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Applications of the Single Well Stirred Tank Model for Dispersion in Flow Injection*

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The single well stirred tank model in which dispersion is modelled by the passage of a slug of fluid through the tank has been used to compare the sensitivity that can be obtained by the use of three types of flow injection manifold, which incorporate on-line chemical reaction. These manifolds are the single-line manifold, the double-line manifold and the single-line manifold used in the reverse mode (*i.e.*, the reagent is injected into the sample which constitutes the carrier stream). The model indicates that each manifold type will give the same sensitivity, but that operating conditions and throughput will be different for each. The model calculations for the determination of phosphate, based on parameter values from the literature, suggest that the commonly applied guideline of designing "medium dispersion" manifolds for on-line chemical derivatisations is sub-optimal in terms of maximising sensitivity and that the guideline should be that the dispersion coefficient has a value of <2 . Practical problems related to refractive index and base-line absorbance effects mean that the double-line manifold is the most suitable for trace analysis and the design of such a manifold is illustrated for the determination of chloride with a detection limit of 11 p.p.b.

Keywords: *Flow injection; dispersion model; sensitivity comparison; design guideline; chloride determination*

In order to achieve the best detection limit for an analytical procedure it is necessary to maximise the sensitivity and minimise the factors that contribute to the over-all noise. For flow injection (FI) procedures that involve an on-line chemical reaction, the sample solution is mixed with the reagent solution. The extent of this mixing is a parameter to be optimised because although limited mixing may reduce the extent of sample dilution, it may not permit complete formation of the reaction product owing to an insufficient excess of reagent over determinand at the time when the analytical measurement is made. In most FI procedures this time corresponds to the maximum of the transient product concentration profile.

As part of a continuing study of the design of an FI manifold for the spectrophotometric determination of trace anions the factors affecting both the sensitivity and the noise in various manifold designs have been evaluated.^{1,2} It has been shown that significant contributions to base-line noise arise from the pulsations due to the peristaltic pump and the mixing of streams with different physical properties at confluence points. It has also been found that detection limits can be severely affected by the use of reagents which absorb at the analytical wavelength and by the differences in refractive index between sample and reagent solutions. The noise contributions can be considerably reduced by the use of pulse dampers and of manifold components, downstream of confluence points, designed to promote mixing between merging streams. Such components include tightly coiled open tubular reactors (OTRs) and packed bed reactors (PBRs). It has been suggested that the single-line manifold (SLM) is limited with regard to the sensitivity, *i.e.*, the slope of the calibration graph, by the onset of double peaks³ and that the reverse FI mode, in which the reagent is injected into the sample, has greater sensitivity than the normal mode.⁴

In this paper the relative sensitivities of three possible manifold configurations are examined. These configurations include the single-line manifold in normal mode (nSLM), the double-line manifold (DLM) and the SLM used in reverse mode (rSLM). The DLM is used in the normal mode. The

basis for comparison is to consider all the dispersion effects to be modelled by the plug flow through a single well stirred tank. The performance of each of the three manifolds will be illustrated by reference to an example taken from the literature,⁵ namely, the determination of orthophosphate by measurement of the absorbance due to the product of the reaction in acid solution in the presence of a reducing agent, between the determinand and molybdate. This reaction is typical of many spectrophotometric methods in common use in that it is normally carried out with a large concentration excess of reagent over determinand.

Theoretical

Manifold Design and Terminology

The extent to which the product of an on-line chemical reaction is formed depends on several factors. These include the stability constant and rate of the reaction under consideration, and the concentration excess of reagent over determinand at the peak maximum. This last factor is in turn controlled by the concentration of the reagent (c_0^r) and the concentration of the determinand (c_0^d). For any given analysis the concentration excess of reagent over sample will be least for the standard of maximum concentration ["top" standard (c_0^{dtop})].

