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Kanji Tamamushi[a]; David J. Wilson[a]
[a] DEPARTMENT OF CHEMISTRY, VANDERBILT UNIVERSITY, NASHVILLE, TENNESSEE

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Line Shapes in Gas Chromatography. An Improved Numerical Integration Method

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KANJI TAMAMUSHI and DAVID J. WILSON*

DEPARTMENT OF CHEMISTRY
VANDERBILT UNIVERSITY
NASHVILLE, TENNESSEE 37235

Abstract

Line shapes in gas chromatography are modeled by numerical integration of the differential equations describing mass transfer. The numerical dispersion which usually introduces substantial error into such calculations is greatly reduced by the use of one of three so-called asymmetrical upwind algorithms for handling the advection term. The effects of the various parameters in the model, which assumes a Langmuir adsorption isotherm, are illustrated.

INTRODUCTION

The problem of calculating line shapes in gas chromatography has been around for many years and has been attacked by a variety of different approaches. Line shapes are determined by the interplay between eddy diffusion, molecular diffusion, advection, the nature of the partitioning of the volatile solute between the moving vapor phase and the stationary liquid phase, and the resistance to mass transfer between the moving and stationary phases. For many purposes the use of Gaussian peaks and the Van Deemter equation is quite adequate. The early work on line shape calculations has been reviewed by Giddings (*1*).

A general method for doing line shape calculations by means of a

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*To whom correspondence should be addressed.

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stochastic approach was developed by Giddings (*1–6*). Houghton has used perturbation methods for taking the effects of diffusion and nonequilibrium mass transport into account (*7*). Vink has carried out line shape calculations using a mesh technique for solving the partial differential equation (*8, 9*); our approach here carries on in this tradition. Yamazaki (*10*) and Kocirik (*11*) have used moment methods in the analysis of nonequilibrium chromatographic line shapes. Olson has determined the effect of carrier gas expansion in the column on peak width (*12*).

A number of special functions from analysis have been used in attacking the line shape problem. These include the Poisson distribution (*1*), Bessel functions (*1*), Gaussians (*13*) and exponentially modified Gaussians (*14*), a linear combination of the Cauchy function with a Gaussian (*13*), the Edgeworth series (*15*), the Gram-Charlier series (*16*), and a combination of the hyperbolic tangent joined to a Gaussian (*17*).

We investigated the effect of the finite rate of mass transport of solute between the moving and stationary phases by means of a time constant approach (*18*). A later paper of ours dealt with the effects of velocity and diffusion constant variation along the length of the gas chromatographic column, of the finite rate of mass transport, of finite sample injection time interval, and of departures from Henry's law behavior of the solute (*19*). Mott and Grushka studied the dependence of gas chromatograph peaks on the Chesler-Cram parameters (*20, 21*). Least squares fits of the Gram-Charlier series to experimental elution profiles were made by Vidal-Madjar and Guiochon (*22*). Pauls and Rogers investigated band broadening by use of exponentially modified Gaussians (*23*).

Dondi and co-workers have carried out statistical analyses of gas chromatograph peaks using the Gram-Charlier series and the Edgeworth-Cramer series (*24*), and have used the Edgeworth-Cramer series to determine peak parameters (*25*). Foley and Dorsey have developed improved equations for calculating figures of merit for ideal and skewed peaks (*26*).

If one uses a model with a nonlinear isotherm (departures from Henry's law behavior), one must give up the hope of obtaining exact analytical solutions to the partial differential equation governing the line shapes. Such departures from linearity are of particular interest in connection with preparative columns, which are usually run at relatively high loadings. One's choices are then 1) to use the linear theory, realizing that this may be a relatively poor approximation; 2) to use a series or moment method, which may give very good fits, but leaves obscure the working of the mechanisms affecting the line shapes; or 3) to resort to numerical integration of the partial differential equation, which is by no means as free from difficulties as one would like. Here we shall be concerned with the third alternative. One of the major problems with numerical integration of such equations is the occurrence of numerical dispersion, an artifact generally associated with the advection term which results in erroneous and extensive broadening of the peaks.

