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Short communication

Nonsteady-state flow in gas chromatography during fast changes in inlet pressure

Tal M. Nahir*

Department of Chemistry, California State University, Chico, CA 95929-0210, USA

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Abstract

The steady-state assumption for describing the flow in a capillary gas chromatography column fails when changes in inlet pressure are introduced at a fast rate. To accommodate the possibility of nonsteady-state conditions, or a transient behavior, a second-order nonlinear differential equation for the pressure is suggested. Good agreement between the new theoretical model and representative experimental results is shown when the inlet pressure is increased at a rate of several hundred kPa per minute; in contrast, predictions from traditional steady-state calculations are relatively poor.

Keywords: Nonsteady-state flow; Pressure programming; Holdup time; Computer simulation; Gas chromatography

1. Introduction

In a previous report, we discussed the analysis of isothermal flow through a capillary gas chromatography (GC) column when the inlet pressure was programmed to change at a single rate [1]. For the special case of a near-vacuum outlet pressure, we developed theoretical expressions for retention times using steady-state assumptions, and the predictions were experimentally confirmed for relatively slow programmed changes in either inlet pressure or flow rate. In addition, we provided preliminary evidence for the failure of the steady-state model when rapid changes in inlet pressure were introduced. As a result, it became clear that some modification of the theoretical framework was required to explain the significant inconsistencies between experimental observations and traditional models for flow in GC columns when the inlet pressure was changing at a very fast rate.

More recently, we considered the changes in flow inside a column when a pressure pulse was incorporated into a GC run, and suggested a new approach for analyzing time-dependent processes when the inlet was subjected to abrupt changes in pressure [2]. Similar to the analysis of mass transport in a developing char layer [3], our proposed new theoretical model included the basic set of relationships normally associated with motion inside GC columns which was expanded by combining a one-dimensional continuity equation with Poiseuille's law and the ideal gas law. The result was a nonlinear second-order partial differential equation for the pressure inside the column during an isothermal process:

$$\frac{\partial p}{\partial t} = \frac{r_c^2}{16\eta} \cdot \frac{\partial^2 p^2}{\partial z^2} \quad (1)$$

where p is pressure, t the time, z the distance from the inlet, r_c the column radius, and η is carrier-gas viscosity. Given a desired set of initial and boundary conditions, Eq. (1) was solved numerically to provide pressure profiles, and retention times were calculated for several pulse experiments.

In this work, we apply the time-dependent model to explain results from experimental measurements of isothermal holdup times during fast programming of inlet pressure. The analysis also shows that the assumption of steady-state conditions leads to erroneous predictions.

2. Experimental

Isothermal runs at 40 °C were carried out with an initial absolute inlet pressure of 200.4 kPa (gauge pressure

* Fax: +1-530-898-5234.
E-mail address: tnahir@csuchico.edu (T.M. Nahir).

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of 100.0 kPa versus 100.4 kPa ambient pressure). An Agilent 7683 Series Injector was used to introduce 1.0 μl air samples at a 10:1 split ratio into a Hewlett-Packard HP-5 MS column (30 m × 0.250 mm, 0.25 μm nominal dimensions) in a Hewlett-Packard HP 6890 Plus Series GC System with helium as the carrier gas. Detection was accomplished by a Hewlett-Packard HP 5973 mass-selective detector operating at a very low pressure of several mPa pressure (measured by a Hewlett-Packard 59864B ionization gauge controller). Mass spectra were taken in the *m*/*z* range from 27.0 to 33.0 at 41.95 Hz, and holdup times were recorded at the apex of air peaks.

Changes to the inlet pressure were introduced using a linear program. At the fastest rates, a slight discrepancy was noticed between the set and the measured magnitudes (as displayed on the front panel of the chromatograph). For instance, at 500 kPa/min, the actual pressure was larger than the set value by about 10 kPa during the initial 10 s (approximately) after injection. While this pattern was noted repeatedly, its effects were not included in the theoretical calculations. In addition, no adjustments were made in the computations to compensate for the permeation of carrier gas through the column walls [4].

The ratio of the length of the column to its radius was calculated from a constant-pressure isothermal run with an absolute inlet pressure of 200.4 kPa at 40 °C. Using a measured holdup time of 0.964 minutes, the magnitude of L/r_c was obtained from:

$$t_m = \frac{32}{3} \cdot \frac{L^2}{r_c^2} \cdot \eta \cdot \frac{p_{in}^3 - p_{out}^3}{(p_{in}^2 - p_{out}^2)^2} \quad (2)$$

where t_m is holdup time, $\eta = 0.373 \times T^{0.698}$ μPa s for helium [5], p_{in} is inlet pressure, and p_{out} is outlet pressure [6]. Assuming an actual column radius of 125 μm, a column length of 28.72 m was calculated.