If the ratio of concentrations at time $t = 0$ is given by $R_0^{r/d}$ and the ratio of the concentrations of reagent to determinand at the peak maximum is given by $R_p^{r/d}$, then the ratio of these two ratios, $R_p^{r/d}/R_0^{r/d}$, is equal to the ratio of dispersion coefficients, D/D^r , where D is the dispersion coefficient of the injection material given by c_0^d/c_p^d and D^r is the dispersion coefficient of the reagent defined in an exactly analogous way as for the injected determinand solution, namely as c_0^r/c_p^r . This ratio of dispersion coefficients will be referred to as the α -value.

The Single Well Stirred Tank Model

Single-line manifold (normal mode)

Equations for the well stirred model developed previously⁶ give rise to the following relationships for D and D^r :

$$D = [1 - \exp(-V_i/V)]^{-1} \quad \dots \quad (1)$$

$$D^r = [\exp(-V_i/V)]^{-1} \quad \dots \quad (2)$$

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Thus the relationships between D and D^r are $D = D^r/(D^r - 1)$ and $D^r = D/(D - 1)$. These two equations can be combined into:

$$1/D + 1/D^r = 1 \quad \dots \quad (3)$$

The relationship between the hypothetical volume of the tank, V , and the volume injected V_i is given by the following equation,

$$V_i = V \ln D^r \quad \dots \quad (4)$$

From the definition of α given above it follows that

$$\alpha = D - 1 \text{ or } D = \alpha + 1 \quad \dots \quad (5)$$

from which, when the top standard is injected

$$D = (R_p^{r/d}/c_0^d)c_0^{\text{dtop}} + 1 \quad \dots \quad (6)$$

$$= \beta c_0^{\text{dtop}} + 1 \quad \dots \quad (7)$$

$$\text{where } \beta = R_p^{r/d}/c_0^d \quad \dots \quad (8)$$

$$\text{and } \alpha = \beta c_0^{\text{dtop}} \quad \dots \quad (9)$$

The sensitivity of the method, b , being the slope of the calibration graph is given by

$$b = kc_p^d/c_0^d = k/D \quad \dots \quad (10)$$

where k is the constant of proportionality between absorbance, A , and the concentration measured, c_p^d .

Single-line manifold (reverse mode)

By analogy with equations (1) and (2), the dispersion coefficients for the determinand species (in the carrier stream) and for the reagent (the injected solution) are given by

$$D = [\exp(-V_i/V)]^{-1} \quad \dots \quad (11)$$

$$D^r = [1 - \exp(-V_i/V)]^{-1} \quad \dots \quad (12)$$

The α -value (D/D^r) is thus given by

$$\alpha = D - 1 \quad \dots \quad (13)$$

As equation (13) is identical with equation (5) the same α -value is obtained regardless of which solution is the injectate and which is the carrier. This symmetry is reflected in the form of the relationship between the dispersion coefficient values given in equation (3).

Double-line manifold

Equations for the DLM have also been derived previously.^{7,8} The relationship between the dispersion coefficient for the injected material, D , and the various model parameters (see Fig. 1) is given by

$$D = \{f^d[1 - \exp(-V_i/Vf^d)]\}^{-1} \quad \dots \quad (14)$$

where $f^d = u^d/Q$, $f^r = u^r/Q$ and $Q = u^r + u^d$ and u^d , u^r and Q are the determinand stream, reagent stream and total flow-rates, respectively. The reagent dispersion coefficient, D^r , is equal to f^r , the fraction of the total flow contributed by the reagent carrier stream. The α -value for this manifold is therefore given by

$$\alpha = D/D^r = D/(1 - f^d) \quad \dots \quad (15)$$

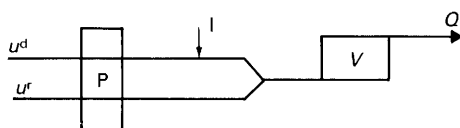
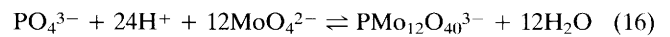


Fig. 1. Schematic diagram of the model for the DLM. u^d , Flow-rate of the determinand carrier stream; u^r , flow-rate of the reagent stream; P, pump; I, injection point; V, volume of the well stirred mixing tank; and Q, total flow-rate. The model assumes (a) plug flow between the injection point and the tank and (b) complete mixing at the confluence point

The sensitivity is given by equation (10).