This problem of excessive numerical dispersion in the numerical integration of diffusion-advection equations is one which frequently arises in connection with the modeling of the dynamics of contaminants in groundwater; Anderson has given an excellent summary of the situation and of a number of techniques used to circumvent the difficulty (*27*). Leonard has shown that numerical dispersion can be greatly reduced by the use of so-called asymmetrical upwind algorithms for representing the advection term in these equations (*28*). We have utilized Leonard's QUICK algorithm and several others also based on Taylor's series expansions, finding that symmetrical representations for advection lead to unstable behavior, as do asymmetrical downwind formulas; but asymmetrical 3- or 4-point formulas are quite stable (i.e., free from oscillatory behavior) and result in drastically reduced numerical dispersion (*29, 30*). One constructs a set of coupled ordinary differential equations defined on mesh points in the space of the problem, and then integrates this set forward in time by means of any one of a number of standard methods. We have found fairly simple predictor-corrector methods to be quite satisfactory (*31*).

Here we examine the application of three of these upwind asymmetrical algorithms for the advective term to the calculation of gas chromatograph peak shapes. We assume that the partitioning of the solute between the moving and stationary phases is governed by a Langmuir isotherm, and we also assume local equilibrium between the moving and stationary phases. This last assumption could be relaxed without causing any difficulties with the upwind asymmetrical algorithms.

ANALYSIS

The mathematical formulation of the gas chromatography model just described is as follows.

$$\frac{\partial m(x,t)}{\partial t} = A \frac{\partial}{\partial x}\left(D \frac{\partial c_g}{\partial x}\right) - \frac{\partial}{\partial x}(v c_g) \qquad (1)$$

$$c_l = \frac{c_l' c_g}{c_g' + c_g} \qquad (2)$$

$$m = (f_v c_g + f_l c_l)A \tag{3}$$

where $m(x,t)$ = mass of solute per unit length of column a distance x from the head of the column at time t

A = cross-sectional area of column

D = axial dispersion constant, dependent on volumetric flow rate of gas

v = volumetric flow rate of gas at x

$c_g(x,t)$ = solute concentration (g/cm^3) in the vapor phase at x,t

$c_l(x,t)$ = solute concentration (g/cm^3) in the liquid phase at x,t

c_l' = Langmuir isotherm parameter

c_g' = Langmuir isotherm parameter

f_v = voids fraction in the column

f_l = liquid phase volume fraction in the column

Equation (1) is our dispersion-advection equation for the column. Equation (2) is the equilibrium expression for the partitioning of solute between the liquid and vapor phases. Equation (3) relates the mass of solute per unit length in the column to the solute concentrations in the liquid and vapor phases. The nonlinearity of Eq. (2) precludes the solution of the system in closed form and dictates a numerical solution. This is usually done by replacing the partial differential equation by a set of coupled ordinary differential equations involving the values of m and c_g at a discrete set of points x_i. The most physically intuitive algorithm for this is the one generally used to derive the partial differential equation in the first place,

$$\frac{dm_i}{dt} = \frac{AD}{\Delta x^2}(c_{g,i+1} - 2c_{g,i} + c_{g,i-1}) + \frac{1}{\Delta x}(v_{i-1}c_{g,i-1} - v_i c_{g,i}),$$

$$i = 1, 2, \ldots, N \tag{4}$$

$m_i \Delta x$ = solute mass in ith volume element of the column

(The variables c_g, c_l, and m in Eqs. (2) and (3) are also subscripted.) The peaks obtained by solution of this system in the limit $c_l' \to \infty$, $c_g' \to \infty$, $c'/c_g' = K_H$ (a linear isotherm) are very much broader than the peaks given by the exact solution to this special case, however. This excessive spreading remains even if one sets the axial dispersion constant equal to zero, establishing that the advection term is the source of this erroneous dispersion.

