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The Principles of Flow Injection Titration

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The term "flow injection analysis" (FIA) covers a wide range of analytical techniques and methodologies[1] and, to some extent, defies concise definition, as whatever is proposed, an aspect of FIA will be found which is not embraced by the definition. However, many FIA methods are based on the basic principle of exploiting controlled dispersion for analytical purposes. Thus, the basic flow injection (FI) experiment can be considered as monitoring the product of the reaction between a discrete volume of sample solution injected into a continuously flowing reagent stream at a downstream, flow-through detector.

A variety of processes occur during the residence time of the injected material within the system, to cause the sample and reagent solutions to interdisperse. Predominant among these are convection (the development of concentration gradients due to the parabolic velocity profile between the centre of the tube and the wall, which arises from laminar flow) and diffusion. Many manifolds also produce secondary flow patterns due to tube coiling, dead volumes, well stirred volumes and flow-rate fluctuations during the injection processes. Manifolds may also contain confluence points and packed-bed reactors, which will contribute to an already complex flow pattern. The net result of all these contributions to dispersion is that, depending on the design of the manifold, peak shapes vary from "exponential" to "Gaussian." Although the shape may defy an accurate mathematical description (except in the special circumstances to be discussed later), the essence of the analytical usefulness of FIA lies in the fact that, for a given manifold design, the peaks are highly reproducible and thus the peak maximum can be taken as an analytical parameter to be related directly to the concentration of the determinand.

Titrations in Flowing Streams

Although there are many variations on the basic theme of conducting a titration with flowing streams of reagent (titrant) and sample (titrand), most of them can be related to the work of Blaedel and Laessig.[2] Their original version of the flow titration consisted of merging the titrant at flow-rate u_R with the titrand flowing at u_S. For a reaction $n_S S + n_R R \rightarrow P$, where S, R and P are titrand, titrant and product, respectively, and n_S and n_R are the stoicheiometric coefficients of S and R, respectively, the equivalence condition is given by

$$C^S u_S / n_S = C^R u_R / n_R \quad \ldots \quad \ldots \quad \ldots \quad (1)$$

where C^S and C^R are the concentrations of S and R, respectively. If C^S, u_S and C^R are kept constant (as, of course, are n_S and n_R) and u_R is varied, then when equivalence is reached, as indicated by monitoring the extent of the reaction downstream from the confluence point, u_R is directly proportional to C^S, and C^S may be calculated from equation (1). Ashworth *et al.*[3] have described a method in which u_S was varied and Fleet and Ho[4] developed a method in which a linear variation of C^R was produced. Thus, C^S could be calculated from either a knowledge of C^R when the equivalence condition was satisfied, or from the time, t, taken to reach equivalence from the start of the gradient formation, provided that the C^R, t relationship was known. This concept was extended by Pungor *et al.*,[5] who devised a method in which two linear gradients of C^R were produced in the form of an isosceles triangle. Thus, two equivalence conditions were obtained, one on the rising gradient of C^R and one on the falling gradient. The time interval between the equivalence conditions was therefore proportional to C^S. The quantitative analytical measurement is now made in the time domain: all that the monitoring system has to do is indicate when the equivalence condition is achieved.

Flow Injection Titrations

Růžička *et al.*[6] described two versions of a flow injection (FI) titration. The principle of the first can be considered as a variation of Pungor's method. Rising and falling concentration gradients were produced by the injection of a discrete volume, V_i, of titrand into a sample carrier stream which had passed through a well stirred mixing chamber of volume V before merging with the titrant stream. Equations for the rising and falling concentration gradients were derived on the basis of the tanks-in-series model for dispersion. The model was reduced to a single tank of volume V and the initial concentration in the tank was taken as $C_0^S V_i / V$, where C_0^S was the injected sample concentration. Thus, the assumption was made that the injected material was washed into the tank in zero time. The gradients produced from this assumption are an infinitely fast rise (to concentration $C_0^S V_i / V$) followed by an exponential fall of the form $C^S = (C_0^S V_i / V) \exp(-u_S t / V)$. It was shown that the time interval between the two equivalence conditions (the first being at time zero) was proportional to the logarithm of the injected concentration.

