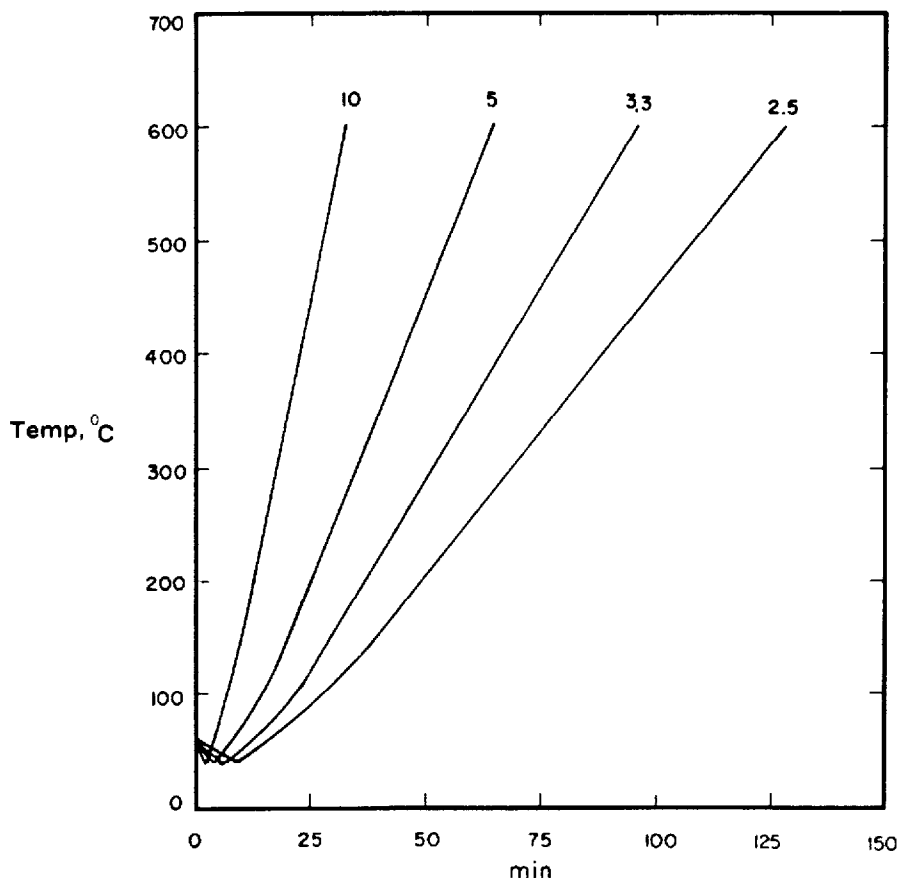
Fig. 2. Temperature (T) *vs.* time profile to produce constant column linear velocity during pressure programming using a linear (laminar flow) restrictor. Numbers next to curves are pressure program rates in atm/min starting from 80 atm and a column temperature and initial restrictor temperature of 40°C.

Turbulent-flow restrictors

It has been shown that turbulent-flow devices produce smaller increases in linear velocity *vs.* pressure than laminar-flow devices[7]. Mass flow still decreases with increasing restrictor temperature as in laminar-flow devices. This combination suggests turbulent-flow restrictors might give a wider range of linear velocity control than laminar-flow devices. Unfortunately, at the mass flows and pressures employed in capillary SFC, no restrictor type produces true turbulent flow. Integral restrictors[19] which have steep internal tapers (decreasing from 50 μm to less than 1 μm I.D. within less than 1 mm) leading to a pinhole opening and other pinhole types, however, produce nearly turbulent flow. Turbulent-flow calculations using Lapple's method as well as a detailed discussion of turbulent-flow restrictor modeling have been previously described[1].