Another algorithm which one might consider for representation of the advection term is

$$\frac{-\partial(vc)}{\partial x} = \frac{1}{\Delta x}(v_{i-\frac{1}{2}}c_{i-\frac{1}{2}} - v_{i+\frac{1}{2}}c_{i+\frac{1}{2}}) \tag{5}$$

which on linear interpolation to represent the quantities at the half-integral points gives

$$\frac{-\partial(vc)}{\partial x} = \frac{1}{2\Delta x}(v_{i-1}c_{i-1} - v_{i+1}c_{i+1}) \tag{6}$$

This algorithm, and all other algorithms we have tried which are antisymmetric about the point *i* (so-called symmetrical formulas) turned out to be very unsatisfactory. As one integrates the equations forward in time, the solutions acquire a highly oscillatory character, with the oscillations increasing without apparent limit as the integration proceeds. (See Ref. *29* for illustrations of some very similar calculations.)

Leonard's exhortations on the advantages to be gained by the use of assymmetrical upwind algorithms in integrating partial differential equations such as the diffusion-advection equation (*28*) and our own experience with using this approach on groundwater problems (*29, 30*) dictated their use in the gas chromatography problem. Leonard has proposed the use of the so-called QUICK algorithm, a 3-point asymetrical formula of the form

$$\frac{-d}{dx}(vc)_i = \frac{1}{\Delta x}\left[\frac{-1}{2}(vc)_{i-2} + 2(vc)_{i-1} - \frac{3}{2}(vc)_i\right] \tag{7}$$

This formula also represents $[(vc)_{i-\frac{1}{2}} - (vc)_{i+\frac{1}{2}}]/\Delta x$ as well.

We have derived two asymmetrical 4-point upwind formulas to represent the advection term: These are

$$\frac{-\partial(vc)_i}{\partial x} \cong \frac{1}{\Delta x}[(vc)_{i-\frac{1}{2}} - (vc)_{i+\frac{1}{2}}] \cong \frac{1}{\Delta x}\left[-\frac{1}{8}(vc)_{i-2} + \frac{7}{8}(vc)_{i-1} - \frac{3}{8}(vc)_i - \frac{3}{8}(vc)_{i+1}\right] \tag{8}$$

and

$$\frac{-\partial(vc)_i}{\partial x} \cong \frac{1}{\Delta x}\left[-\frac{1}{6}(vc)_{i-2} + (vc)_{i-1} - \frac{1}{2}(vc)_i - \frac{1}{3}(vc)_{i+1}\right] \quad (9)$$

All of these formulas are obtained by writing Taylor's series for the desired quantity expanded about the $i-2$, $i-1$, i, and $i+1$th points (or $1-2$, $i-1$, and i in the case of Eq. 7), and then using the set of equations to eliminate the higher derivatives.

We note that use of any of these asymmetrical upwind algorithms eliminates the interpretation of the compartments into which the column is mathematically partitioned as theoretical transfer units (theoretical plates).

Our discrete approximation to the partial differential equation then is taken as Eq. (4), with the advective term replaced by Eqs. (7), (8), or (9), and the algebraic Eqs. (2) and (3) adjoined. We then solve Eq. (3) for $c_{l,i}$ (the subscript i now replaces the continuous variable x), substitute this result in Eq. (2), and rearrange to obtain a quadratic equation in $c_{g,i}$:

$$0 = c_{g,i}^2 + \left(c_g' + \frac{f_l}{f_v}c_l' - \frac{m_i}{f_v A}\right)c_{g,i} - \frac{mc_g'}{f_v A} \quad (10)$$

This is solved by the quadratic formula; the positive sign must be taken to avoid negative values of $c_{g,i}$.

