Journal of Chromatography, 463 (1989) 153–158
Elsevier Science Publishers B.V., Amsterdam — Printed in The Netherlands

CHROM. 21 057

Note

Non-steady pressure profiles in chromatographic columns

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(First received June 15th, 1988; revised manuscript received October 18th, 1988)

The pressure change produced from steady-state flow at a tubular reactor inlet alters the pressure profile and makes it dependent on time, t. This perturbation travels down the reactor, and at time t_L arrives at the outlet. This time t_L is the so-called "response time". A pressure-programmed gas chromatographic column is a good example of this type of tubular reactor.

The treatment of non-steady flow is much more difficult. Non-steady profiles have been obtained as a numerical solution for a non-linear partial differential equation. Special cases, which correspond to sudden pressure jumps at the inlet[1] or to continuous pressure programming[2], have been solved.

Response time has been measured in different cases: (a) discontinuous inlet-pressure changes in packed columns[1] or capillary columns[3] and (b) pressure programming in packed columns[4].

This paper describes a method for calculating non-steady pressure profiles in chromatographic columns. The pressure profiles are calculated in accordance with the response time for the case of a continuous pressure variation.

EXPERIMENTAL AND RESULTS

The pressure profile at any given time t is assumed to be the section of the graph of the function $p(x,t)$ which is represented by a sum of the form:

$$p(x,t) = p_0(x,t) + p_1(x,t) + \ldots + p_n(x,t) \quad (1)$$

where x is the distance between a point in the column and the inlet section of the column; $p_0(x,t)$ represents the stationary profile at any time t with an inlet pressure which may vary according to

$$p_e = p_{e0} + h(t) \quad (2)$$

The expression of the function $h(t)$ reflects the type of pressure variation imposed.

The additional terms $p_i(x,t)$ allow the description of the exact pressure profile

0021-9673/89/$03.50

observed. Thus, it is possible to consider a "quasi-unchanged" pressure distribution. This distribution is always described by the basic equation

$$\frac{\kappa}{2\eta} \cdot \frac{\partial^2 p^2}{\partial x^2} = \frac{\partial p}{\partial t} \tag{3}$$

where κ is the column permeability and η the carrier gas viscosity.

Let us introduce the following set of reduced variables, each of which is dimensionless:

$$\begin{aligned} p^* &= p/p_s \quad \text{(reduced pressure)} \\ x^* &= x/L \quad \text{(reduced distance)} \\ t^* &= t/\tau \quad \text{(reduced time)} \end{aligned} \tag{4}$$

where p_s is defined as the outlet pressure. The reference time τ is defined as

$$\tau = 2\eta L^2/\kappa p_s \tag{5}$$

where L is the column length. When these reduced variables are used, the mathematical analysis is simplified and eqn. 1 is transformed to

$$\frac{\partial^2 p^2}{\partial x^2} = \frac{\partial p}{\partial t} \tag{6}$$

if the asterisk is removed. The term $p_0(x,t)$ corresponding to steady-state flow, at time t, is the solution of the equation

$$\frac{\partial^2 p_0^2(x,t)}{\partial x^2} = 0 \tag{7}$$

After two integrations we obtain the quadratic form

$$p_0^2 = A - Bx \tag{8}$$

where

$$A = p_0^2(0,t) = p_e^2$$

and

$$B = p_e^2 - p_0^2(1,t) = p_e^2 - 1$$

so that eqn. 8 may be written as

$$p_0(x) = | \ p_e^2 - (p_e^2 - 1)x| ^{\frac{1}{2}} \tag{9}$$

which represents the classical James–Martin expression[5]. The shape of the function $p_0(x)$ is given in Fig. 1 and a net decompression appears near the column outlet.

