Random walk simulation of flow injection analysis.  
Evaluation of dispersion profiles

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Abstract

The use of the random walk model for simulating peak shapes in flow injection analysis (FIA) is investigated. Studies are limited to the case of dispersion in straight tubes with laminar flow (no reaction), but more precise peak shape data than has previously been available is provided. Peak shapes obtained with the random walk model are compared with experimental results and predictions made by other theoretical approaches. Comparisons utilize a wide variety of conditions, including those treated by other authors. Favorable agreement is obtained in all cases, although some differences with experimental results are observed. The computational aspects of the random walk algorithm are considered and guidelines for its implementation are provided. The versatility of the algorithm is demonstrated through the presentation of simulation results for modified laminar flow profiles, asymmetric flow profiles, and conditions of infinite radial diffusion.

Keywords: Flow injection; Dispersion profiles; Random walk simulation

In recent years, considerable effort has been directed towards obtaining a better understanding of peak shapes in flow injection analysis (FIA). Because of the interaction of diffusion, convection and chemical kinetics, the problem is non-trivial and is made more complex by the wide variety of geometries, manifolds and flow strategies that continue to appear. Achieving a better appreciation of factors that affect the shape of flow injection profiles is important because FIA has become a widely used tool for automated analysis. Furthermore, the use of modified FIA methods such as merging zones [1,2], flow reversals [3], and sinusoidal flow [4] underscore the need to be able to theoretically predict concentration distributions in a flowing stream.

A variety of methods for modeling concentration profiles in open tubes have been developed. These have been reviewed by several authors [5–8] and an extensive discussion will not be given here. Methods include single parameter descriptions of the dispersion of the sample plug [9], solution of the convection–diffusion equations [10–13] or tanks-in-series model [14,15], and discrete simulation [16,17]. Models have considered both the case of dispersion only and dispersion with chemical reaction. Descriptions based on the calculation of a single parameter are often useful in assessing the performance of a particular experimental system, but are of limited utility for more comprehensive studies that require an accurate description of concentration profiles. Numerical solution of the differential equations associated with the convection–diffusion or tanks-in-series models have produced results that are in good agreement with experimentally observed profiles, but these approaches are computationally intensive and often limited in terms of
the experimental geometries for which they are valid. In the work presented here, discrete simulations based on the random walk model developed by Betteridge et al. [16] are used. Although this method is also computationally intensive, it has several advantages which have been pointed out by the authors. Most notably, certain changes in the experimental parameters that are difficult to incorporate into other models are easily accommodated by the random walk model since the simulation treats individual molecules. Moreover, tentative physical models that explain the observed effects of changing system parameters (e.g. coiling, flow, injection profile, connections) may be more easily tested with the random walk model. Since the ultimate objective of these studies is to obtain a better understanding of the physical and chemical processes occurring within the FIA system, the ability to develop and test models for a variety of configurations is of critical importance.

In their original work [16], Betteridge et al. demonstrated that trends in peak height for the simulated results were in general agreement with experimental observations, but did not provide detailed comparisons of predicted concentration profiles with experimental measurements or the results of other models. This was due to the limited computational capabilities which prevented the simulation of more than a few thousand molecules in a reasonable time period. This resulted in concentration profiles with large amounts of stochastic noise, making them unsatisfactory for detailed comparisons. Such comparisons are important for evaluating the potential of the random walk approach to modeling FIA profiles, however.

In the work presented here, a comparison of peak profiles obtained by the random walk model with experimental and other theoretical results is provided. To keep the scope of the study reasonable, comparisons are limited to the case of dispersion of the sample plug in a straight tube with laminar flow (no reaction). Future studies will consider different flow geometries and chemical kinetics. In the comparisons presented, experiments conducted in our laboratory as well as those carried out by Korenaga et al. [6] and Wada et al. [13] are used to evaluate the random walk approach. In addition, theoretical peak and bolus shapes predicted by solution of the convection–diffusion equation by Wada et al. [13] and Vanderslice et al. [10,12] are considered. The effect of changing the flow profile and mixing characteristics of the flow system using the random walk model are considered. Finally, some observations on implementing the random walk model are discussed.