Comparison of manifolds

To compare the sensitivities obtained with each of these manifold designs and to examine typical performance parameters, an example of an FI method for which a considerable amount of literature exists has been chosen, namely the determination of phosphate for which the following reaction is the first stage



One source of information⁵ concerning the FI format of this reaction gives the following data for an SLM: $V_i = 30 \mu\text{l}$, $c_0^{\text{dtop}} = 40 \text{ p.p.m.}$ ($1.29 \times 10^{-3} \text{ M}$), $c_0^r = 0.005 \text{ M}$ ($(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}$ (0.035 M Mo) and $D = 4$. In using these data for illustrative purposes, it is assumed that the values represent an optimised parameter set, *i.e.*, that the conditions produce the maximum sensitivity which can be obtained with this reagent if the top standard in the calibration sequence has a concentration of 40 p.p.m.

Single-line manifold (normal mode)

From equations (3)–(5), it can be calculated that for this manifold $D^r = 4/3$, $V = 104 \mu\text{l}$ and $\alpha = 3$. From equations (6) and (7) it may be calculated that, for the top standard, $R_p^{r/d} = 81.4$ and $\beta = 2326$. The ratio of reagent to determinand at time $t = 0$ is 27.13.

The sensitivity of the procedure obtained from equation (10) is $0.25k$. If the assumed constraints apply the sensitivity is fixed. However, as the sensitivity is inversely proportional to the dispersion coefficient [equation (10)], the sensitivity may be increased if the α -value can be decreased [equation (5)]. Equations (8) and (9) show that for a given chemistry and reagent concentration, α will decrease if the top standard concentration is decreased. Examples of the changes that can be produced are given in Table 1, together with an indication of the injection volume necessary for a manifold of hypothetical mixing volume of $104 \mu\text{l}$. The relationship between bk^{-1} ($1/D$) and the concentration of the top standard is given in Fig. 2.

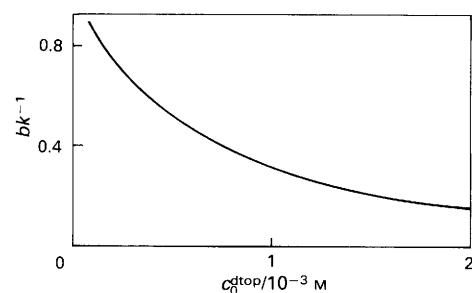


Fig. 2. Plot of bk^{-1} versus concentration of the top standard

Table 1. Increase in sensitivity obtained for SLM in normal mode by reducing the concentration of the top standard

$c_0^{\text{dtop}}/10^{-5} \text{ M}$	α	D	$bk^{-1}(1/D)$	$V_i/\mu\text{l}$
200*	4.65	5.65	0.177	20.3
100	3.33	4.33	0.301	37.0
25.0	0.581	1.581	0.632	104
3.12	0.0726	1.0726	0.932	280

* This value corresponds to approximately 64 p.p.m. of phosphorus.

Table 2. Manifold parameters for DLM as a function of top standard concentration

$c_0^{\text{dtop}}/10^{-5} \text{ M}$	α	D	$bk^{-1}(1/D = f^d)$	$V_i/\mu\text{l}$	$V_i/\mu\text{l}^*$
200	4.65	5.65	0.177	81.4	20.3
100	3.33	4.33	0.301	106	37.0
25.0	0.581	1.581	0.632	291	104
3.12	0.0726	1.0726	0.932	429	280

* Injection volumes for the SLM with the same hypothetical mixing chamber volume.