In the second version of the FI titration described by Růžička *et al.*,[6] the merging stream configuration was no longer used, and a single-line manifold was employed instead (see Fig. 1). Injection of a volume V_i of titrand into a continuously flowing stream of titrant and passage through the well stirred mixing chamber was also found to produce peak profiles, the width of which was proportional to the logarithm of the sample concentration. The same approximation was used in deriving the basic equation.

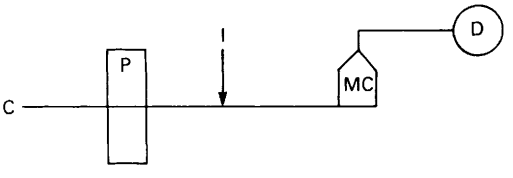

Fig. 1. Manifold for flow injection titration. C, Carrier stream of reagent (titrant); P, peristaltic pump; I, injection of sample (titrand); MC, mixing chamber; D, detector

The second flow injection version of the flowing stream titration was examined in detail by Pardue and Fields,[7,8] who derived equations relating the concentration of injected material to elapsed time, taking into account both physical dispersion in the mixing chamber and chemical reaction. They pointed out that it was not necessary to have any titrand (*i.e.*,

C^R could be zero throughout) as the physically dispersed peak profile was such that the width (at any height) was proportional to a logarithmic function of the injected concentration. Their peak-width equation was used by Stewart and Rosenfeld[9] as the basis for extended range calibrations of a number of analytical spectrometries using the type of manifold shown in Fig. 1 with a real mixing chamber. This idea was adapted by Tyson[10] to the extended range calibration of an atomic absorption spectrometer in which the kinetic response of the nebuliser was taken as modelling that of a well-stirred tank. The useful working range was extended up to 1000 mg l^{-1} for magnesium.

Peak Width Equations

For the case in which no chemical reaction occurs [see Fig. 2(*a*)] the width of an exponential peak produced by passage of a discrete volume V_i through a tank of volume V (in which the concentration, C, = 0 when t = 0) is given by[10]:

$$\Delta t = (V/u) \ln [(C_o/C') - 1] - (V/u) \ln (D - 1) \quad . . \quad (2)$$

where Δt is the peak width at concentration C', C_o is the injected concentration and D is the dispersion coefficient defined by $D = C_m/C_p$, where C_p is the concentration at the peak maximum. It is readily shown[11] that $D = [1 - \exp(-V_i/V)]^{-1}$. When $C_o/C' \gg 1$, equation (2) reduces to

$$\Delta t = (V/u) \ln C_o - (V/u) \ln C'(D - 1) \quad . . \quad (3)$$

and Δt is directly proportional to the logarithm of the injected concentration.

When a chemical reaction occurs between the injected "titrand" and the carrier stream "titrant," equations (2) and (3) are still valid for the situation in which the "titrant" is in excess in the profile centre [Fig. 2(*b*)], but when the "titrand" is in excess in the profile centre [Fig. 2(*c*)] then the flow injection titration condition has been achieved as there must be equivalence points on the rise and fall curves. It has been shown[12] that the peak width between the equivalence points, Δt_{eq} (for a 1 : 1 reaction), is given by

$$\Delta t_{eq} = (V/u) \ln C_o^S - (V/u) \ln C_o^R(D - 1) \quad . . \quad (4)$$

No approximations are involved and Δt_{eq} is directly proportional to ln C_o^S. When the product of the reaction is followed, as shown in Fig. 2(*c*), there is no difficulty in locating the equivalence points as they are the individual maxima of the doublet peak.