THEORETICAL CONSIDERATIONS

The random walk model, originally used by Einstein to treat Brownian motion [18], has been widely applied to the physical sciences. The principles of this method have been discussed elsewhere [19] and will not be treated in detail here. The procedure used in this work is essentially the same as that employed by Betteridge et al. [16] with modifications made for some studies. The basic algorithm is summarized as follows. Initially, a predetermined number of molecules (typically 5000) are randomly distributed in a tube of radius \( R \) and length \( L \). This represents the sample plug. It may be argued that a more uniform distribution of \( x, y, \) and \( z \) coordinates would be more logical, but a random distribution in a cylindrical volume is more easily implemented and avoids bias that may be introduced by regular spacing, especially on repetitive runs. Once the initial molecular coordinates have been established, the molecules are moved in discrete time intervals of \( \Delta t \). Steps corresponding to molecular diffusion and convection contribute to a molecule’s motion, so an extra term must be included for the latter effect. In the original simulation, a parabolic flow profile was assumed such that,

\[
U = U_{\text{max}} \left(1 - \frac{r^2}{R^2}\right)
\] (1)
where $U$ is the flow velocity at a distance $r$ from the center of the tube, and $U_{\text{max}}$ is the maximum flow velocity (equal to twice the average flow velocity, $U_{\text{avg}}$). Therefore the motion of the molecule in the $z$ direction uses a step of $Q \Delta l + U \Delta t$, where the latter term is calculated at the $x$ and $y$ values after the step. To obtain detector profiles, the number of molecules which have passed the detector (a distance $l$ from the injection point) after each one second interval is recorded. This continues for a specified period of time. To provide data for contour plots of flow profiles (bolus shapes), the simulation is stopped after a predetermined period and the number of molecules within smaller sections of the tube are counted. In both cases, simulations are repeated a sufficient number of times to provide good averaging.

Obviously, two of the factors that will affect the quality of simulation results are the total number of steps taken as the molecules move down the tube and the average size of each step. Assuming that the step size is sufficiently small, an insufficient number of iterations would be expected to lead to significant variations in the peak profiles obtained between runs. Generally this is not a problem because typical FIA conditions usually ensure an adequate number of steps and the large number of molecules employed averages out differences. The problem of insufficient step size is more critical since it can lead to systematic errors in two ways. First, axial movement of the molecule by convection is calculated from the new $x$ and $y$ coordinates rather than from the average flow velocity between the new and old positions. This is intended to reduce computation time and assumes that velocity differences will be small and average out. It would be useful to know what the magnitude of this effect is and if it becomes significant for larger step sizes. To this end, some of the simulations employed in this work computed an average axial velocity between points 1 and 2, $U_{12} = \frac{U_{\text{max}}}{R^2 \Delta x} [ A \Delta x^2 - B \Delta x - C \Delta x^2 ]$ (2)

where $U_{12}$ is the average flow velocity between points 1 and 2, $\Delta x = (x_2^2 - x_1^2)$; $A = R^2 - b^2$; $B = b m$; $C = (1 + m^2)/3$; $m = (y_2 - y_1)/(x_2 - x_1)$; $b = y_1 - mx_1$.

Another factor that relates to step size is the interaction of molecules with the walls of the tubing. Because the random walk simulation is based on Cartesian coordinates, it is possible to take steps in the $x$ and $y$ directions which can put the molecule outside the radius of the tubing. If this happened in the original simulation of Betteridge et al. [16], the $x$ and $y$ coordinates of the molecule were left at their previous value and movement in the axial direction due to convection was taken to be half of the value it would have been if the molecule really had remained at the same $xy$ coordinates. This seems like a reasonable approximation to the more logical approach of "bouncing" the molecule off the wall and is much less computationally demanding. Nevertheless, it is likely to affect the results as the step size becomes larger, as the region to which the approximation must be applied becomes more significant. We have attempted to determine the maximum permissible step size to obtain reliable results and also which of the two factors (mean velocity or wall interaction) is more critical in causing deviations as the step size becomes larger.