Calculations of column linear velocity resulting from turbulent restrictor mass flow *vs.* pressure for an arbitrarily chosen restrictor size of 2 × 100 μm are presented in Fig. 3. The general shape of the curves are similar to those for the laminar-flow
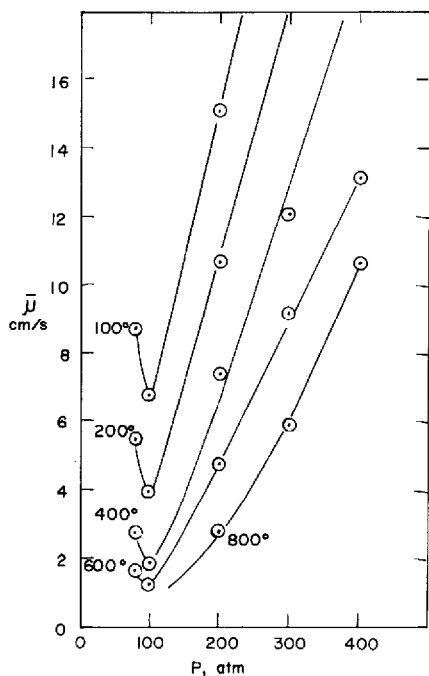
Fig. 3. Predicted column linear velocity using Lapple's method. Assumed column temperature is 40°C. Numbers next to curves are restrictor temperatures.

restrictor in Fig. 1 except the curves tend to exhibit less increase in linear velocity with increasing pressure, as expected. Constant linear velocity conditions could be represented with horizontal lines.

Heated-zone design

Very short restrictors are usually assumed to operate adiabatically. However, at low pressures and flow-rates, heat transfer may be adequate to maintain isothermal conditions. As pressure and mass flow increase, heat is more rapidly carried away by the expanding fluid and the device may operate more nearly adiabatically. The heated zones in most standard gas chromatographic detectors are not designed for use with such restrictors. There is typically a very large heated-zone I.D. compared to restrictor O.D., which tends to severely limit heat transfer. This is inadvertently compensated for by the heated-zone length being much too long. In very short restrictors the fluid upstream of the actual restriction must not be heated excessively compared to the column since this will drop fluid density and solute solubility in the restrictor below that in the column. For volatile solutes this is no problem since increased temperature will prevent such compounds from being lost. Some compounds, however, are thermally labile and their breakdown products are not volatile. In this case, tailing or loss of solutes can result.

EXPERIMENTAL

Instrumentation and chemicals

A Suprex Model 200 syringe pump was used to control the pressure of carbon dioxide supplied to the restrictors. Mass flows were measured with Sierra mass flow meters, and checked with bubble flow meters. The linear velocities reported in Figs. 4 and 5 are calculated values based on the measured mass flow-rates through integral (steep tapered) restrictors mounted in the heated zones described below. These mass flows together with the chosen column geometry, and column density vs. pressure and temperature[20,21] relationships allows direct calculation of linear velocity. These values of column linear velocity have been randomly checked chromatographically. A Hewlett-Pachard Model 5890 gas chromatograph with two standard flame ionization detectors was used as the chromatographic oven and detector. Hexane was injected through an injection valve and "tee" arangement. The "tee" was located in the oven, and the injection valve was a Valco Model 2WI4W.06 mounted on the gas chromatograh. The column was a methyl silicone 10 m × 50 μm I.D. column from J.&W. Scientific. Constant-pressure chromatograms were collected with a Hewlett-Packard Model 3396 recording integrator. Hexane solvent peaks were assumed to be unretained and therefore a direct measure of the column linear velocity. This chromatographic set-up was not used throughout the experiment because the heated zone located at the base of the flame ionization detector was of conventional design, had inappropriate geometry, and a maximum temperature of 400°C.
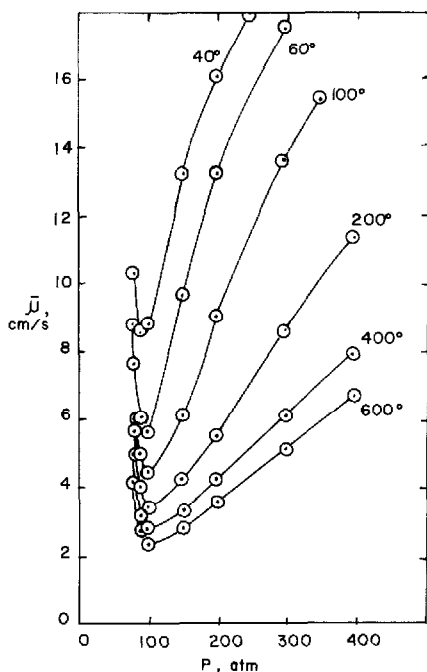

