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Applications of controlled dispersion flow injection techniques

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SUMMARY

The factors affecting dispersion in flow injection analysis (FIA) are discussed with particular reference to the design of practical manifolds for analyses based on on-line chemical reactions. The advantages of the modelling approach are pointed out and some simple models for dispersion behaviour based on the passage of discrete volumes of fluid through well stirred mixing chambers are described and some relevant equations quoted. The use of this modelling approach is illustrated with calculations of the reagent to sample concentration ratio required to achieve a desired concentration ratio at the peak maximum, showing the advantage of the merging stream manifold over the single line manifold in this respect. The use of the models as the basis of a peak width method allowing extended range calibrations of common spectrometric techniques to be made is described. The information available from the doublet peak obtained when the reagent is in deficit in the peak centre is described. The use of two novel models (two tanks in series and two tanks in parallel) for describing entire peak shapes is illustrated with the results of some curve fitting calculations. Some limitations of the models are discussed, including the dependence of dispersion of flow rate and results presented which demonstrate that dispersion coefficient is largely independent of flow rate.

Keywords: Flow injection analysis, Flow models, Dispersion, Peak width methods, Doublet peak methods.

Many flow injection (FI) procedures are based on the on-line generation of a reaction product which is monitored at a flow through detector. Normally this product is produced as a result of the reaction between the injected sample and a reagent stream. Thus the manifold used has to be designed to achieve several functions.

Firstly, there must be mixing between the sample and reagent to an extent sufficient to achieve the desired degree of reaction for measurement to be made. In the majority of cases the measurement is made at the maximum of the product peak, which usually corresponds to the maximum in the physically dispersed injected sample profile.

Secondly, the injected material must not unnecessarily diluted, as this reduces the sensitivity (and degrades the detection limit) and decreases the rate at which samples can be analysed.

Thirdly, there must be adequate residence time in the system for the required degree of reaction to occur.

Thus for any given chemistry, selected as the basis of a FI determination, the manifold must be designed to achieve the above requirements. If it is assumed that the reactions in question are fast compared with the rate at which sample and reagent mix, then the design of the manifold reduces to achieving the desired compromise between mixing, dilution and throughput.

If a suitable manifold is to be designed, then both the factors which control dispersion and the way in which they affect dispersion need to be known. For a single line manifold, it is often stated that the factors involved are tube dimensions (length and internal diameter), flow rate and volume injected. If a quantitative basis for dispersion is to be established, then some underlying mechanism for the dispersion is required.

This is the point where the theory and the practice of flow injection analysis (FIA) begin to divide, as nearly all of the theoretical treatments of the dispersion behaviour of liquids flowing in closed circular pipes are based on ideas of a combination of convection (the production of concentration gradients due to the difference in flow velocity between stream lines in a fluid moving under laminar flow) and diffusion. Although it is possible to produce equations for these processes, the production of solutions to these equations applicable to practical FI situations is not so straightforward.

Usually a number of simplifying assumptions have to be made, such as the volume injected being infinitely small, the detector viewing an infinitely thin slice across the tube and the manifold consisting of a straight tube.
of uniform bore. Although equations for dispersion behaviour under these sorts of conditions have been produced [1], they are of limited value because, in practice, the dispersion behaviour of an FI system depends not only on the factors already mentioned but also on the method of injection, the presence of different diameter tubes in the manifold, the detector geometry, the presence of confluence points (a very common design feature) and the extent of coiling or other physical contortion of the flow lines. The secondary flow patterns introduced due to all these factors may well dominate the underlying basic diffusion-convection behaviour.

It is possible to relate the extent of dispersion produced to a number of experimental variables using a purely empirical approach and analysis of the data by the use of a multiple regression method [2]. This approach is unsatisfactory in that it requires a considerable amount of experimentation and the resulting equations are only applicable to the particular conditions and manifold components used.