Table 3. Comparison of injection volumes for three manifold designs

$c_0^{\text{dtop}}/10^{-5} \text{ M}$	α	D	bk^{-1}	V_i DLM/ μl	V_i nSLM/ μl	V_i rSLM/ μl
200	4.65	5.65	0.177	84.8	20.3	180
100	3.33	4.33	0.301	111	37.0	152
25.0	0.581	1.581	0.632	303	104	47.6
3.12	0.0726	1.0726	0.932	447	280	7.29

Double-line manifold

By combining equations (10) and (14), the sensitivity (b) is given by

$$b = kf^d - kf^d \exp(-V_i/Vf^d) \dots \dots \dots (17)$$

In order to maximise the value of b the first term on the right-hand side of equation (17) should be made as large as possible and the second term should be made as small as possible. This latter term can be reduced to zero for an infinitely large value of V_i ; under these circumstances a dispersion coefficient of $1/f^d$ is obtained. Substituting this value into equation (15) gives an α -value for maximum sensitivity of $D - 1$. This value is the same as that obtained for the SLM.

It can be shown⁸ that the injection volume required to give a peak height of 99% of that obtained under infinite volume conditions is given by $4.6V/D$. The implications for the manifold design parameters of fractional flow-rate for the determinand carrier stream (f^d) and volume injected (V_i) are shown in Table 2. For comparison, the corresponding injection volumes for the SLM are also given in Table 2. These values indicate that for the same total flow-rate, the throughput of the DLM would be less than that of the SLM.

Single-line manifold (reverse mode)

As can be seen from equation (13), the α -value for this manifold configuration is the same as that for the nSLM and the DLM and thus is capable of producing the same sensitivity as these two manifold designs. However, the operating parameters of this manifold differ markedly from those of the nSLM in that the increased sensitivity that can be obtained by decreasing the concentration of the top standard is achieved by decreasing the volume of reagent injected. A comparison of injection volumes is given in Table 3.

Discussion

The single well stirred tank model for dispersion shows that, contrary to previous reports,^{3,4} all of these manifolds are capable of producing the same sensitivity when the constraints of the same α and β values are applied. However, the model indicates that the throughput will be considerably different for the nSLM and the DLM. Although the peak width will be narrow for the high sensitivity rSLM, the concept of sample throughput has less meaning in this instance, as the sample is the carrier stream and it is likely that this type of manifold would only be employed in situations where intermittent monitoring of a process stream was required, and also because the main consideration here is manifold design for maximum sensitivity. One possible reason for the consideration that the DLM provides for higher sensitivity than the SLM is that a study of the parameters of both manifolds, which investigated

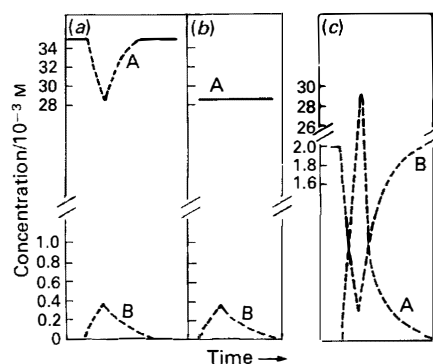


Fig. 3. Concentration gradients of A, reagent and B, determinand for (a) the SLM, (b) the DLM and (c) the rSLM

the effect of increasing the volume injected for a fixed concentration, would show the SLM to be limited by the appearance of double peaks, whereas the DLM would show a more gradual transition to a limiting sensitivity value (it is not possible for double peaks to be formed with this manifold) as there is no reagent concentration gradient in a DLM. There has been very little discussion of the role of $R_p^{\text{r/dtop}}$ values in manifold design in previous publications and it is likely that comparisons have been made between manifolds in which a variety of $R_p^{\text{r/dtop}}$ values would have been produced.

In comparing the nSLM with the rSLM it can be shown that if a given manifold is switched from one configuration to the other (*i.e.*, the roles of sample and reagent are reversed) an increase in sensitivity will be obtained if the dispersion coefficient (D) of the manifold is >2 . Dispersion coefficient values greater than 2 are likely to be encountered as many manifolds designed for on-line reaction will have been designed as so-called "medium dispersion" manifolds,⁹ for which D is normally taken to have a value of between 3 and 10. Thus, it is likely that a manifold designed according to this specification will show an increase in sensitivity when used in the reverse mode. When $D = 2$, no change in the sensitivity will be obtained on changing from normal to reverse mode.

