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Flow Injection Techniques for Extending the Working Range of Atomic Absorption Spectrometry and u.v.-Visible Spectrophotometry

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R. FLOW INJECTION TECHNIQUES FOR EXTENDING THE WORKING RANGE OF ATOMIC ABSORPTION SPECTROMETRY AND U.V.-VISIBLE SPECTROPHOTOMETRY

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Nearly all of the chemical manipulations required for conventional u.v.-visible and atomic absorption spectrometries can be done by FIA techniques [R1]. In general, these are simpler, safer, faster and cheaper than the con-ventional procedures. Most FIA applications concern solution u.v.-visible spectrophotometry [R2] though flow injection techniques have been applied to AAS [R3]. This section examines the ways in which flow injec-tion techniques can extend the working range of AAS and solution u.v.-visible spectrophotometry (SS). Any such development will also have potential for a calibration strategy.

CONTROLLED DISPERSION

The factors which control dispersion in FIA are well known, if not as yet well understood. Some of the controlling factors, such as the extent of coiling, the nature of the injection process, the number of discontinuities in the tubing, and the type of flow cell are either not variable in practical situations or are only capable of providing a limited range of dispersion or both. From a practical view-point, the volume injected, tube dimensions, flow rate and timing of selected operations are important, together with the appropriate manifold design. Most variable dispersion manifolds designed primarily to dilute the sample have been used for flame AAS. The preferred approach for SS appears to be the time-based measurements described below.

Volume injected. The volume injected is normally readily changed (by changing the external loop of the valve), but not readily varied from one injection to another. Large dispersions may be achieved; up to 100 (dispersion being defined as the dilution factor of the injected material at the point of measurement) at the peak maximum [R4]. Thus, the working range is increased by the same factor at either end. It is possible to vary the volume reproducibly from one injection to another by controlled timing, either of the partial injection of the contents of a large loop, or of the aspiration of

the sample in valveless 'controlled dispersion analysis' [R5]. Injection of a portion of the dispersed sample zone into another carrier stream (zone sampling) produces dispersions at the peak maximum of up to 130 [R6]. The timing of this second injection may also be controlled.

Carrier tube dimensions. A range of values may be obtained by arranging a number of flow lines in parallel. The injected material is switched down the most appropriate line. When this technique, with dispersions at peak maxima values ranging from 2.52 to 14.9 [R7], is used a working range of 1—40 $\mu g\ ml^{-1}$ can be expanded to 2.5—600 $\mu g\ ml^{-1}$. One of the problems is that with fixed volume injection, a large dispersion means a large peak width.

Flow rate. This parameter does not provide a sufficient range of dispersions in a single line manifold, but may be used in conjunction with a merging stream configuration [R8]. The total flow rate will vary, which can cause problems with atomic absorption detectors. This can be offset by splitting the flow just prior to the detector.

TIME-BASED MEASUREMENTS

The factors which give rise to reproducible peak heights also provide reproducible peak shapes. Measurement along the rise or tail of the peak gives a variety of dispersions. In addition to the greater dilution, zones on the rise or tail usually have a greater reagent-to-sample ratio, which may be of benefit. Time-based methods also apply when the peak maximum is 'off scale'.

Peak tail. Measurements on this part of the peak have been used to provide 'electronic dilution' [R9]. This requires accurate and precise control over the delay period between injection and measurement. In conjunction with 'stopped-flow', it provides a basis for adjusting the 'initial' conditions of kinetic methods [R10].

Peak rise. Under normal FIA conditions, the peak rise is too fast to yield usable measurements. However, if it is spread out by the deliberate insertion of a gradient-forming device (such as a well-stirred mixing chamber), points on the rise curve can form the basis of a calibration technique [R11]. The time at which the mixing chamber effluent had the same absorbance as the sample is substituted into the known concentration/time equation.

Peak width. This is the most widely used of the time-based methods. Although first introduced as a flow injection 'titration' technique [R12], the concept has wider applications and the more general term, 'peak width' is used here rather than 'variable-time kinetic method' [R13]. All peak width methods allow the conventional calibration range to be extended upwards for several orders of magnitude [R14, R15]. This aspect, strangely enough, is hardly ever mentioned.