An alternative approach to the production of equations useful for partial FI situations is by the use of models [3]. A very large number of flow models have been described in the chemical engineering literature [4] some of which, for example the « tanks-in-series » model, have been applied to FI manifolds.

In this paper the basis and use of some simple models based on the passage of finite volumes of fluid through well-stirred tanks are described.

**BASIS OF THE MODELS**

All the models are based on the passage of an injected volume, \( V_o \), of concentration \( C_o \), at volumetric flow rate \( Q \) through a well-stirred tank of volume \( V \). The basis for the model is shown in Fig. 1a. The time taken to reach the peak maximum, \( t_r \), is thus \( V_o/Q \) and if the concentration at the peak maximum is \( C_p \), the dispersion coefficient at the peak maximum of the injected material, \( D \), is given by \( C_o/C_p \).

The equation for the rise curve is given by

\[
C = C_o[1 - \exp(-Qt/V)]
\]

(1)

where \( C \) is concentration and \( t \) is time.

At the peak maximum,

\[
C_p = C_o[1 - \exp(-V_o/V)]
\]

(2)

and the equation for the fall curve is

\[
C = C_o\exp[-Q(t - t_r)/V]
\]

(3)

The peak width, \( \Delta t \), at sted concentration \( C' \) is given by

\[
\Delta t = (V/Q)\ln[(C_o/C') - 1] - (V/Q)\ln(D - 1)
\]

(4)

and the dispersion coefficient, \( D \), is given by

\[
D = [1 - \exp(-V_o/V)]^{-1}
\]

(5)

**EXTENSION OF THE MODEL**

This model can be extended to account for the merging stream manifold as shown in Fig. 1b. The single input stream to the tank is replaced by a sample carrier stream flowing a rate \( u \) and a reagent stream flowing at rate \( q \). The total flow rate, \( Q \), is obviously \( u + q \). The equation for the peak dispersion coefficient of the sample is now modified to

\[
D = f[1 - \exp(-fV_o/V)]^{-1}
\]

(6)

where \( f \) is the ratio \((q + u)/u, \) i.e \( Q/u \).

An extension of the model specifically designed to model the response of an atomic absorption spectrometer [5] introduces a second outflow from the tank. The inputs are now, sample line at flow rate \( pu \), diluent at flow rate \( q \), outflow to detector, \( Q \) and outflow to waste \((1 - p)u \). The term \( p \) was defined as \( p = u/(1 - hu) \) where \( b \) is a factor obtained from the model curve fitting procedure.

The basic model has been extended in two further ways by the incorporation of a second mixing chamber either in series (as shown in Fig. 1c) or in parallel (as shown in Fig. 1d).

**APPLICATIONS OF THE MODELS**

As can be seen from the equations above the models account for the effect of the volume injected on the
dispersion into the terms connected with the volume(s) of the mixing stages. The role of a confluence point is modelled by dilution in proportion to the relative flow rates.

Reagent to Sample Ratio

To ensure that the chemical reaction used as the basis of the determination proceeds to the desired extent, it is necessary to control the concentration ratio of reagent to sample at the point of measurement (usually the peak maximum). On the basis of the single tank model, the dispersion coefficient of the reagent at the peak maximum, \( D^R \) (defined as \( \frac{C^S}{C^R} \)) is given by \( \exp(V/Q) \) and thus there is a simple relationship between sample dispersion and reagent dispersion,

\[
D^R = \frac{D}{D - 1}
\]

From this it is possible to calculate that the ratio of reagent to sample at the peak maximum, \( R^R^S \), is related to the initial concentration ratio, \( R^R^S \), by the equation,

\[
R^R^S = \frac{R^R^S Q}{qD}
\]

Thus, for example, if a peak ratio of reagent to sample concentrations of 10 is required, then an initial ratio of 2.5 will be all that is needed required if the dispersion coefficient is 5. However, if the dilution this produces is unacceptable and a dispersion coefficient of 1.1 is needed, then the initial concentration ratio will need to be 100.