Determination of p_1

Only p_1 will be calculated. We substitute the sum $p_0 + p_1$ for the variable p in eqn. (6). After linearization, the following equations, with dimensionless parameters, are obtained:

$$\frac{\partial^2 p^2}{\partial x^2} \approx \frac{\partial^2(p_0^2 + 2p_0p_1)}{\partial x^2} = \frac{\partial p_0}{\partial t} = \frac{2p_e p_e' - 2p_e p_e' x}{2|p_e^2 - (p_e^2 - 1)x|^{\frac{1}{2}}} \tag{10}$$

where p_e' is the derivative of the function p_e with respect to reduced time. A first integration with respect to x gives

$$\frac{\partial(p_0^2 + 2p_0p_1)}{\partial x} = \alpha + \frac{2p_e p_e'}{(p_e^2 - 1)^2} \cdot p_0 + \frac{p_e p_e'}{p_e^2 - 1}\int p_0 \mathrm{d}x \tag{11}$$

where α is a constant. A second integration gives

$$p_0^2 + 2p_0p_1 = \alpha x + \beta + \frac{4}{3} \cdot \frac{p_e p_e'}{(p_e^2 - 1)^3}\left(\frac{p_0^5}{5} - p_0^3\right) \tag{12}$$

where β is a constant.

For $x = 0$, we have $p_0 = p_e$ and $p_1 = 0$, hence β may be calculated as the initial conditions:

$$\beta = p_e^2 - \frac{4}{3} \cdot \frac{p_e p_e'}{(p_e^2 - 1)^3}\left(\frac{p_e^5}{5} - p_e^3\right) \tag{13}$$

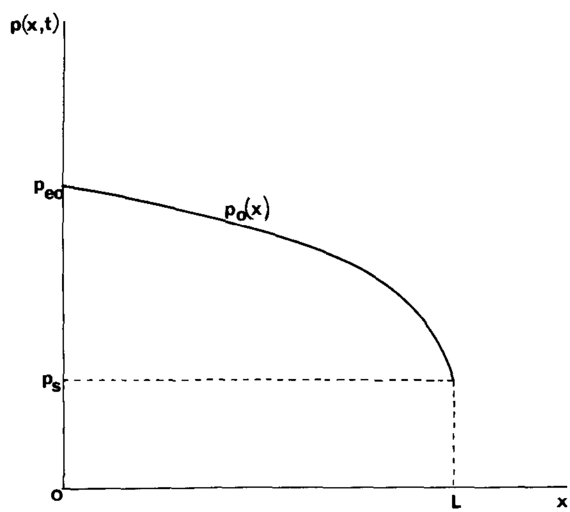

Fig. 1. Plot of $p(x,t)$ *versus* x.

TABLE I

EFFECTS OF THE REFERENCE TIME τ AND THE PROGRAMMING RATE b ON THE TERM p_1

τ	κ/η*	p_e	b**	x*	p_0	p_1
4	1	2	10^{-3}	0.5	1.58	$-1.94 \cdot 10^{-4}$
40	10^{-1}	–	–	–	–	$-1.94 \cdot 10^{-3}$
400	10^{-2}	–	–	–	–	$-1.94 \cdot 10^{-2}$
4	1	2	10^{-3}	0.25	1.80	$-1.42 \cdot 10^{-4}$
–	–	1.2	–	–	1.15	$-2.00 \cdot 10^{-4}$
4	1	2	10^{-3}	0.5	1.58	$-1.94 \cdot 10^{-4}$
–	–	–	10^{-2}	–	–	$-1.94 \cdot 10^{-3}$
–	–	–	10^{-1}	–	–	$-1.94 \cdot 10^{-2}$
40	10^{-1}	2	10^{-3}	0.25	1.80	$-1.42 \cdot 10^{-3}$
–	–	–	–	0.50	1.58	$-1.94 \cdot 10^{-3}$
–	–	–	–	0.75	1.32	$-1.50 \cdot 10^{-3}$

* Values are expressed in s atm m^{-2} for a column of length $L = 2$ m and outlet pressure $p_s = 1$ atm.
** Values are expressed in atm s^{-1}.