Calculations were performed using Microsoft Visual Basic 4.0 with 200 equal-length column segments, and the motion of a compound through the column was simulated at discreet time intervals, δt, whose magnitude is given in Eq. (3). Starting at the time of injection, pressure profiles were computed in response to changes in inlet pressure according to either Eq. (4) for the transient model or Eq. (5) for the steady-state model. At each time step, the motion of an unretained compound was digitally simulated by calculating an incremental distance given by the product of δt and u from Eq. (6) for the column segment where the compound was located. This pattern of first computing a new pressure profile and then an incremental progress toward the outlet was repeated until the sum of the calculated distance increments exceeded the length of the column; the corresponding sum of time intervals was the retention time (or holdup time in the case of an unretained compound).

3. Results

Several isothermal runs were performed with the inlet pressure programmed to increase linearly with respect to time at a range of constant rates, g_p, from an identical initial pressure. In addition to experimentally measuring holdup times, the theoretical magnitudes of t_m were predicted according to models based on either transient (i.e. nonsteady-state) or steady-state behavior. Transient-model calculations were performed using well-established procedures for numerical solutions of nonlinear partial differential equations [7]. To satisfy the stability requirement, the solution of Eq. (1) was performed at discreet time increments of:

$$\delta t = \frac{4\eta}{3r_c^2 p_{max}} \cdot \left(\frac{L}{j}\right)^2 \quad (3)$$

where j is the number of equal-length distance increments inside the column, and p_{max} is equal to (or greater than) the magnitude of the largest pressure during the analysis. The pressure in the segment of interest, i, for the transient case was obtained according to:

$$p_i' = p_i + \frac{1}{12p_{max}} \cdot (p_{i-1}^2 - 2p_i^2 + p_{i+1}^2) \quad (4)$$

where the magnitude of the pressure at the point of interest, p_i', is calculated from three earlier (by δt) pressures: one at a point closer to the inlet (at a distance of $-L/j$ from i) shown as $i-1$, another at i itself, and one at a point closer to the outlet ($+L/j$ from i). Note that all calculations here assume that the outlet pressure is constant, and that the inlet pressure changes incrementally (according to the desired pressure program and as the experiment progresses) by a

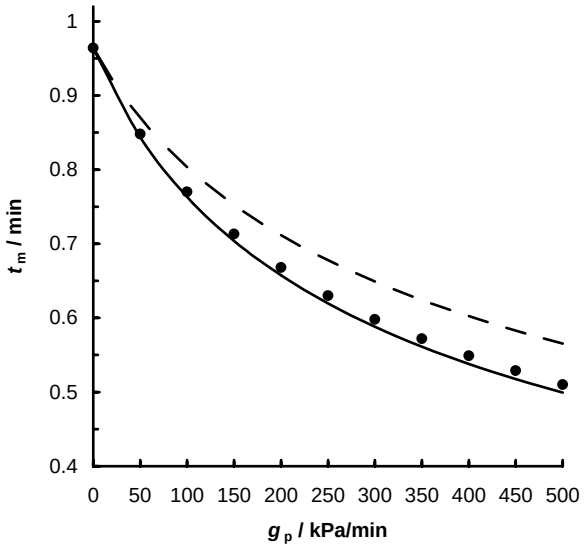

Fig. 1. Comparison of experimental holdup times (circles) with predictions from transient (solid line) and steady-state (dashed line) models for several inlet-pressure programs with constant rates, g_p. All runs were at 40 °C with an initial absolute inlet pressure of 200.4 kPa.

magnitude equal to the product of g_p and δt, the time increment from Eq. (3). Thus, pressure profiles were calculated according to Eq. (4) for i values corresponding to all column increments excluding the first and last segments. For comparison, the steady-state pressure profiles were calculated from

$$p_i = p_{in}\left[1 - \frac{i}{j}\left(1 - \frac{p_{out}^2}{p_{in}^2}\right)\right]^{1/2} \quad (5)$$

Note that Eq. (5) corresponds to the solution for Eq. (1) if the pressure profiles are assumed to be established instantaneously (i.e. when the process is time-independent) [2].

As Fig. 1 shows, the discrepancy between actual measurements and predictions from the steady-state model increases as the magnitude of g_p increases. In contrast, holdup times calculated according to the transient model show a substantially better agreement with experimental results.

4. Discussion

The failure of the steady-state model to predict correct holdup times when changes in inlet pressure happen at a relatively fast rate is related to the fact that the effects of flow-related events at the inlet cannot be assumed to always propagate through the column on a time scale which is insignificant when compared to that of a complete run. Therefore, it would seem inappropriate to presume that the corresponding adjustments in pressure profiles throughout the whole column would occur instantaneously as suggested by steady-state assumptions.