The situation where there is no reagent in the carrier stream applies to AAS and to the measurement of preformed coloured products. To derive a relationship between peak width and concentration, some assumptions have to be made about peak shape. So far, only exponential peak shapes have been

considered, for which the peak width at any height is directly proportional to a simple logarithmic function of the concentration injected [R14].

When a reagent is present in the carrier stream, in either a single-line manifold or a merged reagent-stream manifold, the peak width will bear the same relationship to concentration as the situation above, provided that the reagent concentration does not fall below that equivalent to the sample concentration at any point on the dispersed profile.

When the sample concentration exceeds this reagent concentration over a portion of the profile (this can always be achieved in a single-line manifold by injection of a large enough volume), there are points on the rise and tail at which the concentrations of sample and reagent are in their stoichiometric ratios. These are the 'equivalence points' of the flow injection 'titration'. An approximate expression for the time between them has been derived for the single-line manifold [R12, R16] and the merging stream manifold [R12]. Again, this is a logarithmic function. The practical difficulties of locating the equivalence points have not been discussed in any detail and, despite the additional simplification introduced, good correlations are obtained between the width at any height and the logarithm of the concentration [R17].

Double peaks. A new peak-width method has been proposed [R18] in which the separation between the double peaks produced when the reagent

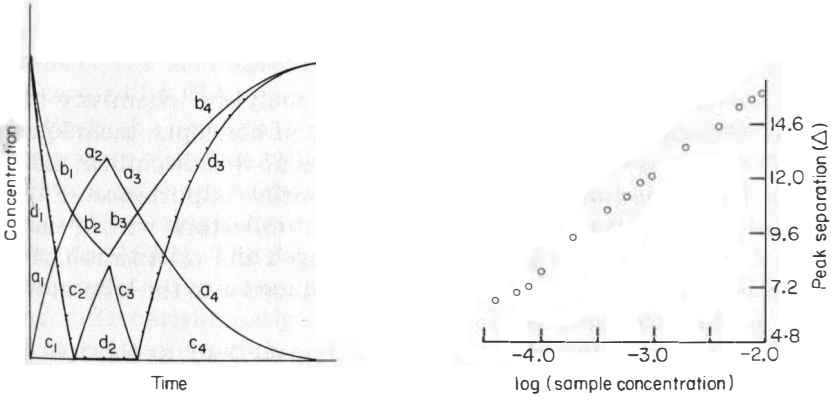

Fig. R1. Formation of double peaks in a single-line manifold. Curves a_1, a_2, a_3, a_4 and b_1, b_2, b_3, b_4 represent the physical dispersion of the sample and reagent respectively. Curves a_1, b_2, b_3, a_4, c_1, c_2, c_3 and d_1, d_2, d_3, represent the product, sample and reagent profiles when reaction occurs. It is assumed that the rate of the product-forming reaction is fast compared with the mixing process and that the thermodynamics ensure 'complete' reaction across the profile. This ensures that the product concentration profile (which is what, in practice, is measured) is an accurate representation of the dispersed sample or reagent profile, depending on which is in excess.

Fig. R2. Plot of peak separation against the logarithm of the injected sample concentration. The carrier stream was 1×10^{-4} M 1,10-phenanthroline flowing at 2.5 ml min^{-1} through a tube 35 cm long. The volume injected was 370 μl and the wavelength 508 nm. A least-squares linear regression gave: slope 3.92, intercept 23.6, standard deviation of residuals 0.197 and correlation coefficient 0.998.

'runs out' is related to the logarithm of the concentration. The basis of this is shown in Fig. R1, and the results for the determination of iron(II) over the range 4×10^{-5} to 1×10^{-2} M are given in Fig. R2. This method allows the time values of the equivalence points readily to be located. The peak heights are also related to concentration and permit extension of the lower end of the calibration down to 4×10^{-6} M.

CONCLUSION

Flow injection methods have more to offer than being just a more convenient way of carrying out existing analytical methods. In addition to opening up new reactions for analytical exploitation and a number of possibilities for manipulating sample and reagent concentrations, the availability of reproducible concentration gradients offers entirely new ways of obtaining analytical information. The challenge to analytical chemists is to discover them!