Fig. 4. Calculated column linear velocity from measured mass flows at different restrictor temperatures. Assumed column temperature is 40°C. Numbers next to curves are restrictor temperatures.
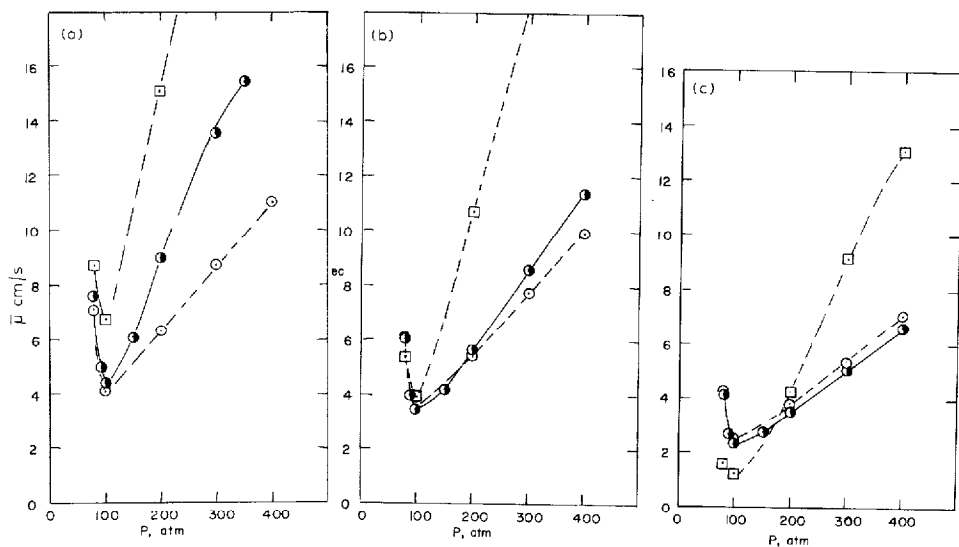
Fig. 5. Comparison of measured to predicted linear velocities. Column temperature is 40°C. □ = Predicted results from Poiseuille model; ○ = predicted results from Lapple's method; ◑ = results from measured mass flows. Restrictor temperature: (a) 100°C; (b) 200°C; and (c) 600°C.

Carbon dioxide was SFC grade supplied in aluminum cylinders from Scott Specialty Gasses. "Integral" (steep tapered) restrictors were purchased from J.&W. Scientific. It was recognized that decreasing wall thickness would minimize heat transfer problems but problems in fabrication and the fragility of thin-wall restrictors with short taper lengths made the thick-wall material more attractive. Linear restrictors were pieces of small I.D. tubing (5 and 10 μm) purchased from SGE.

Heated zones were constructed of 316 stainless steel. Zones consisted of up to three stackable units, each approximately 1 cm thick and equipped with its own heater and temperature sensor. Units could be run simultaneously or individually to determine the minimum length of heated zone required for adequate heat transfer. Several versions of the inner diameter of the heated zones have been tried. All produce intimate contact between the restrictor outer diameter and the zone block, without an air gap.

RESULTS AND DISCUSSION

Heated-zone lengths

All heated-zone lengths gave the same mass flow at the same temperature, even at 600°C. This suggests that zones can be made less than 1 cm long and still allow adequate heat transfer while not loosing solutes to the wall of the restrictor.