Several other modifications were also made to the simulations in order to examine their effect on peak shapes. One of these was variation of the usual laminar flow profile by changing the power term in Eqn. 1. The modified equation was,

$$U = U_{\text{max}} (1 - r^P/R^P)$$ (3)

where $P$ was varied between 1 and 4. It can be shown that, for the modified profile,

$$U_{\text{max}} = \frac{U_{\text{avg}} (P + 2)}{P}$$ (4)

The effect of changing the symmetry of the flow profile was also investigated. Non-radially symmetric velocity profiles are known to arise when FIA tubes are coiled or otherwise deformed. To examine the role of this asymmetry with minimal computational burden, an approximation to Søberg's model [20, Fig. 3.9, p. 111] was used.
The equation applied was:

\[
U = N \left[ 1 - e^{-k(1-r')} \right] \times \left[ 1 - (x')^2 - (y')^2 + 2a(1+y') \right]
\]

where \(U\) is the flow velocity at \(x', y'\); \(N\) is a constant obtained by numerical integration to provide the correct \(U_{max}\); \(k\) is an adjustable constant set to 10 in this work; \(r'\) is the reduced radial position of the molecule = \(r/R\); \(x', y'\) are the reduced \(x\) and \(y\) coordinates of the molecule = \(x/R, y/R\); \(a\) is an asymmetry factor between 0 and 1. The second term in square brackets is a quadratic function which gives a maximum flow velocity centered at \(x' = 0, y' = a\) and a minimum value of zero (within the confines of the tube) at \(x' = 0, y' = -1\). The first term in square brackets forces the flow velocity to zero at the walls of the tube.

Another change that was made for some studies was the introduction of infinite radial diffusion. This was done to examine the amount of dispersion in the limiting case. To simulate an infinite rate of radial mass transfer, increments in \(x\) and \(y\) were no longer used, but rather the \(xy\) position itself was totally randomized within the cylinder. This avoids the problem of collisions with the walls as the steps become larger.

EXPERIMENTAL

Apparatus

The apparatus used to obtain the experimental flow profiles in this work is shown in Fig. 1. A very simple arrangement consisting of a pump, injection valve, tubing, and detector was used. Two types of pumps were employed to examine possible differences in profiles due to pulsations: an eight-roller peristaltic pump (Ismatec model SA, Cole-Parmer, Chicago, IL) and a stepper motor-driven syringe pump (Sage Instruments model 341A, Cambridge, MA). Both pumps were calibrated before each run. For sample injection, a manually operated six-port, two-way valve (Rheodyne model 5020, Cotati, CA) fitted with a polytetrafluoroethylene (PTFE) sample loop was employed. Other workers have used special injection methods to avoid the changes in flow dynamics introduced by valve fittings and sample loop coiling [21], but we wished to obtain experimental results from a more standard FIA system. The volume of the sample loop was precisely measured by mass difference to be 232 \(\mu\)l. It was later determined that, for the geometry used, minor changes in the plug volume had relatively little effect on the simulation.

Both stainless steel (SS) (Supelco, Oakville, Ont.) and PTFE tubing (Chromatographic Specialties, Brockville, Ont.) were used in these experiments. Both were nominally 0.8 mm i.d. \(\times\) 1.6 mm o.d., but internal diameters were more precisely measured as 0.801 mm (SS) and 0.875 mm (PTFE) by mass difference. In each case, the length of tubing was approximately 2 m and it was kept as straight as possible to avoid secondary flow which will increase radial mass transfer. Some bends at the injector and detector were unavoidable, but were kept to a minimum. Flanged fittings were used at the injector and detector for the PTFE tubing, while connection via short pieces of Tygon tubing was used for the stainless steel. The total length (exit of injector to entrance of detector) was 227.0 cm in the case of the PTFE and 219.4 cm in the case of the stainless steel.

The detector employed was a Hewlett-Packard 8452A diode array spectrophotometer (Hewlett-Packard, Palo Alto, CA) equipped with a 30-\(\mu\)l, 1-cm flow cell (Hellma, Jamaica, NY). Absorbance measurements at the wavelength of
maximum absorbance for the sample (404 nm) were acquired at 2-s intervals with an integration period of 1 s. These detector conditions introduce minimal broadening to the profiles obtained here. Because of the difficulties involved in thermostating the long reactor, all measurements were made at room temperature. Although changes in temperature will affect dispersion [22], the variations observed in this work were not significant enough to affect comparisons with simulation results.

Reagents
All solutions were prepared in distilled water from materials of ACS reagent grade or better. The carrier used was 1 M KCl and all samples were 3 mM potassium hexacyanoferrate(III) in 1 M KCl. The diffusion coefficient for K$_2$Fe(CN)$_6$ under these conditions was taken as $7.6 \times 10^{-6}$ cm$^2$ s$^{-1}$ at 25°C [23].

