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Models for Dispersion in Flow Injection
Part 2.* Two Tanks in Parallel Model

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The application of two models based on the stirred mixing tanks, the well stirred tank and the two tanks in parallel models, is discussed, and results are presented for flow manifolds with both flame atomic absorption spectrometric and solution spectrophotometric detectors. Both models can be applied to the description of the dispersion generated by the nebuliser/spray chamber of a flame atomic absorption spectrometer. They can also be applied to flow injection manifolds under conditions giving rise to peaks having exponential-like rise and fall curves.

Keywords: Flow injection; dispersion; flow models; well stirred tank; two tanks in parallel

Flow injection (FI) is a technique that has undergone considerable and rapid development since its introduction. However, the underlying theory of the technique has not been so well developed and, as yet, there is no theoretical basis for the description of dispersion behaviour in FI manifolds. The design of manifolds to achieve the required degree of mixing and sample throughput is based largely on empirically established guidelines. As part of a continuing study of the potential of models for dispersion behaviour, the use of simple models, based on well stirred mixing tanks, has been evaluated and results for the single well stirred tank (WST) model and the two tanks in parallel (TTP) models are discussed here. The ultimate aim of the studies is to allow a prediction of the physical dispersion and peak shape produced by the flow in any given manifold.

The fundamental mechanisms of diffusion and convection (distortion due to laminar flow) are well known, the combination of these two processes having been expressed by Taylor1,2 as the diffusion - convection equation. As was discussed briefly in an earlier paper,3 Taylor's approximate solutions for this equation are not generally applicable to all conditions encountered in FI and hence a variety of methods have been employed for the description of dispersion. These have drawn on earlier work from both the chemical engineering4,5 and chromatographic6,7 literature. Although all the methods that have been described in the literature can be applied to FI manifolds under the appropriate conditions, the variety of manifold and reactor designs requires that new models and theoretical descriptions for dispersion should be developed. Hence there is a continued interest in the investigation of the factors affecting sample dispersion and the development of both new and existing models in FI.

For example, Stults et al.8 have investigated the effect of temperature on dispersion and have shown that the value of the dispersion coefficient, D (related to reciprocal peak height), decreases with increasing temperature over the range 20–70 °C, both in the absence and presence of a chemical reaction. The role of chemical reaction kinetics has been considered by Hungerford and Christian9 and van Opstal et al.10 using the tanks in series (TIS) model. These latter workers applied their results to the optimisation of single bead string reactors (SBSRs) in FI. Locascio-Brown et al.11 have examined the dispersion behaviour of liposomes in FI manifolds, dispersion being qualified in terms of peak asymmetry and mean residence time. Crowe et al.12 have used a random-walk simulation to investigate dispersion in merging zone systems with chemical reactions, while Garn et al.13 have discussed dispersion in systems containing mixing tanks and stream-sampling to achieve high dilutions.

The response of an atomic absorption spectrometer to discrete nebulisation and FI sample introduction has been modelled by an impulse input coupled with axially dispersed plug flow and an absorbance - concentration (A - c) relationship based on a mass balance model for the function of the nebuliser, spray chamber and burner.14

The use of impulse/response functions has been employed to model the behaviour of individual components in an FI manifold.15 The approach was to deconvolute the impulse/ response functions obtained with and without the extra element. This was carried out in the Fourier domain using a fast Fourier transform (FT) algorithm.

Finally, Kolev and Pungerčev16–19 have given extensive descriptions of models for single-line manifolds based on axially dispersed plug flow.

Theoretical

WST Model

The WST model has been described previously.20,21 In this model, all dispersion processes are represented by a single well stirred tank, the sample concentration being measured directly at the tank outlet. The differential equation describing the concentration - time (c - t) profile for such a device is

\[ \frac{dc}{dt} = -\frac{dc}{dt} \]