The system of differential equations is readily integrated by the following predictor-corrector method (31):

Starter:

$$m_i(\Delta t) = m_i(0) + \frac{dm_i}{dt}(0)\Delta t \quad (11)$$

Predictor:

$$m_i^*(t + \Delta t) = m_i(t - \Delta t) + \frac{dm_i}{dt}(t)\cdot 2\Delta t$$

Corrector:

$$m_i(t + \Delta t) = m_i(t) + \frac{\Delta t}{2}\left[\frac{dm_i}{dt}(t) + \frac{dm_i^*}{dt}(t + \Delta t)\right]$$

One starts initially with the total mass of the sample in the first compartment of the column. Equations (10) and (2) are used to calculate $c_{l,1}$ and $c_{g,1}$. It is then possible to integrate the differential equations forward one step in time, leading to a new set of values of the m_i. These give new $c_{l,i}$ and $c_{g,i}$. And so on.

It is necessary to modify the differential equations for $i = 1, 2$, and N, since the general equation requires nonexistent values of the $c_{g,i}$ for these values of i. We write

$$\frac{dm_1}{dt} = \frac{AD}{\Delta x^2}(c_{g,2} - c_{g,1}) - \frac{1}{\Delta x}(vc_g)_1 \tag{12}$$

$$\frac{dm_2}{dt} = \frac{AD}{\Delta x^2}(c_{g,3} - 2c_{g,2} + c_{g,1}) + \frac{1}{\Delta x}[(vc_g)_1 - (vc_g)_2 \tag{13}$$

$$\frac{dm_N}{dt} = \frac{AD}{\Delta x^2}(-c_{g,N} + c_{g,N-1}) + \frac{1}{\Delta x}[(vc_g)_{N-1} - (vc_g)_N] \tag{14}$$

Initial exploratory work with this approach was carried out on an Apple IIe, for which a program in Applesoft BASIC was written, debugged, and compiled. A typical run on the Apple IIe took about 2 h. This work indicated that numerical dispersion was very substantially reduced by use of any of the asymmetric upwind algorithms. A Fortran 77 program was therefore written, and the bulk of the computations were carried out on a DEC 1099 computer. Most of the runs took well under a minute of CPU time. The runs with $N = 200$ and $t = 0.1$ s took about 68 s; when t was reduced to 0.05 s, these runs took about 144 s. The results were tabulated and also displayed as graphs on the line printer. In most of the figures we shall be comparing results of the three asymmetric upwind algorithms—Eqs. (7), (8), and (9)—with the theoretical plate model for advection given in Eq. (4). We shall call Eqs. (7), (8), and (9) the first, second, and third algorithms;

$$\frac{-\partial}{\partial x}(vc)_i \cong \frac{1}{\Delta x}[(vc)_{i-1} - (vc)_i] \tag{15}$$

will be called the fourth algorithm.

All parameters are given in cgs units. Unless stated otherwise, the following parameters have the values indicated.

solute mass injected = 10^{-6} g
$\Delta t = 0.1$ s

$f_v = 0.75$
$f_l = 0.05$
column length = 250 cm
column cross-sectional area = 0.25 cm^2
$v = 1.00$ mL/s
$c_g' = 3.2 \times 10^{-4}$ g/mL
$c_l' = 5.0 \times 10^{-3}$ g/mL

Since we are interested in exploring the numerical dispersion resulting from the advection term, we have set the dispersion constant equal to zero in these runs. Since we are assuming instantaneous achievement of local equilibrium in the column, we would expect that, for runs with loadings in the linear range of the isotherm, we should see a very sharp spike coming off the column. Departures from this behavior are due to numerical dispersion.

Figure 1 compares the four algorithms for modeling advection for a column partitioned into 50 compartments ($N = 50$). $\Delta t = 0.1$ s here. The two 4-point algorithms give peaks which are somewhat narrower than the 3-point algorithm and which are less than half as wide as the peak obtained using the theoretical plate model. Figure 2 displays an identical set of runs, except that here $N = 150$. The peak widths obtained with the 4-point formulas are again somewhat less than that obtained with the 3-point formula, and are less than a third the peak width resulting from the