Computational aspects
Simulations were run on a 16 MHz IBM PC/AT compatible computer (Tristar Computers, Tempe, AZ) with a math coprocessor. The random walk program was written in Turbo C++ (Borland Corp., Scott's Valley, CA). This allowed the use of linked lists for molecular coordinates and decreased computation time significantly by permitting molecules which had passed the detector to be eliminated from the simulation. Normally, the program displayed the detector response at 1-s intervals by counting the number of molecules which had $z$ coordinates beyond the detector. In some cases, the axial and radial distributions at a fixed time were recorded by stopping the simulation. A single run typically contained 5000 molecules, but 10 to 200 repetitions (equivalent to $5 \times 10^4$ to $10^6$ molecules) were normally averaged to obtain smooth profiles. The replicate runs with smaller arrays maximized computational efficiency and minimized the amount of data lost in the event of inadvertent program termination. A run with 5000 molecules and one step per second, with a simulated flow-rate of 1 ml/min and a tube length of 2 m, typically took about 5 min if no special calculations were added to the algorithm, an improvement of several orders of magnitude over the original work [16]. The program obtained variable simulation parameters from a data file, allowing the it to be run in batch mode overnight. Contour maps and three-dimensional displays were generated with the program SURFER (v 4.0, Golden Software, Golden, CO).

RESULTS AND DISCUSSION

Comparison of experimental and simulated profiles
Initial evaluation of the random walk simulation utilized experimental results from the flow injection system described above. Since this experimental apparatus exhibited non-idealities with respect to the model, deviations in the results were anticipated, but it was hoped that these would be minimal and might be accommodated by adjustments to the model to illustrate the versatility of the random walk approach. Results for the peristaltic pump for both the PTFE and stainless steel tubing are shown in Fig. 2. The experimental results appear as smooth curves while the simulated profiles (250,000 molecules) are somewhat jagged due to the stochastic nature of the simulation. For all of the results presented here, the simulated profiles have been normalized to the same area as the experimental profiles for comparison. Figure 2 shows that there is good general agreement between the experimental peak shapes and those obtained by the random walk simulation, although some discrepancies are apparent. Both types of tubing give similar results and the best agreement is obtained for the intermediate flow-rate. At the low flow-rate, the experimental dispersion is somewhat greater, while the opposite is true at the high flow-rate. The theoretically predicted double-peak at the high flow-rate is not observed experimentally, but this is not surprising since it has been previously shown that even a small amount of turbulence can eliminate this from experimental results [10]. Finally, the simulated profile typically starts earlier than the experimental peak in all cases.

It was thought that discrepancies between experimental and simulated results in Fig. 2 might arise from pump pulsations in the case of the
Fig. 2. Comparison of simulated and experimental dispersion profiles obtained with a peristaltic pump for PTFE and stainless steel (SS) tubing at different flow-rates (FR). Experimental results are represented by the dashed lines. See text for further details.

Fig. 3. Comparison of simulated and experimental dispersion profiles obtained with a syringe pump for PTFE and stainless steel (SS) tubing at different flow-rates. Experimental results are represented by the dashed lines. See text for further details.
peristaltic pump, so a syringe pump was also employed. The results in Fig. 3 show that larger deviations are generally observed with the syringe pump for both types of tubing. The time shifts are also more apparent, with simulation results leading the experimental results in all cases. The trends in dispersion are the same in this case as for the peristaltic pump. The reason for the greater discrepancies in this case are not clear, but could result from stepper motor pulsations for the syringe pump (about 170 pulses/min at 0.5 ml/min) which would cause a more turbulent flow, or a larger pressure surge on injection. The type of tubing seems to be more important in this case than for the peristaltic pump, indicating that factors such as elasticity or wettability may be important.

These results indicate a reasonably good qualitative agreement between experimental and simulated peak shapes, but suggest that some non-idealities in the experimental system may be responsible for discrepancies observed. The discrepancies are larger than what is expected on the basis of small variations in temperature or