If a plug of sample of concentration \( c_0 \) and volume \( V_s \) enters the tank at a flow-rate \( q \) starting at time \( t = 0 \), equation (1) can be solved to give

\[ c = c_0 \left[ 1 - \exp \left( -\frac{q}{V_m} \right) \right], \quad 0 < t < t_p \]  \hspace{1cm} (2a)

\[ c = c_0 \left[ 1 - \exp \left( -\frac{q}{V_m} \right) \right], \quad t = t_p \]  \hspace{1cm} (2b)

\[ c = c_p \exp \left( -\frac{q}{V_m} \right), \quad t > t_p \]  \hspace{1cm} (2c)

where \( c_p \) is the concentration at the peak maximum, \( t_p \) is the time to the maximum (\( = V_s/q \)) and \( V_m \) is the tank volume. Hence a single-line manifold can be represented by a hypothetical manifold containing a length \( l \) of tubing of internal radius \( a \) (Fig. 1). In this instance, \( t \) in equations (2a)–(2c) is replaced by \( (t - t_s) \) where \( t_s = \pi a^2 l/q \). It should be noted that this model differs from the TIS model for a single tank (\( N = 1 \)) by the injection conditions assumed. For the WST model, these correspond to "time" injection,22 whereas the TIS model assumes a "delta" injection function, resulting in a single exponential decay function.
The TTP model was first derived to model nebuliser response to the WST model, it can be shown that the resulting stirred tanks connected in parallel (Fig. 2). The sample absorption spectrometry (FAAS) and consists of two well tank is independent of the tank volumes. By comparison with points and that the fraction of the flow diverted through each confluence point. It is assumed further that no mixing occurs in the connecting tubing or at the splitting and confluence curves for step changes in concentration in flame atomic concentration is assumed to be measured immediately at the mixing tank: \( P \), pump: \( S \), sample: \( V \), valve; \( W \), waste; \( C \), Carrier: \( D \), detector; \( V_1 \), volume of tank 1; and \( V_2 \), volume of tank 2.

**TTP Model**

The TTP model was first derived to model nebuliser response curves for step changes in concentration in flame atomic absorption spectrometry (FAAS) and consists of two well stirred tanks connected in parallel (Fig. 2). The sample concentration is assumed to be measured immediately at the confluence point. It is assumed further that no mixing occurs in the connecting tubing or at the splitting and confluence points and that the fraction of the flow diverted through each tank is independent of the tank volumes. By comparison with the WST model, it can be shown that the resulting \( c - t \) profile is given by

\[
\begin{align*}
\frac{c}{c_0} &= c_0 \left[ 1 - f_1 \exp \left( \frac{-f_1 q t}{V_1} \right) - f_2 \exp \left( \frac{-f_2 q t}{V_2} \right) \right], 0 \leq t < t_p \\
\frac{-\ln(c/c_0)}{q} &= \frac{V_1}{V_2}, 0 < t < t_p \\
\frac{-\ln(c/c_0)}{q} &= \frac{V_2}{V_1}, t > t_p
\end{align*}
\]

and all other symbols are as defined in Figs. 1 and 2.

It should be noted that if the flow fraction through each tank is made a function of the tank volume, \( f_1 = V_2/(V_1 + V_2) \), then equations (3a)–(3c) reduce to equations (2a)–(2c) with \( V_m = V_1 + V_2 \). Some typical \( c - t \) profiles calculated for the model are shown in Fig. 3.

![Fig. 1](image1.png)

**Fig. 1.** (a) Real and (b) hypothetical manifolds for the WST model. \( C \), Carrier; \( D \), detector; \( f \), tube length; \( f' \), hypothetical tube length; \( M \), mixing tank; \( P \), pump; \( S \), sample; \( V \), valve; \( W \), waste; \( V_1 \), sample volume; and \( V_m \), tank volume

![Fig. 2](image2.png)

**Fig. 2.** The TTP model. Distances \( A-A' \) and \( B-B' \) are assumed to be negligible. \( f_1 \), Fraction of flow through tank 1; \( f_2 \), fraction of flow through tank 2; \( V_1 \), volume of tank 1; and \( V_2 \), volume of tank 2

**Fitting of the Models to Experimental Data**

In order to assess the conditions for which different models could be applied to simple FI manifolds, a database of experimentally recorded peak shapes was compiled, covering a range of conditions. The peak shapes were stored on a mainframe computer (Honeywell DPS6/4) as \( c - t \) profiles normalised with respect to the initial sample concentration \( c_0 \). Programs were written in FORTRAN 77 which allowed these peak shapes to be plotted, analysed and compared with \( c - t \) profiles predicted for various models. These included the convection, diffusion and TIS models for comparison.

Consideration of the equations for the WST model suggested that the data could be linearised by the following transformations:

\[
\begin{align*}
\frac{-\ln(1 - c/c_0)}{q} &= \frac{V_1}{V_2}, 0 < t < t_p \\
\frac{-\ln(c/c_0)}{q} &= \frac{V_2}{V_1}, t > t_p
\end{align*}
\]

Hence values of \( V_m \) can be calculated from the slopes of the linear portions of the rising and falling parts of experimental peak shapes plotted according to equations (5a) and (5b), respectively.