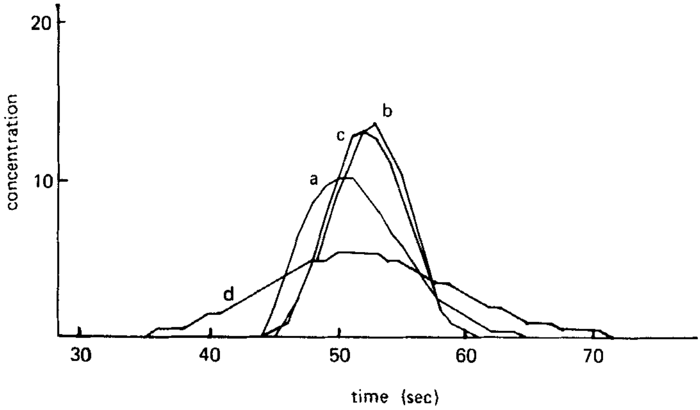

FIG. 1. Gas chromatograph line shapes. $N = 50$. (a) First algorithm (3-point); (b) second algorithm; (c) third algorithm; (d) fourth algorithm (theoretical transfer unit model). Other parameters are given in the text.

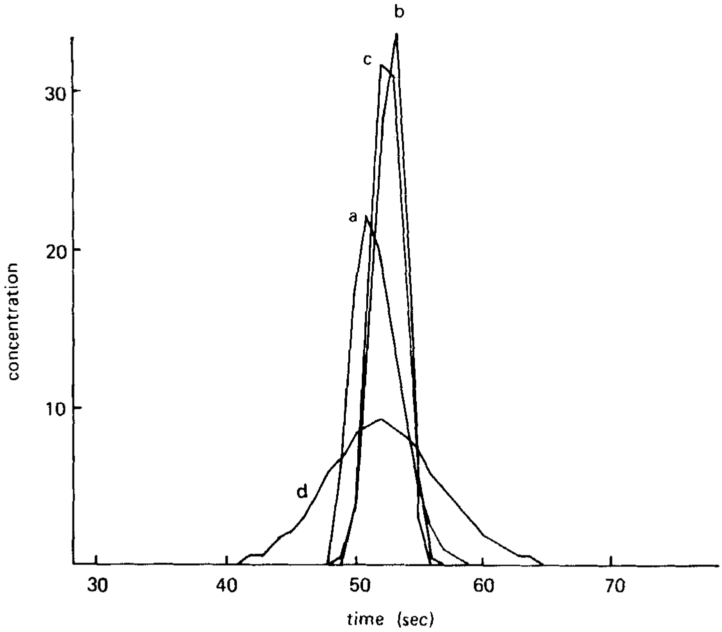

FIG. 2. Gas chromatograph line shapes. $N = 150$. The curves are labeled as in Fig. 1. Other parameters are given in the text.

theoretical plate treatment. We have set $N = 200$ in Fig. 3. The same pattern seen in the first two figures is repeated, except that the width of the peaks obtained with the 4-point algorithms is now about a fourth of the peak obtained with the theoretical plate model. In the calculations given in Fig. 3 it was necessary to use $\Delta t = 0.05$ s in the 3-point algorithm to avoid instability; $\Delta t = 0.1$ s proved satisfactory in the other algorithms.

The curves in Fig. 4 show the expected peak narrowing as N is increased from 50 to 200; line width appears to be varying as $N^{-1/2}$. Figures 5 and 6 present similar plots for the second and third algorithms; it is apparent that both algorithms are capable of producing quite narrow peaks for values of N equal to or above 150.

Figure 7 shows the effects of varying the gas flow rate. The peaks were obtained with the second algorithm. The relative positions of the peak maxima are exactly as one would expect from the various flow rates.