Fig. 4. Effects of simulated tube length (L, cm) and mean flow velocity (u, cm s\(^{-1}\)) on simulation results; for comparison with experimental results given in Ref. 6. Fig. 4. Other conditions given in text.
viscosity and it is believed that the assumption of a parabolic flow profile may not be valid for certain time periods (e.g. immediately following injection) or in certain regions of the tube (e.g. at connections). Valve switching on injection temporarily interrupts the flow and can result in a surge of pressure. Although this can be avoided by using stopped-flow or hydrodynamic injection techniques, these methods introduce new problems arising from the need to bring the flow rate from zero to its desired value. Connections were minimized, but non-idealities such as reduced or enlarged diameters through flanged unions may contribute to variations in the flow. Deviations from a linear geometry at the injector and detector will also contribute to secondary flow. These contributions could be minimized by employing valves or detectors of a different design, but these were not used in this work. It is expected that modified flow patterns near the injector will have the greatest effect, since they are amplified as the sample plug moves to the detector. In most cases, changes in the flow profile should increase radial mass transfer. This would be consistent with the delayed appearance times and reduced dispersion observed for the experimental peaks. The discrepancies observed in these studies are consistent with results obtained by Wada et al. [13] who used an alternative method to generate the theoretical curves.

To provide further evidence that the random walk model provides results consistent with experimental profiles under a variety of conditions, experimental results obtained by other authors were considered. One fairly extensive study was carried out by Korenaga et al. [6] under carefully controlled conditions. These authors examined the effect of flow velocity, tube length, tube diameter and diffusion coefficient on sample dispersion in straight tubes. We have used the conditions employed in the flow velocity/tube length study ($D = 3.8 \times 10^{-6}$ cm$^2$ s$^{-1}$, i.d. = 1 mm, sample volume = 10 µl) (see Ref. 6, Fig. 4) to generate corresponding profiles from the simulation. These results are presented in Fig. 4 with the same format as the original reference for easy comparison. Very good agreement was obtained between experimental peak shapes given in the reference and the simulation results presented here, although some of the experimental peaks are substantially broader. Also, the values of the concentration ratio, $C/C_0$, were more than an order of magnitude lower for the simulation results. Closer scrutiny of the experimental results through area calculations indicates that the values reported by Korenaga et al. are in error by a scaling factor which would place the magnitude of their measurements in agreement with ours. The effects of tube diameter and diffusion coefficient (see Ref. 6, Figs. 5 and 6) were also examined with the random walk simulation and are shown in Figs. 5 and 6, respectively. For Fig. 5, conditions used were as in Fig. 4 but with $l = 120$ cm, flow velocity = 2.3 cm s$^{-1}$, and tube diameters as given in the figure. Again, there is good qualitative agreement between the simulation

![Fig. 5. Effect of simulated tube diameter (d) on simulation results; for comparison with Ref. 6, Fig. 5.](image-url)
peak shapes and the experimental profiles given in Ref. 6, but the experimental peaks are generally broader. For Fig. 6, only two sets of results are reported rather than the three in the original reference, as no diffusion coefficient was estimated for the sub-micron pigment ink used by the authors. Conditions used here were: sample volume = 10 μl, I = 40 cm, d = 1 mm, and flow velocity = 0.45 cm s⁻¹ (diffusion coefficients given in the figure). Agreement with experimental results is not as good for the smaller diffusion coefficient, but double peaks are indicated for both experimental and simulated results. It is likely that the short tube length contributes to disagreement in this case, since this will enhance errors arising from non-ideal connections.

Comparison with other theoretical results

Previous studies have demonstrated good agreement between experimental FIA profiles and theoretical results obtained through numerical solution of the convection–diffusion equation. It was therefore of interest to determine whether the discrepancies observed for the random walk approach were due experimental limitations or fundamental differences with the convection-diffusion model. To this end, profiles obtained with the random walk model were compared with those reported by Wada et al. [13] and Vanderslice et al. [10]. Figure 7 shows results for comparison with the former (see Ref. 13, Fig. 4b). The random walk simulations employed 250,000 molecules with the following conditions: $D = 5.4 \times 10^{-6}$ cm² s⁻¹, i.d. = 0.50 mm, tube length (not including sample loop) = 50 cm. The sample plug lengths and flow rates are given in the figure. As before, results are presented in the same format as the original reference with the reduced time, $t^*$, plotted on the abscissa ($t^* = tU_{max}/L$ where $t$ is the time, $U_{max}$ is the maximum flow velocity, and $L$ is the initial length of the sample plug). Comparison of Fig. 7 with the original reference produces excellent agreement in peak shape and height under all conditions. Further comparisons were made with Vanderslice et al. [10] under different conditions. The results of the random walk simulation ($10^6$ molecules) are shown in Fig. 8 and correspond to Figs. 8 and 9 of Ref. 10. Note that in this case the reduced time and reduced distance are given by the more usual definitions $\tau = Dt/a^2$ and $X = Dx/a^2U_{max}$, respectively. Conditions used for the simulation are given in the figure caption. Once again excellent agreement was obtained between the random walk model and solution of convection–diffusion equation, including details of the predicted "double-hump" (profiles with double maxima are predicted to occur under certain conditions, but are rarely observed in practice for dispersion only because of experimental limitations). This indicates that the two methods are consistent with
one another and suggest that equally valid results can be obtained by alternative routes.