The analysis for the fit of the TTP model to experimental data was performed as described previously. The initial and final gradients of plots of either \( -\ln(1 - c/c_0) \) or \( -\ln(c/c_0) \) versus \( t \) were used to calculate values of \( V_1 \) and \( V_2 \) for a range of values of \( f_1 \) (where \( f_1 + f_2 = 1 \)) as

\[
G_1 = f_1 q V_1, G_2 = f_2 q V_2
\]

[Equations (3a)–(3c) are mathematically symmetrical, therefore it does not matter whether \( G_1 \) or \( G_2 \) is assigned to the initial gradient.] Initially, the parameters of the model \( (V_1, V_2 \) and \( f_1) \) giving rise to the “best fit” were determined by a visual comparison of the experimental and model \( c - t \) profiles. In order to provide a more objective basis for the comparison, a SIMPLEX optimisation procedure was adopted using the National Algorithm (Nag) Library sub-routine E04CCF. The optimisation was based on minimising the root mean square (RMS) value of the residuals between actual and predicted concentration values for each point collected from the experimental \( c - t \) profile. The software routine automatically performed expansion, contraction, translation and reflection of the simplex until the simplex value (the RMS value of the function calculated for the simplex vertices) was less than a user-defined tolerance. This tolerance was estimated from the
Experimental errors associated with recording the \( c - t \) profile and calculating residuals was typically of the order of \( 10^{-4} - 10^{-5} \). The method was tested first on model data and found to perform satisfactorily.

For both models, the start of the peak was matched for the experimental and predicted \( c - t \) profiles by calculating a hypothetical tube length, \( L \), from the appearance time \( t_a \) using the equation \( t_a = \pi a^2/q \).

**Experimental**

**Application of the Models to FI-AAS**

The application of the WST and TTP models to FI-AAS was investigated using the apparatus described previously. Steady-state growth curves were recorded using a fast chart recorder for a 1.00 \( \mu \)g ml\(^{-1} \) magnesium solution (\( L = 15 \) cm, \( d = 0.58 \) mm) for sample flow-rates of 1.23, 2.18, 3.16, 4.20 and 5.76 \( \mu \)l min\(^{-1} \) into the nebuliser of a flame atomic absorption spectrometer (Pye Unicam SP9). Separate calibration graphs were constructed for each flow-rate to allow calculation of the \( c - t \) profiles from the absorbance-time \( (A-t) \) data. Growth curves were also obtained for tube lengths of 10.0–160.0 cm (\( d = 0.58 \) mm) with both AAS and UV-visible detection. In this instance the sample solution was potassium permanganate (5.00 \( \mu \)g ml\(^{-1} \)), the detector conditions for both methods being as described previously. The flow-rate was held constant at 5.8 \( \mu \)l min\(^{-1} \), which corresponded to the natural aspiration rate of the nebuliser of the atomic absorption spectrometer for the fuel and oxidant flow-rates used.

**Application of the Models to FI**

The use of the WST and TTP models was evaluated for both slug and time injections using the experimental database that was compiled using the apparatus described previously. The sample solution was tartrazine (0.020 g l\(^{-1} \)) in distilled water. Distilled water was used as the carrier stream throughout.

**Results and Discussion**

**Application of the Models to FI-AAS**

Both the WST and TTP models were originally developed for FI-AAS, as it had been observed that the growth curves obtained for step changes in concentration at the nebuliser resembled exponential growth curves. Earlier results obtained for different flame atomic absorption spectrometers showed that both models could be applied to such growth curves. It was therefore of interest to investigate the application of these models further, particularly the TTP model.

<table>
<thead>
<tr>
<th>( q/\mu l ) min(^{-1} )</th>
<th>( G_1/\text{s}^{-1} )</th>
<th>( G_2/\text{s}^{-1} )</th>
<th>( f_1 )</th>
<th>( V_f/\mu l )</th>
<th>( V_s/\mu l )</th>
</tr>
</thead>
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<tr>
<td>5.76</td>
<td>1.0079</td>
<td>0.5958</td>
<td>0.800</td>
<td>76.20</td>
<td>32.22</td>
</tr>
<tr>
<td>4.20</td>
<td>0.9771</td>
<td>0.5218</td>
<td>0.800</td>
<td>57.31</td>
<td>26.84</td>
</tr>
<tr>
<td>3.16</td>
<td>0.9570</td>
<td>0.6670</td>
<td>0.800</td>
<td>44.06</td>
<td>15.80</td>
</tr>
<tr>
<td>2.18</td>
<td>1.1174</td>
<td>0.5947</td>
<td>0.700</td>
<td>22.74</td>
<td>18.31</td>
</tr>
<tr>
<td>1.23</td>
<td>0.9233</td>
<td>0.1519</td>
<td>0.800</td>
<td>17.76</td>
<td>27.00</td>
</tr>
</tbody>
</table>