A similar expression can be derived for the model for the merging stream manifold. Here the reagent is diluted at the confluence point but is not affected by the volume of the mixing tank. The corresponding equation is

\[
R^R^S = \frac{R^R^S Q}{qD}
\]

Thus, for example, if the flow rates of samples and reagent are equal and a ratio of reagent concentration to sample concentration of 10 at the peak maximum is required, an initial concentration ratio of 0.1 would be required if the dispersion coefficient was 10. However, if the dilution this produces is unacceptable and a dispersion coefficient of 1.1 is needed, then the initial concentration ratio would need to be 100.

Peak Width Methods

As was shown in equation (4), the width of the peak produced by the single tank models at a concentration \( C^R \) is proportional to a logarithmic function of the injected concentration. This allows the conventional working range of a technique which normally uses peak height as the quantitative parameter, to be extended by several orders of magnitude. The technique has been applied to a number of different detection modes [6].

There are several different ways in which peak width methods may be used. In the case of flame atomic absorption spectrometry (FAAS), an extended range calibration may be obtained either by the injection of standards covering the extended range [7] or by measurement of the peak width at several values of \( C^R \), ie at a variety of heights above the base line [8]. In these ways working ranges of up to 1,000 mg l \(^{-1}\) for elements such as Mg, Cr, and Ni have been obtained. Although the best results are obtained with the insertion of a real mixing device into the manifold, in order to generate exponential shaped peaks, it has been found that, for some instruments [7], the nebuliser behaves as a single well stirred tank. The variation in peak width with flow rate for an atomic absorption spectrometer has been modelled by the extended tank model [5] described above.

Equation (4) may be applied to methods based on the spectrophotometric monitoring of a reaction product when the reagent is in excess across the entire peak profile. When the reagent is in deficit in the peak centre, then a double product peak is obtained, the peaks of which correspond to the element of fluid in which the sample and reagent are in their stoichiometric ratios and thus may be considered as 'end-points' in a flow injection 'titration'. Such methods, are normally used in a mode in which one of the reactants is monitored, rather than the product of the reaction, and thus the doublet peaks are not observed. However, it is possible to extract useful analytical information from the doublet peak.

Doublet Peak Methods

For a single line manifold, the concentration of reactants at equivalence of a 1 : 1 reaction, is given by

\[
C_{eq} = \frac{C^S}{C^R}(C^R + C^S)
\]

Substitution of this expression into the peak width equation above gives

\[
\Delta t_{eq} = \frac{(V/Q)\ln C^S - (V/Q)\ln C^R}{(D - 1)}
\]

and thus the peak width between the two peaks is directly proportional to the logarithm of the concentration of the injected sample. If the peak width obtained when the concentrations of reactants are in standard states is designated \( \Delta t_{eq}' \), then the equation takes a form analogous to the Nernst equation namely

\[
\Delta t_{eq} = \Delta t_{eq}' + 2.303V/Q \log \frac{C^S}{C^R}
\]

This method has been used for the determination of Cu\(^{2+}\) by monitoring the formation of the Cu-edta complex [9] and for the determination of OH\(^-\) by monitoring its reaction with bromothymol blue [10]. In both cases, linear calibration plots over several orders of magnitude were obtained using tubular reactors, ie it was found not necessary to use a real mixing chamber.

The peak separation can also be used to calculate the stoichiometric ratio of the reactants and the peak height can be used as the basis for the calculation of
the stability constant \([10]\). For a \(1:1\) reaction the equation is

\[
K = \frac{C_q}{(C_{eq} - C_{eq})^2} \tag{13}
\]

where \(C_q\) is the concentration of the product at the equivalence point (the peak maximum) and \(C_{eq}\) is the concentration of sample or reagent due to physical dispersion at the peak maximum and is given by equation (10) above. Preliminary results for the determination of the stability constant for the Cu-edta system have shown the validity of the method \([11]\).