We conclude that the use of either of these 4-point upwind asym-

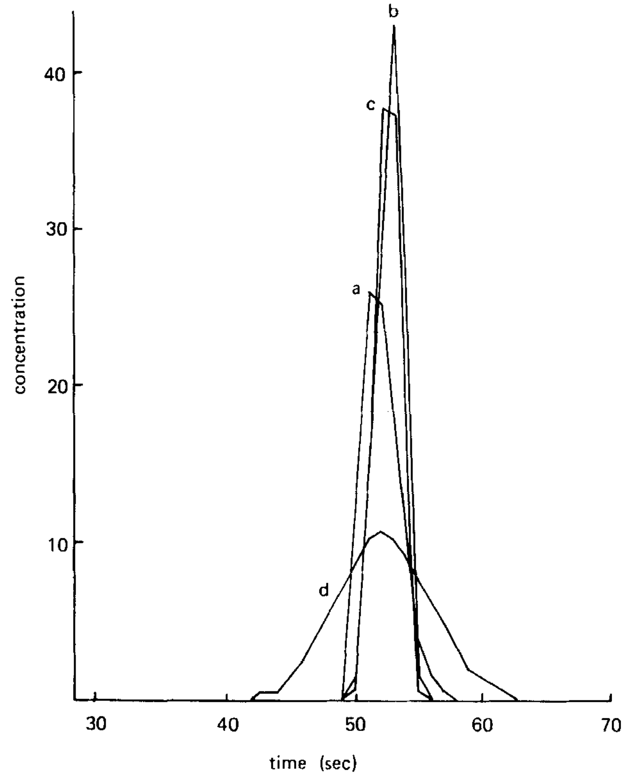

FIG. 3. Gas chromatograph line shapes. $N = 200$. The curves are labeled as in Fig. 1. $\Delta t = 0.05$ s for Curve a (first algorithm); $\Delta t = 0.1$ s for Curves b, c, and d. Other parameters are given in the text.

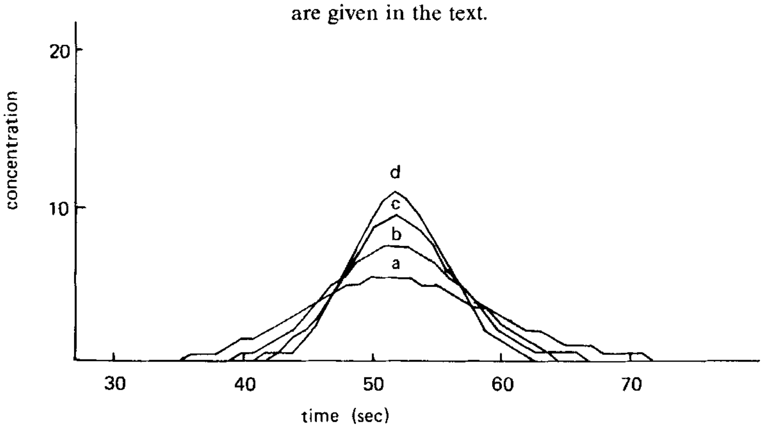

FIG. 4. Effect of N on gas chromatograph line shapes. $N = 50, 100, 150, 200$ (a–d). Curves were calculated with the fourth algorithm (theoretical transfer unit model).