The \( c - t \) profiles obtained at different flow-rates are shown in Fig. 4. It was found that, within experimental error, these profiles were the same except for that obtained at the lowest flow-rate. Changing the sample flow-rate will change the rate at which the sample enters the flame, which will in turn change the steady-state absorbance value obtained. The shape of the growth curve, and the time taken for the steady state to be reached, will be determined primarily by the fuel and oxidant flow-rates and by the aerosol formation mechanisms associated with the nebuliser/spray chamber. Hence if a change in sample flow-rate did not affect the nebuliser/spray chamber performance, the \( A-t \) curves would be different, but the \( c - t \) curves would be the same (as separate calibration graphs were prepared for each flow-rate, thus correcting for the effect of sample flow-rate on absorbance). However, it is known that sample flow-rate does affect nebuliser performance; a decrease in flow-rate results in an increased proportion of small droplets in the aerosol, thus increasing the amount of sample usefully entering the flame. This could explain the observed difference in the \( c - t \) curves. If the rate of transport of small droplets into the flame is determined only by the fuel and oxidant flow-rates, then the initial portion of the \( c - t \) growth curve will be due to this rapid process and will be independent of sample flow-rate. However, those processes involving large droplets, which are less well understood, may be slower and have a more significant effect of low sample flow-rates, giving rise to the later, less rapid rate of growth observed in Fig. 4 for a flow-rate of 1.23 \( \mu l \) min\(^{-1} \).

Results for the fit of the TTP model to the \( c - t \) profiles are summarised in Table 1 and the experimental and predicted growth curves for a flow-rate of 4.20 \( \mu l \) min\(^{-1} \) are shown in Fig. 5. Good agreement (as determined by a visual comparison) was found for the four highest flow-rates. Poorer agreement was obtained for the lowest flow-rate. The decrease in the values of the model parameters \( V_f \) and \( V_s \) with sample flow-rate reflects the fact that in the model, decreasing the flow-rate increases the time taken for the steady-state maximum to be reached for a step change in concentration, whereas the \( c - t \) profile is not dependent on sample flow-rate (except as described above).
The results for the fit of both the WST and TTP models to growth curves obtained at constant flow-rate for different tube lengths are summarised in Tables 2 and 3. It should be noted that a tube length of 10.0 cm could not be used with the UV-visible spectrophotometer because of the physical size of the sample compartment.

The WST model was found to provide a good fit to the experimental data for tube lengths of less than 50 cm for AAS detection, but was not as applicable to the curves obtained with UV-visible detection. The failure of the model for longer tube lengths probably reflects the increasing contribution of the connecting tubing to the overall dispersion and hence the shape of the growth curve. This is in agreement with earlier results obtained for the variation of the dispersion coefficient with flow-rate. The results suggest that for short tube lengths, the dispersion due to the nebuliser/spray chamber dominates that occurring in the connecting tubing. This is reflected by the values of $V_{m}$ obtained, which are remarkably constant for tube lengths up to 40.0 cm for AAS detection, but show greater variability for UV-visible detection. (As the detector contributes little to the observed dispersion for the latter situation, these results approximate closely to the dispersion due to the manifold excluding a detector.)

The results obtained for the TTP model show better agreement with the experimental data than the WST model, although the TTP model also breaks down for longer tube lengths. It is interesting to note that the model parameters for the TTP model and a tube length of 40.0 cm are equivalent to those for the WST model. In general, the TTP model will fit any $c-t$ profile that can be described by the WST model, as this equivalence condition exists (see above); the reverse, however, is not generally true.