**Curve Shapes**

Although the models based on the single tank perform quite well in describing peak height and width behaviour, the overall curve shape is not well described. In practice, due to the effects of the injection process and the mode of operation of the detector, peaks have an initial curved portion near the baseline of the rise curve have rounded tops and the fall curve is not the reverse of the rise curve. This latter feature is due to the fact that not all elements of the injected sample slug are subjected to the same dispersion effects. As the usual method of injection is to actuate the valve and allow the carrier stream to sweep the entire contents of the loop into the manifold, the rear of the sample slug traverses the length of the loop as well as the rest of the manifold and is thus subject to greater dispersion effects.

A comparison of the best fits of the two tank models (tanks in series and in parallel) is shown in Fig. 2 for the physical dispersion of a solution containing 0.02 g l\(^{-1}\) of tartrazine, 82 \(\mu\)l of which were injected into a carrier stream flowing at 1.2 ml min\(^{-1}\) through a tube of 50 cm length and 0.58 mm internal diameter to a detector cell volume of 8 \(\mu\)l. As can be seen from the figure, the best fit is given by the tanks in series model which accounts for the initial curvature and rounded peaks quite well.

**LIMITATIONS OF THE MODELS**

Apart from the extended model used for atomic absorption spectrometry \([5]\), none of the models accounts for the effects of flow rate on the dispersion coefficient, the models predict that dispersion coefficient is independent of flow rate \(\text{see equation (5)}\). Nor do the models predict an appearance time, and as the models are based on exponential curve shapes, they predict an infinitely long rise time to the steady state and an infinitely long washout time.

Thus in order to calculate realistic values for the throughput rate, some boundary condition has to be placed on the washout curve. This is somewhat arbitrary, but the end of the peak can be set at a value such as 1 % of the peak maximum. This may not be suitable in cases where an extended calibration range is being employed where a value of 0.001 % may have to be set if the top standard is three orders of magnitude above the top of the normal working range. This, in turn, will give rise to unrealistically long values of washout times for the lower concentrations.

The inability to predict the effect of flow rate on dispersion coefficient may not be as serious a defect of the models as it might first appear. The variation of \(D\) with \(Q\) is shown in Fig. 3 for different lengths of 0.58 mm internal diameter tubing, from which it can be seen that over the range of flow rates typically encountered in FIA (0.5 to 5.0 ml min\(^{-1}\)), \(D\) is almost independent of \(Q\). In practice it is unlikely that \(D\) would be tailored to the desired value by control of \(Q\), as the volume injected is a much more powerful parameter for controlling \(D\). It is more likely that \(Q\),
together with the tube length, would be used for producing the required residence time for the reaction to occur.

At present, work has not developed to a stage where the volume of the mixing tank, \( V \), can be accurately predicted from the nature and dimensions of the manifold components. However, it may be calculated from a few simple experiments and the models will then satisfactorily predict the effect of changing the injected volume.

It has also been found that, particularly at low flow rates, the dispersion coefficient of a given manifold is a function of the diffusion coefficient of the molecular species in question. The models do not allow variations due to changes in diffusion coefficient to be accounted for. This is a general problem in flow injection work and means that small molecules should not be used as tracers to calculate dispersion coefficients if the manifold is subsequently to be used for chemistries involving large molecules.

**CONCLUSIONS**

Models for the dispersion behaviour observed for typical flow injection systems based on the passage of discrete volumes through well stirred mixing chambers can be used to describe such behaviour. The calculations are straightforward and the models readily account for the effect of the most powerful control of dispersion namely, volume injected. The models also provide guidelines for manifold design and provide a basis for the comparison of the performances of different manifold designs (such as the single line vs merging stream) for the same chemistry.

The models also provide the basis for new analytical methods based on the use of mixing chambers, particularly methods based on the use of the doublet peak obtained for the product profile in an FIA titration.

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