Integral restrictor mass flows

The mass flow of carbon dioxide through an integral restrictor (steep tapered) was measured as a function of both pressure and temperature, and the results are presented in Table I. This information was then used to calculate mobile phase linear

TABLE I

MASS FLOW ($\cdot$ 10^5 g/s) THROUGH AN INTEGRAL RESTRICTOR AS A FUNCTION OF PRESSURE AND TEMPERATURE

T (°C)	P (atm)						
	80	90	100	150	200	300	400
40	5.70	8.13	10.74	20.57	26.57	31.24[a]	—
60	4.85	5.67	6.73	14.95	21.84	31.33	—
80	4.52	5.16	5.92	11.41	17.65	27.76	—
100	4.22	4.79	5.40	9.50	14.74	24.27	28.57[b]
200	3.37	3.79	4.25	6.61	9.40	15.35	21.54
300	2.70	3.00	3.34	5.16	6.98	10.86	14.86
400	2.31	2.55	2.82	4.31	5.85	9.10	12.53

[a] Collected at 250°C.
[b] Collected at 350°C.

velocity expected at different column pressures and temperatures, an example of which is shown in Fig. 4.

These empirical results were compared to calculated values for both very laminar- (Fig. 1) and nearly turbulent-flow (Fig. 3) restrictors. The results appear remarkably like the calculated values in general shape and trends but more closely resemble the turbulent-flow calculations. Comparisons, as in Fig. 5a–c, indicate the degree of fit between the calculated and measured results at different restrictor
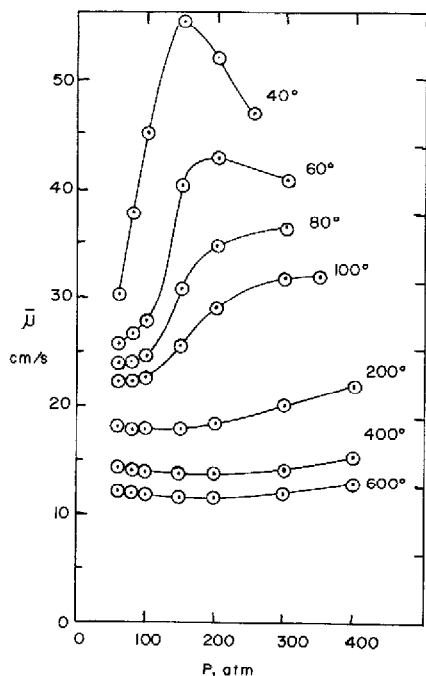

Fig. 6. Mass flow results of Fig. 4 replotted as linear velocities with column temperature increased to 200°C.

temperatures. The real restrictor acted less like a turbulent-flow device than expected. The discrepancies could arise from several sources. The restrictor could have a larger aspect ratio than estimated for the calculations or heat transfer may not be adequate to keep the restrictor at the set temperature (although the latter seems unlikely since both short and long heated zones gave the same result). We were somewhat surprised to find a more gradual than expected internal diameter taper in the commercially available integral restrictors when viewed under a microscope. This suggested that the discrepancies may be due to use of too small a restrictor aspect ratio in the calculations.

Real capillary columns are seldom operated at 40°C. The same mass-flow measurements used to calculate the linear velocities in Fig. 4, for a column temperature of 40°C, would yield the linear velocities in Fig. 6, if the column temperature were 200°C. This temperature is actually rather high for capillary SFC and represents an opposite extreme of the performance envelope. The results in Fig. 6 indicate that contrary to normal operation, where linear velocity increases from modest to large amounts during pressure-programmed runs, linear velocity can be decreased by at least a factor of three over the full pressure range and actually by larger amounts over narrower pressure ranges if restrictor temperature is programmed to counter the effects of increasing column pressure. Most chromatograms are collected using column conditions between the extremes represented by Figs. 4 and 6.

CONCLUSIONS

Restrictor flow can be accurately modeled and predictably controlled by changing restrictor temperature. The control concept employs changes in the fluid properties to throttle flow through a fixed restrictor. Since control is accomplished independent of column conditions it can be viewed as a means to independently control solute solubility through column density changes, and column efficiency through linear velocity control.

Work is progressing in interfacing a short, high-temperature heated zone into the base of a flame ionization detector with a programmable temperature controller so that chromatograms may be collected to determine the extent of expected efficiency improvements during pressure programming.

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