### Table 2. Fit of the WST model to rise curves obtained for AAS and solution spectrophotometric detection.

<table>
<thead>
<tr>
<th>Detector</th>
<th>$l$ (cm)</th>
<th>$V_{m}$ (µl)*</th>
<th>Fit</th>
</tr>
</thead>
<tbody>
<tr>
<td>AAS</td>
<td>10.0</td>
<td>115.89</td>
<td>YY</td>
</tr>
<tr>
<td>AAS</td>
<td>20.1</td>
<td>105.66</td>
<td>Y</td>
</tr>
<tr>
<td>AAS</td>
<td>30.1</td>
<td>116.99</td>
<td>Y</td>
</tr>
<tr>
<td>AAS</td>
<td>40.0</td>
<td>115.48</td>
<td>YY</td>
</tr>
<tr>
<td>AAS</td>
<td>50.4</td>
<td>155.20</td>
<td>Y</td>
</tr>
<tr>
<td>AAS</td>
<td>80.5</td>
<td>210.46</td>
<td>X</td>
</tr>
<tr>
<td>AAS</td>
<td>110.0</td>
<td>183.41</td>
<td>X</td>
</tr>
<tr>
<td>AAS</td>
<td>160.0</td>
<td>210.80</td>
<td>?</td>
</tr>
<tr>
<td>UV</td>
<td>20.1</td>
<td>48.61</td>
<td>Y</td>
</tr>
<tr>
<td>UV</td>
<td>30.1</td>
<td>40.22</td>
<td>X</td>
</tr>
<tr>
<td>UV</td>
<td>40.0</td>
<td>43.16</td>
<td>Y</td>
</tr>
<tr>
<td>UV</td>
<td>50.4</td>
<td>54.02</td>
<td>?</td>
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<tr>
<td>UV</td>
<td>80.5</td>
<td>—</td>
<td>X</td>
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<tr>
<td>UV</td>
<td>110.0</td>
<td>—</td>
<td>X</td>
</tr>
<tr>
<td>UV</td>
<td>160.0</td>
<td>—</td>
<td>X</td>
</tr>
</tbody>
</table>

* Calculated from the slope of the linear portion.

### Table 3. Fit of the TTP model to rise curves obtained for AAS and solution spectrophotometric detection.

<table>
<thead>
<tr>
<th>Detector</th>
<th>$l$ (cm)</th>
<th>$f_1$</th>
<th>$V_{m}$ (µl)</th>
<th>$V_{m}$ (µl)</th>
<th>Fit</th>
</tr>
</thead>
<tbody>
<tr>
<td>AAS</td>
<td>10.0</td>
<td>0.300</td>
<td>34.77</td>
<td>70.01</td>
<td>Y</td>
</tr>
<tr>
<td>AAS</td>
<td>20.1</td>
<td>0.500</td>
<td>52.83</td>
<td>58.86</td>
<td>Y</td>
</tr>
<tr>
<td>AAS</td>
<td>30.1</td>
<td>0.500</td>
<td>58.49</td>
<td>58.13</td>
<td>Y</td>
</tr>
<tr>
<td>AAS</td>
<td>40.0</td>
<td>0.500</td>
<td>57.74</td>
<td>57.73</td>
<td>Y*</td>
</tr>
<tr>
<td>AAS</td>
<td>50.4</td>
<td>0.500</td>
<td>77.61</td>
<td>55.24</td>
<td>Y</td>
</tr>
<tr>
<td>AAS</td>
<td>80.5</td>
<td>0.400</td>
<td>84.18</td>
<td>66.29*</td>
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</tr>
<tr>
<td>AAS</td>
<td>110.0</td>
<td>0.500</td>
<td>91.70</td>
<td>61.51*</td>
<td></td>
</tr>
<tr>
<td>AAS</td>
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<td>80.18</td>
<td>X</td>
</tr>
<tr>
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<td>17.74</td>
<td>20.11*</td>
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</tr>
<tr>
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<td>0.500</td>
<td>27.01</td>
<td>19.22*</td>
<td></td>
</tr>
<tr>
<td>UV</td>
<td>80.5</td>
<td>0.400</td>
<td>39.21</td>
<td>38.15*</td>
<td></td>
</tr>
<tr>
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<td>0.400</td>
<td>40.10</td>
<td>28.63*</td>
<td></td>
</tr>
<tr>
<td>UV</td>
<td>160.0</td>
<td>0.500</td>
<td>61.68</td>
<td>32.80*</td>
<td></td>
</tr>
</tbody>
</table>

* Equivalent to the WST model with $V_{m} = 115.48$ µl (see Table 2).