Fig. 2 shows the substantial disparity in theoretical pressure profiles between the steady-state and the transient calculations when the inlet pressure is programmed to rise at a very fast rate. In general, the results show that the system does not adjust fast enough to justify an approximation by a steady-state configuration, and the discrepancy is likely to result in a significant difference between the corresponding computed retention times.

To further illustrate the difference between the results from the two models, we next compute the pressure gradients from the corresponding pressure profiles, and calculate the velocity of the mobile phase according to Poiseuille's law [8] in a distance increment of interest:

$$u = -\frac{r_c^2}{8\eta}\cdot\frac{\partial p}{\partial z} \approx -\frac{r_c^2}{8\eta}\cdot\frac{p_{i+1} - p_i}{L/j} \quad (6)$$

The holdup time is found according to the integral (or the corresponding summation over all column segments):

$$t_r = \int_0^L u^{-1}\,dz \quad (7)$$

Fig. 3 shows a comparison of values predicted for u^{-1} using steady-state and transient models. Note that initially the velocity is higher in the transient case, but that trend is reversed in the second half of the column where the steady-state calculation predicts larger velocities. Since overall the area under the curve is smaller in the nonsteady-state calculation, the magnitude of t_m is overestimated by the steady-state calculation. This is consistent with the results

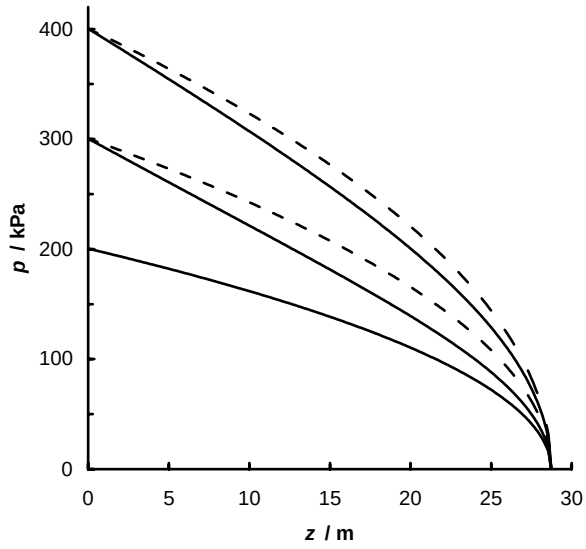

Fig. 2. Time-dependent evolution of pressure profiles when the inlet pressure is increased at a constant rate of 400 kPa/min from 200.4 kPa (absolute pressure) during the initial 0.5 min of an isothermal run at 40 °C. The outlet pressure is that for a detector operating at near vacuum. The solid line shows the transient response according to the numerical solution of Eq. (1), and the dashed line represents steady-state profiles according to Eq. (5).

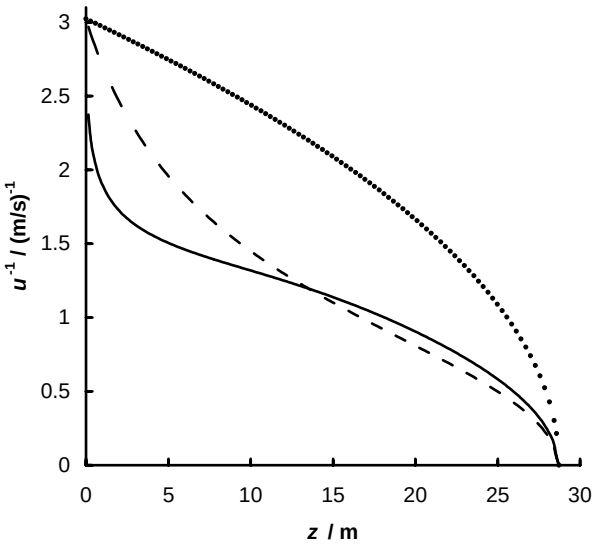

Fig. 3. Dependence of reciprocal velocity on location for an unretained compound inside the column during a fast inlet-pressure program (conditions are the same as in Fig. 2). The solid line shows the transient response, the dashed line represents the steady-state calculation, and the dotted line corresponds to a constant inlet pressure, i.e. $g_p = 0$.

shown for experimental and theoretical holdup times in Fig. 1.

Finally, it appears that the transient model would be necessary to properly describe the system when the inlet pressure is indirectly programmed to increase quickly; this might be the case at fast rates of temperature programming in a "constant-flow" mode [9], since the inlet pressure must be proportionally increased to compensate for higher carrier-gas viscosities as the temperature rises.

Acknowledgements

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