For $x = 1$, $p_0 = 1$ and $p_1 = 0$, we obtain

$$\beta = 1 - p_e^2 + \frac{4}{3} \cdot \frac{p_e p_e'}{(p_e^2 - 1)^3}\left(\frac{4}{5} + \frac{p_e^5}{5} - p_e^3\right) \tag{14}$$

and finally

$$p_1 = \frac{2p_e p_e'}{3p_0(p_e^2 - 1)^3}\left[\frac{4x}{5} + (x - 1)\left(\frac{p_e^5}{5} - p_e^3\right) + \left(\frac{p_0^5}{5} - p_0^3\right)\right] \tag{15}$$

p_1 is a linear function of the space variable x and is dependent on the type of programming of the inlet pressure.

TABLE II

VALIDITY OF THE APPROXIMATION $p^2 \approx p_0^2 + 2p_0p_1$: MAXIMUM VALUES OF b FOR DIFFERENT VALUES OF τ

Column length $L = 2$ m and outlet pressure $p_s = 1$ atm.

τ	κ/η*	*Maximum* b**
400	0.01	$5 \cdot 10^{-3}$
40	0.1	$5 \cdot 10^{-2}$
4	1	$5 \cdot 10^{-1}$

* Values are expressed in s atm m^{-2} for a column of length $L = 2$ m and outlet pressure $p_s = 1$ atm.
** Values are expressed in atm s^{-1}.

TABLE III

COMPARISON OF p (atm) OBTAINED BY THE PRESENT METHOD (A) AND A NUMERICAL METHOD (B)[2]

*Conditions**	*Method*	x^* 0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1
I	A	4.50_0	4.26_4	4.02_0	3.76_4	3.49_5	3.20_8	2.89_7	2.55_3	2.16_0	1.68_1	1.00_0
	B	4.50_0	4.26_5	4.02_1	3.76_6	3.49_7	3.21_0	2.90_0	2.55_6	2.16_3	1.68_4	1.00_0
II	A	2.25_0	2.24_8	2.14_3	2.03_4	1.91_9	1.79_7	1.66_7	1.52_7	1.37_4	1.20_1	1.00_0
	B	2.25_0	2.24_9	2.14_4	2.03_4	1.91_9	1.79_8	1.66_8	1.52_8	1.37_4	1.20_2	1.00_0

* Conditions: I, $p(0,0) = 3.5$, $\tau = 8$, $t = 0.25\tau$, $b = 5 \cdot 10^{-1}$ atm s^{-1}; II, $p(0,0) = 2.15$, $\tau = 8$, $t = 0.25\tau$, $b = 5 \cdot 10^{-2}$ atm s^{-1}.

Application to linear flow programming

Linear programming was chosen to test the present method; the function $h(t)$ is written as

$$h(t) = bt$$

Two parameters have an important effect on the term p_1 (see Table I); the reference time, $\tau = 2\eta L^2/\kappa p_s$, and the programming rate, b. The validity of the approximation $p^2 \approx p_0^2 + 2p_0p_1$ is limited by the values of b. Table II shows the maximum values of b for different values κ/η, with an error for 0.3% in the pressure p, the inlet pressure being 2 atm.

From Table III, it is possible to compare the present method (method A) with a numerical method (method B) used in previous work[3]. Method B gives a polynomial development of the pressure profile. There is good agreement between the two methods.

CONCLUSION

A continuous change in flow causes a departure from a steady state. The assumption that the time-varying pressure profile along the column is the same as that existing in constant-pressure operation for a given inlet pressure value is not satisfactory[6], so we have added a perturbation term to the classical pressure profile of James and Martin[5] to obtain the actual profile. A flow variation at the column inlet give rise to a perturbation that reaches the column outlet at a time t_L, which is usually small. The present method is rigorously applicable to pressure distributions after this time. In the theory, a second-order term is neglected owing to its smallness when the programming rate is not too high; when the permeability of a column decreases, the maximum programming rate likewise decreases. The results are in good agreement with those obtained by numerical methods.

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