---

Fig. 6. Comparison of the WST model (- - -) with experimental peak shapes (-). The experimental conditions and parameters were as follows. (a): $q = 1.23$ ml min$^{-1}$, $l = 50.1$ cm, $V_{i} = 82.0$ µl (time injection), detector volume ($V_d$) = 8.0 µl; $V_m = 63.1$ µl. (b): $q = 1.17$ ml min$^{-1}$, $l = 20.0$ cm, $V_{i} = 74.9$ µl (time injection), $V_d < 0.6$ µl; $V_m = 45.4$ µl. (c): $q = 1.73$ ml min$^{-1}$, $l = 50.0$ cm, $V_{i} = 113$ µl (slug injection), $V_d < 0.6$ µl; $V_m = 104.9$ µl. (d): $q = 1.10$ ml min$^{-1}$, $l = 19.3$ cm, $V_{i} = 53.6$ µl (slug injection), $V_d < 0.6$ µl; $V_m = 56.0$ µl. $d = 0.58$ mm throughout. Values of $V_{m}$ calculated from the peak maximum using equation (2b).
Application of the Models to FI

Because of the peak shape predicted by the WST and TTP models (discontinuous exponential rise and fall), the range of conditions for which the models may be applied is restricted. For this reason, peak shape analysis was only applied to experimental results that could be described as "exponential," "tailed" or "triangular." Some typical results for the WST model are shown in Fig. 6. As expected, good agreement was obtained for short tube lengths and high flow-rates. Sample volume and method of injection were also important factors. This is to be expected, as the model assumes time injection. Therefore, the model will only be valid for slug injection under conditions for which the differences between profiles for time and slug injections are minimal. This will occur when the sample volume (V_s) is small in comparison to the reactor volume (V_r), here defined as the total volume through which the sample must pass between the injector and the detector.

Values of V_m, were calculated from the peak maximum and the rising and falling portions of the experimental profiles. Good agreement was obtained only when the three values of V_m thus obtained were similar. Fig. 6(c) shows the result when this is not the case: in fact the WST model could not be fitted to the tail of this peak at all. This is because for slug injection, elements of sample towards the tail of the sample zone see a progressively larger dispersing volume. Hence differences in the values of V_m obtained from different parts of the peak (or failure to fit the model to the tail of the peak) indicate conditions for which differences between time and slug injections are significant. For slug injection, good agreement between the model and experimental results was obtained for values of V_s/V_r < 1, corresponding to l < 20 cm and V_s < 50 µl (d = 0.58 mm). Partial agreement was obtained for tube lengths up to 70 cm only for sufficiently high flow-rates (>1.5 ml min⁻¹), for which the effects of diffusion are minimised. Better results were found for time injection, the conditions employed being V_s/V_r > 0.3 and l ≤ 50 cm.

Typical results for the TTP model are shown in Fig. 7. These were obtained using the SIMPLEX method described earlier, employing the value of l calculated from the appearance time. For slug injection, the model could be used for V_s/V_r > 0.5 and l < 50 cm (d = 0.58 mm). For time injection, the conditions were V_s/V_r > 0.3 and l ≤ 50 cm. No agreement was found for either time or slug injection for large sample volumes (V_s/V_r > 1). It was also found that although the model parameters derived using the SIMPLEX method fitted the rise portion of the experimental c - t profiles fairly well, they did not necessarily predict peak height accurately. This may be a result of the function chosen for the optimisation, i.e., minimising the RMS of the concentration residuals does not necessarily result in a "good fit" as assessed on a subjective basis.

Conclusions

Both the WST and TTP models can be applied to FI manifolds under the appropriate conditions. These correspond to conditions for which other models (such as the diffusion or axially dispersed plug flow model) are not valid, namely, short tube lengths and moderate or high flow-rates. Although both the WST and TTP models are derived assuming time injection they can be applied to results obtained using slug injection when the sample volume is less than the reactor volume. Both models can be applied to FI-AAS for short tube lengths and to the description of the dispersion introduced by the nebuliser/spray chamber assembly of a flame atomic absorption spectrometer. In this respect, the TTP model would appear to offer a slightly better performance than the WST model. The TTP model was fitted to experimental data using both a subjective (visual comparison) and objective (SIMPLEX optimisation) comparison. The latter gave results that did not
always correspond to a “good fit” when evaluated subjectively. It may be that the method could be improved by introducing a weighting factor into the calculation of the RMS of the concentration residuals, which would allow the “fit” to be biased towards the more significant portions of the peak profile.

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References
Note—Reference 3 is to Part 1 of this series.