As an alternative to the usual comparison of peak profiles, it was decided that a direct examination of bolus shapes would be useful. This was accomplished by stopping the simulation after a predetermined solute residence time and counting molecules in defined volume elements. For this purpose, the tube was divided into 20 concentric radial elements of equal width and 20 axial elements of equal length. Concentrations were calculated as a function of radial and axial position and contour maps were generated using the program SURFER. To ensure an accurate representation, \(10^6\) molecules were used for each set of results. The results are shown in Fig. 9 for different values of the reduced time and are intended to be compared to Figs. 4 and 5 of Vanderslice et al. [12]. Note that the scale for \(\tau = 0.01\) is expanded by a factor of 10 as in the reference. The bolus shapes produced by the simulation are in very good agreement with those obtained in reference 12 except that there appears to be a considerably larger concentration near the walls of the tube. This discrepancy is curious since the peak shapes obtained in Fig. 8 are in excellent agreement with earlier work by the same authors [10]. The bolus shapes obtained here more closely resemble those provided by Wada et al. [13], but a direct comparison has not been made to those results since reaction kinetics were also considered by the authors.

**Effect of step size and wall approximations**

As already noted, the effect of the mean molecular step size \((\Delta l = (2D\Delta t)^{1/2})\) is expected to influence the validity of the original algorithm used by Betteridge et al. [16] because of errors in the calculation of the mean velocity of a molecule in traversing two points and because of approximations made at the walls of the tube. The mean step size can be decreased by reducing the time interval between iterations, \(\Delta t\). This was accomplished in the present work by specifying the number of iterations per second, \(n\), such that \(\Delta t = 1/n\). Increasing \(n\) improves the validity of the simulation, but also increases computation time proportionately, so it was of interest to determine the maximum permissible mean step size for consistent results. To this end, simulations were run under the conditions used for the PTFE tubing at 1 ml/min, but with \(D = 1 \times 10^{-4}\) cm\(^2\) s\(^{-1}\) to make the step size artificially large. The results for 50,000 molecules are shown in Fig. 10 for \(n = 1, 5, 10,\) and 100. The percentage of steps encountering the walls ranged from 31% when \(n = 1\) to 3% when \(n = 100\). The percentage of steps for the limiting profile as \(n\) becomes larger. From these results, it appears that reasonably good agreement was obtained for \(n \geq 20\).

![Fig. 8. Simulation results for comparison with Ref. 10, Figs. 8 and 9. Conditions used: (a) sample volume = 2 \(\mu\)l, i.d. = 0.23 mm, \(D = 2.48 \times 10^{-6}\) cm\(^2\) s\(^{-1}\), \(l = 30\) cm, flow-rate = 0.0615 ml min\(^{-1}\); (b) same, except flow rate = 0.0771 ml min\(^{-1}\).](image)
approximations of the true simulated profile require the mean step size to be no more than about 5 to 10% of the tube radius.

Since two factors (mean velocity and wall interactions) can affect the validity of the simulation, we wished to determine which had the greater effect. Compensating calculations to determine the true mean velocity and to allow molecules to "bounce" off of the wall were added to different versions of the program. In actual fact, it was computationally simpler to reflect the molecule backwards along its original trajectory than truly bounce it off of the wall. This is mathematically equivalent, since it leaves the molecule at the same radial position, and produces results identical to those that would be obtained if the true trajectory were used. Results in Fig. 11 show the profiles obtained with \( n = 1 \) for the same conditions as in Fig. 10, but with various combinations of compensating factors. It was observed

\[
\tau = 0.01 \\
\tau = 0.04 \\
\tau = 0.06 \\
\tau = 0.10
\]

![Fig. 9. Contour maps showing bolus shapes as a function of reduced time (\( \tau \)), reduced radial position, and reduced axial position.](image)

For comparison with Figs. 4 and 5 of Ref. 12.
that approximations made at the wall had the largest effect when the step size was very large. However, the mean velocity calculation plays a very important role as the peak shape begins to approach its limiting value. The inclusion of both compensating calculations produced results very similar to those obtained when the step size was very small.