The proposed model indicates that for fixed values of c_0^{dtop} and $R_p^{\text{r/dtop}}$ (*i.e.*, for a fixed β value) the sensitivity can only be increased by reducing the concentration for the top standard in the sequence. This, in effect, allows the same $R_p^{\text{r/dtop}}$ value to be obtained at a lower value of D . Further, the calculations suggest that the concept of a "medium dispersion" manifold, for which $3 < D < 10$, may not be a helpful guide for manifold design as the best performance may be obtained at D values below 2.

Although the model indicates that the three manifold configurations have the same sensitivity, the physically

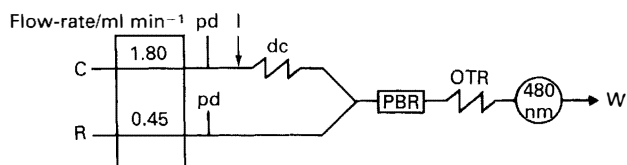


Fig. 4. Schematic diagram of the manifold for the determination of chloride. C, Sample carrier stream (water); R, reagent; pd, pulse damper; I, injection valve (1000 μ l); dc, delay coil (2.1 m \times 0.8 mm i.d.); PBR, packed bed reactor (6 cm \times 2 mm i.d.); OTR, open tubular reactor (1 m \times 0.8 mm i.d.); and W, waste

Table 4. Off-line formation of reaction product between 2 p.p.m. chloride and various reagent dilutions

Absorbance	Reagent dilution factor (D^r)	$D^r/(D^r-1)$ (= D)	c_0^d , p.p.m.	Sensitivity/absorbance p.p.m. ⁻¹
0.025	20.0	1.053	2.11	0.0119
0.031	16.7	1.064	2.13	0.0146
0.034	14.3	1.075	2.15	0.0158
0.039	12.5	1.087	2.17	0.0179
0.056	11.1	1.099	2.20	0.0255
0.069	10.0	1.111	2.22	0.0311
0.073	6.67	1.198	2.40	0.0305
0.093	5.00	1.250	2.50	0.0372
0.121	4.00	1.333	2.67	0.0454
0.130	3.33	1.429	2.86	0.0455
0.145	2.50	1.667	3.33	0.0435
0.153	2.00	2.000	4.00	0.0383
0.159	1.67	2.492	4.99	0.0319
0.156	1.43	3.326	6.65	0.0235
0.143	1.25	5.000	10.00	0.0143

Table 5. Calibration data for chloride

Concentration, p.p.b.	0	10	30	50	70	100	150
Absorbance/ 10^{-3}	0.3	1.0	1.8	3.2	4.4	5.8	8.2

dispersed concentration gradients for each are different, as shown in Fig. 3. The shapes of the profiles for the rSLM are typical illustrations of the situation which causes the appearance of double peaks. This suggests that it may not be necessary to have such a large reagent to sample excess at the peak maximum and that, in an optimisation strategy designed to achieve maximum sensitivity, the value of $R_p^{r/dt^{top}}$ should be carefully studied.

It should be noted that the concentration of the reagent can be controlled. Equations (6)–(10) show that the sensitivity can be increased by increasing the concentration of the reagent.

Application of Model Calculations to the Determination of Chloride

Some of the above concepts were applied to the determination of chloride with a commercially available reagent. Previous work with this system² has indicated that the best detection limits cannot be achieved with the SLM because, at low determinand concentrations, there is considerable base-line distortion due to (a) refractive index effects (the reagent has a refractive index considerably different to that of dilute aqueous salt solutions) and (b) the absorption of the reagent at the analytical wavelength (which would give rise to negative peaks at low determinand concentrations even in the absence of refractive index effects). Both of these effects can be overcome by the use of a DLM. Contributions to base-line noise from pump pulsations and incomplete mixing downstream of the confluence point may be reduced by the use of pulse dampers and a combination of OTR and PBR, respectively.^{2,10} A further source of base-line distortion has been observed with a DLM, namely, the momentary interrup-

tion of the sample carrier stream flow during the injection process. This distortion can be time-resolved from the analytical signal by the insertion of a delay coil in the sample line upstream of the confluence point.¹⁰

In order to determine the optimum $R_p^{r/dt^{top}}$ value an off-line experiment was performed.