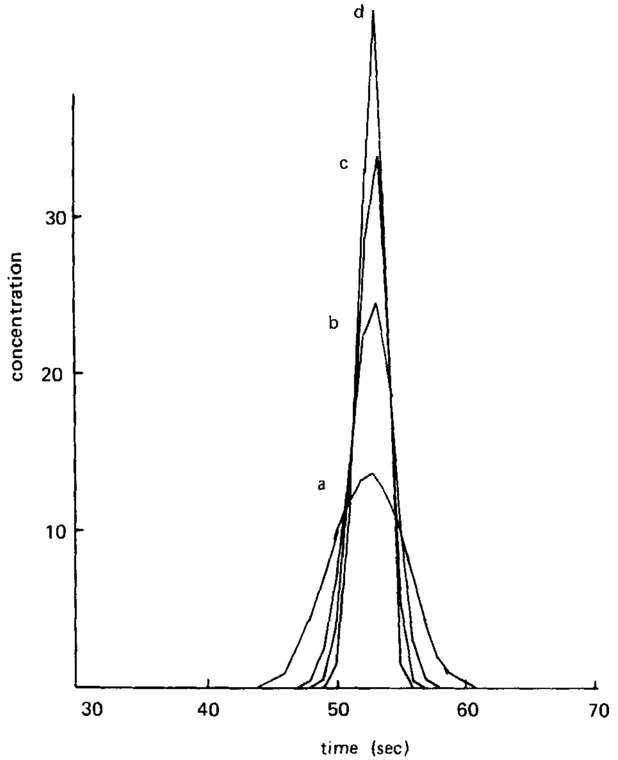

FIG. 5. Effect of N on gas chromatograph line shapes. The second algorithm was used. $N = 50, 100, 150, 200$ (a-d).

metrical algorithms in the modeling of gas chromatography line shapes drastically reduces numerical dispersion in the numerical integration of the relevant equations. With this technique, numerical integration becomes a useful, fast, and economical method for calculating gas chromatographic line shapes for volatile solutes exhibiting departures from Henry's law behavior.

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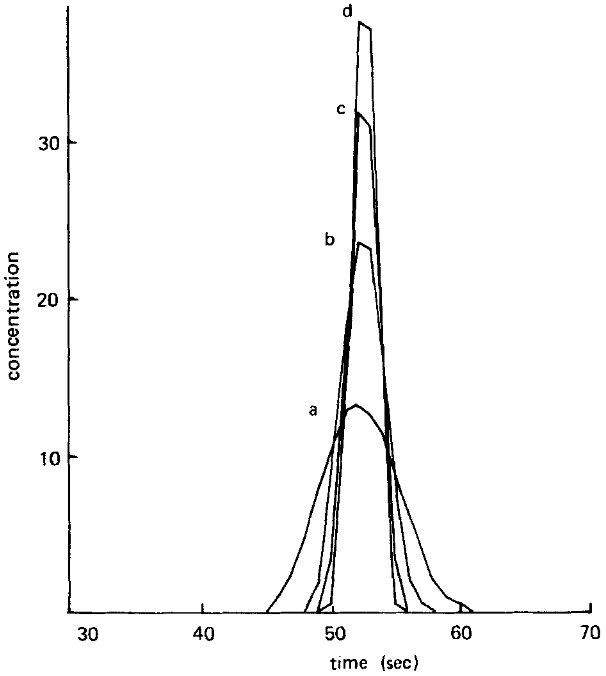

FIG. 6. Effect of N on gas chromatograph line shapes. The third algorithm was used. N = 50, 100, 150, 200 (a–d).

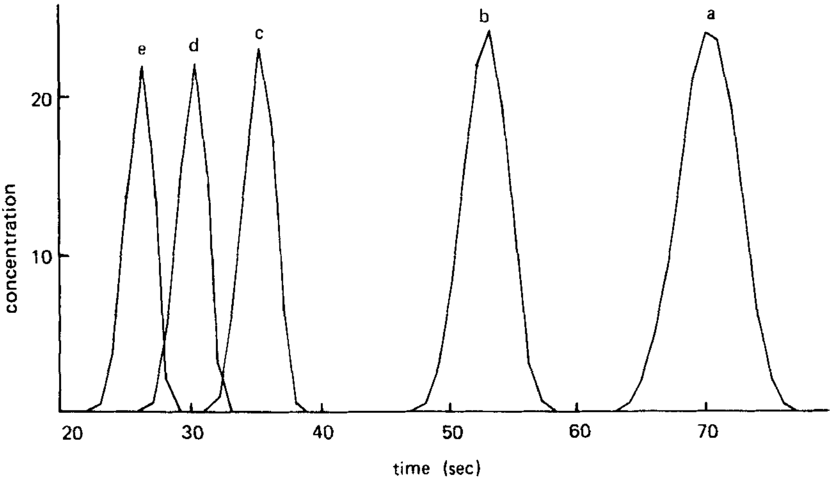

FIG. 7. Effect of flow rate on gas chromatograph line shapes. The second algorithm was used. N = 100, Δt = 0.2 s.

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