However, most reports on the use of FI titrations describe a method in which the concentration of either the titrant or titrand is followed, often by a technique which is linear with respect to the logarithm of the concentration (such as a potentiometric method). There are also several reports in which the absorption of an indicator (acid - base, redox, etc.) is followed to indicate the extent of the reaction. For example, Koupparis *et al.*[13] reported the determination of calcium in the range from 5×10^{-4} to 1×10^{-2} M, by using a reagent stream of 5×10^{-5} M Mg^{2+} - EDTA and 1.3×10^{-5} M calmagnite indicator in 1 M ammonia - ammonium chloride buffer. The measured times ranged from 24.33 to 76.54 s, with a relative standard deviation of 0.2–0.08% (n = 5). The correlation coefficient of the resulting plot of Δt *versus* log C_o was 0.9998. No special effort was made to make measurements at a level corresponding to the equivalence points.

This paper also illustrates the normal way in which FI titrations are applied for analytical purposes, *i.e.*, via calibration with standards. Although, in principle, if the manifold is designed so that equation (4) is valid,[14] a value of C_o^S could be calculated from a single measurement of Δt_{eq} provided that the tank volume, V, flow-rate, u, and reagent concentration are known, it is simpler in practice to "standardise" the system by the injection of titrand solutions of known concentration.

Furthermore, it has been demonstrated that it is not necessary to use a real mixing chamber and that, under appropriate conditions,[12,14,15] short lengths of tubing produce a dispersion pattern which is an acceptable approximation to that of a well stirred mixing chamber.

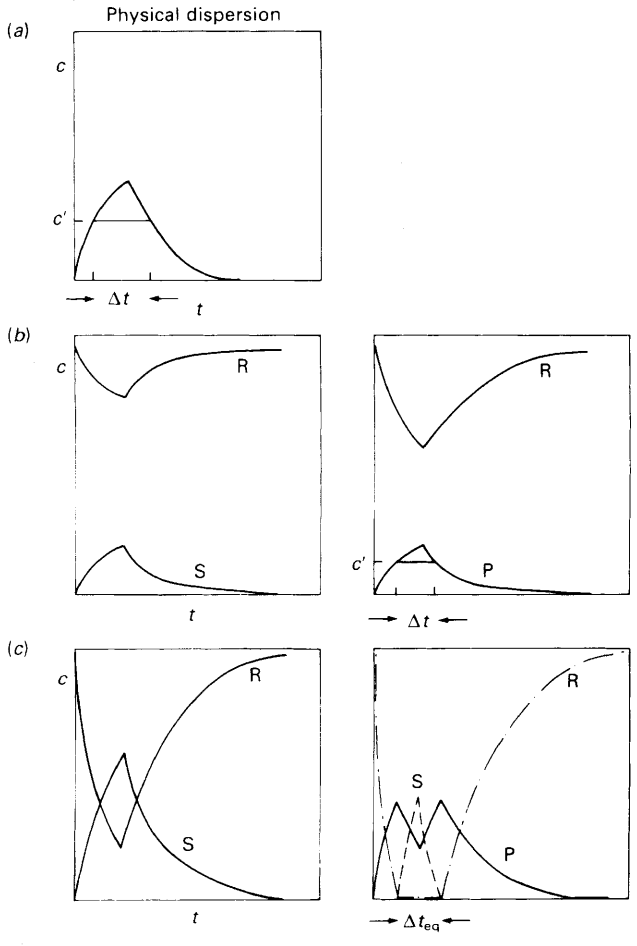

Fig. 2. Peak widths. (*a*) Physical dispersion only, dispersed sample zone monitored at detector. (*b*) Physical dispersion and chemical reaction, reagent in excess in profile centre. (*c*) Physical dispersion and chemical reaction, sample in excess in profile centre

Conclusions

Flow injection titrations provide all the benefits normally associated with FI methodology, *viz.*, low sample and reagent consumption, speed, contamination-free reaction environment and the possible use of "unstable" reagents and reactions, together with the benefit of the greatly increased working range due to the logarithmic response of the system. Flow injection titrations are less precise than the corresponding batch mode and, as with all analytical techniques, accuracy depends on the quality of the standards. As the detector response is not required to have an approximately linear relationship with concentration, only that the response is stable in time, the use of simple, low-cost, transducers capable of accurate measurement of elapsed time between two "trigger" points is possible. The future development of FI titrations could well involve such analytical "time machines."

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