Experimental

The manifold used is shown in Fig. 4. All chemicals used were of analytical-reagent grade. The chloride reagent (BDH, Poole, Dorset, UK) consisted of mercury(II) thiocyanate 0.625 g l⁻¹ (1.97×10^{-3} M), iron(III) nitrate 30.3 g l⁻¹ (7.5×10^{-2} M), nitric acid 3.3 g l⁻¹ (3.67×10^{-2} M) and methanol 15% v/v. Chloride standard solutions were prepared by serial dilution of a stock solution with a concentration of 1000 p.p.m. (BDH).

The absorbance of solutions containing 2 p.p.m. of chloride and various dilutions of the reagent was measured in 10-mm cells by a Philips PU 8600 UV - visible spectrometer. An aqueous solution of tartrazine (0.001% m/v, BDH) was used to establish the physical dispersion coefficient of the manifold. After determination of the optimum α and D values, the appropriate flow-rate ratios and injection volumes were calculated and a calibration for chloride over the range 0–150 p.p.b. was obtained. The detection limit was calculated from the absorbance residuals after an unweighted least-squares regression procedure had been applied to fit a straight line calibration function to the data.¹¹

Results and Discussion

The results for the off-line measurement of the net absorbance for a chloride solution with a concentration of 2 p.p.m. are given in Table 4. This experiment is considered to model the performance of an SLM. The reagent dilution factors are thus analogous to D^r values so that D values can be calculated from equation (3). These values are given in Table 4. From these values an initial concentration of determinand can be calculated as, for each measurement, the "peak" concentration of chloride is 2 p.p.m. Hence a "sensitivity" value for the SLM analogue of this experiment could be calculated.

The results show that a D value of between 1.33 and 1.43 should be used. The model calculations discussed earlier showed that the DLM designed for maximum sensitivity would have the same α -value as the maximum sensitivity SLM and thus the requirement is for an α -value of between 0.33 and 0.43. For a DLM the α -value is controlled by the flow-rate ratio. As a single pump was used and pump tubing is only available in certain discrete sizes, it was not possible to adjust this ratio to exactly the required value. Hence, the value of 0.8 for f^d (rather than a value between 0.70 and 0.75) which arises from the flow-rates of 1.80 and 0.45 ml min⁻¹ for u^d and u^r , respectively.

The injection of 564 μ l of the tartrazine solution gave a physical dispersion coefficient, for $f^d = 0.8$, of 1.29. The volume of the equivalent well stirred tank, V , was calculated from equation (4) to be 200 μ l, hence the volume of 1000 μ l injected is sufficient to produce a physical dispersion coefficient of approximately 99.9% of the infinite volume value.

The calibration data are given in Table 5, from which the detection limit¹¹ is calculated to be 11 p.p.b. As the calibration range can be used for concentrations of up to 2 p.p.m., the dynamic range of the method is over two orders of magnitude. When a chart recording of the response to the standard of lowest concentration (10 p.p.b.) was examined, it appeared that a practical detection limit below the value calculated above could be achieved.

Conclusions

Application of the single well stirred tank model for dispersion shows that the SLM (both normal and reverse mode) and the

DLM all have the same inherent sensitivity for FI methods employing on-line chemical reaction. The model also indicates that the need to maintain a large excess of reagent over determinand at the peak maximum may not be necessary and that the use of the guideline of $3 < D < 10$ for manifolds used for on-line chemical derivatisation probably leads to a sub-optimal design in terms of sensitivity. The guideline should suggest $D < 2$.

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