The inclusion of corrections for the mean velocity and wall interactions may or may not be more computationally efficient than decreasing the step size, since the calculations are quite involved. In practice, decreasing the step size tends to be more straightforward when adding modifications to the algorithm such as asymmetric flow profiles, since these make the corrections more difficult. It should be noted that, for the other simulations presented here, the step size was kept small enough to ensure valid results from the simulation.

**Effect of flow velocity profile**

One of the advantages of the random walk approach is that it is readily adapted to modifications in flow characteristics and other experimental parameters. Since even straight tubing can give rise to flow profiles that are not precisely laminar, the random walk simulation was used to evaluate the contribution that this might have to the peak shapes obtained. The first study investigated modifications to the exponent, $P$, in the normal laminar flow case as discussed in an earlier section. Conditions used were those for the PTFE tubing and the results for a flow-rate of 1 ml/min are shown in Fig. 12. The radial velocity profile appears as an inset. It was found that there was virtually no change in the peak position under these conditions, but dispersion was substantially affected. In all cases, the leading edge of the peak moved to slightly longer times and
became steeper as the flow-rate was increased, and the peaks became narrower. In the case of the 1.5 ml/min flow-rate (not shown), the spike on the leading edge of the profile became more prominent with increasing flow-rate. It is also interesting to note the presence of an isoresponse point on the trailing edges of the peaks. In some instances, agreement between theoretical and experimental results could be improved by adjusting the flow-rate, suggesting that the nature of the flow profile may change with experimental conditions. Other factors will also affect this agreement, however.

The effect of the symmetry of the flow was also investigated with a view towards possibly explaining reduced dispersion in coiled tubes. Equation 5 was used to generate laminar-type profiles with an asymmetric distribution. Results are shown in Fig. 13 for PTFE tubing conditions (1 ml/min) and asymmetry factors of 0 (normal laminar flow), 0.25, 0.5 and 0.75. The addition of the asymmetric flow did not sufficiently explain the effects of coiling. Although dispersion did decrease with increases in the asymmetry factor, changes in peak shape and position are not consistent with experimental observations for coiled tubing. More detailed studies are being carried out to try to more accurately model coiled geometries.

**Effect of diffusion coefficient**

Figure 14 shows the effect of varying the diffusion coefficient over a limited range on the simulation results. The conditions used were those for the PTFE tubing at 1 ml/min. The diffusion coefficient was multiplied by factors ranging from 0.6 to 1.4 and the simulation included 250,000 molecules. As expected, an increase in the diffusion coefficient leads to sharper peaks due to increased radial mass transfer. It is also interesting to note what appears to be an isoresponse point on the tail of the peaks. This behaviour is consistent with changes in peak shape that have been observed by other workers [20, p. 136].

The random walk algorithm can also be used to investigate limiting dispersion for a given set of conditions. Because it is a discrete simulation, the radial component of diffusion can be separated from the axial component. The case of infinite radial diffusion can be achieved by making the $x$ and $y$ coordinates of each molecule completely random (within the confines of the tube) at each step. This should give the smallest dispersion possible for the flow conditions imposed. Figure 15 compares normal and infinite radial diffusion results for the stainless steel experimental conditions at 1 ml/min. The tall peak defines the limit to which dispersion can be reduced by coiling.
knitting or other means. The next highest peak is the experimentally observed profile when the tubing is coiled to a diameter of about 2 cm. The final two curves show simulated and experimental results when uncoiled tubing is used. It is apparent that the reduction in dispersion obtained by coiling is not at the theoretical limit, although further reduction may be limited in practice. It is unlikely that other models could be used to make this type of prediction. Further work needs to be done to determine how the random walk model may be adapted to the case of coiled tubing.

Conclusions
From the results presented here, it is evident that the random walk model can be used as effectively as other approaches for modeling peak shapes in FIA. It has been shown that modifications to flow parameters can be easily incorporated to test physical models. Agreement with experimental flow profiles is reasonably good. Differences probably arise from invalid assumptions regarding the true flow characteristics which will be affected by factors related to injection, connections, pump pulsations, tube wettability, and so on. Further work with the random walk algorithm may permit a better understanding of how these non-ideal conditions affect the flow dynamics.

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