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Flow Injection Sample Introduction Methods for Atomic-absorption Spectrometry

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The essential features of flow injection analysis are described and the use of flow injection methodology for sample introduction for flame atomic-absorption spectrometry is briefly reviewed. A flow injection analogue of the standard additions method has been devised and applied to the analysis of chromium in some BCS standard steels. The results showed good agreement with the certificate values. The use of a concentration gradient forming mixing chamber to provide a novel method of rapid, single-standard calibration is described and the results of preliminary experiments with magnesium show the method to be viable. The potential usefulness of both methods is critically evaluated.

Keywords: Flow injection; atomic-absorption spectrometry; standard additions method; sample introduction; concentration gradient generator

The term "flow injection analysis" (FIA) is generally understood to encompass analytical techniques in which a discrete sample volume is injected into a continuously flowing carrier stream after which the sample undergoes controlled mixing with a reagent (or reagents) and finally the reaction product is measured by a flow-through detector. The concept of FIA was first proposed by Růžička and Hansen in 1975,¹ although a variety of non-segmented flow systems had been described earlier. In its simplest form, the mixing of sample and reagent is achieved by using the reagent as a carrier stream and controlling the dispersion of the sample between the point of injection and the downstream detector. In general, dispersion is a function of volume injected, tube dimensions (both length and diameter) and flow-rate. The predominant mechanisms are (a) the convective flow patterns developed in the laminar flow of a fluid in a closed circular pipe (the stream lines at the tube walls have zero velocity and that in the centre has twice the average velocity, with a parabolic velocity profile between these two extremes) and (b) the radial diffusion of the sample molecules. The latter mechanism allows molecules to move from one stream line to another and thus all the molecules in the sample zone are eventually transported down the tube and cross-contamination from one sample zone to another may be avoided by suitable timing of the injection cycle. In this basic format, FIA may be considered to be high-performance liquid chromatography without the column, whereas the more complex manifolds that allow merging zone and other reagent addition procedures may be considered as AutoAnalyzer systems without the air bubbles.

Most FIA methods are based on a spectrophotometric measurement of the reaction product. As a steady-state signal is not achieved, the FIA system must consist of a high-precision sample injection valve and pumping unit so as to achieve good reproducibility of the peak height. In practice, the precision achievable depends on the particular pumps and injection valve used, the nature of the detection system, complexity of the flow injection manifold, etc. Values of less than 1% relative standard deviation are routinely reported for the over-all precision based on peak height. This high precision, which may be achieved at a relatively modest cost, allows some of the kinetic restrictions governing the use of reactions forming the basis of a spectrophotometric method of analysis to be relaxed and thus as well as adapting existing methods for FIA, new chemistries may be devised. Further, the peaks may be only a few seconds wide and very rapid sample throughputs are possible with suitably automated equipment.

Not surprisingly, given the emphasis on controlled chemical reaction through the controlled dispersion of FIA, these techniques have not found much use as sample introduction methods for atomic-absorption spectrometry. Such applications that have been reported have either used flow injection techniques as a precise method of introducing small sample volumes to the instrument² or as a means of adding spectroscopic buffers, releasing agents, etc.,³ and may be thought of as the flow injection analogues of "discrete nebulisation" and "branched capillary nebulisation."

However, it is suggested here that the controlled, precise dispersion characterisation of FIA has considerably more to offer and in this paper the possibilities of FIA for calibration purposes are outlined and results presented for (a) the determination of chromium in steel by the standard additions method (in which iron exerts a depressive effect) and (b) calibration for magnesium using a variable dispersion device.

Quantifying Dispersion

Although Gaussian shaped peaks are expected from FIA systems, in practice the dispersion necessary for analytical purposes is rarely large enough for the peaks to achieve a Gaussian shape. In most FIA systems the peaks are skewed with the rising and falling curves approximating to exponentials. This is particularly true when an atomic-absorption spectrometer is used as a detector as the basic action of the nebuliser and the instrument response characteristics play a major role in determining peak shape. A simple model has been proposed to account for these peak shapes⁴⁻⁶ and these will not be discussed further here. It is common practice in FIA not to quantify dispersion in terms of the peak width at some particular height (as is done in chromatography) but to define dispersion, D , as the ratio of the concentration injected, C_m , to the concentration at the peak maximum, C_p . Thus for a sample plug in a reagent stream,

$$D = C_m/C_p \quad \dots \quad \dots \quad \dots \quad \dots \quad \dots \quad (1)$$

The carrier stream reagent concentration will also vary across the sample plug from C_m^R to C_p^R at the peak maximum. The reagent dispersion, D^R , is defined in an analogous manner, *i.e.*,

$$D^R = C_m^R/C_p^R \quad \dots \quad \dots \quad \dots \quad \dots \quad \dots \quad (2)$$

and on the basis of the simple model mentioned above it has been shown⁶ that

$$D^R = \frac{D}{D-1} \quad \dots \quad \dots \quad \dots \quad \dots \quad \dots \quad (3)$$

FI Standard Additions Method

In this method the sample is used as the carrier stream and the standards are injected in sequence. If the concentration of a standard, C^s , is lower than the sample carrier stream concentration, C^x , then the change in concentration at the peak maximum, ΔC_p , will be negative.

Also, if $C^s > C^x$ then $\Delta C_p > 0$ and if $C^s = C^x$ then $\Delta C_p = 0$. Thus a graph of ΔC_p versus C^s will intersect the C^s axis at C^x . In order for the method to compensate for any interference effect in the sample, the dispersion must be such that the concentrations at the peak maximum are such that the interference also affects the added standard to the same extent as it does the sample. The effect of varying the dispersion has already been described for the interference of phosphate on calcium.⁵ If the required minimum ratio of interferent to analyte species, $R_{1/a}$, is known, the relationship between concentration of interferent, sample concentration, C^x , and standard concentration, C^s , may be readily calculated from equations (1)–(3) above,⁶ bearing in mind that the analyte concentration at the peak is made up of contributions from carrier stream and injected solution, as follows:

$$C_m^R = [C_i^s/(D-1) + C^x]R \quad \dots \quad \dots \quad \dots \quad \dots \quad \dots \quad (4)$$

where C_m^R is the concentration of interferent in the carrier stream and C_i^s is the concentration of the top standard in the calibration sequence.

The validity of this approach was evaluated by using it to adjust the concentration of iron (interferent) in the determination of chromium in steel.

Variable Dispersion Calibration Methods

The dispersion may be varied by either changing the volume injected or by changing the tube dimensions between the injection point and the nebuliser, the flow-rate being kept constant at a value giving a satisfactory nebuliser performance. Previously it had been

observed⁴ that a graph of signal *versus* flow-rate showed a broad maximum at a flow-rate slightly greater than the nebuliser's "natural" flow-rate. Experimentally, varying the volume injected required the sample loops on the injection valve to be changed and although this is a straightforward procedure it has nothing to recommend it as an alternative to serial dilution in calibrated flasks as a means of producing solutions of known concentration for calibration points. However, changing the tube dimensions by switching the injected volume down a set of lines in parallel is experimentally simple and rapid and is, at present, being evaluated⁷ as a calibration method.

As different points along the rising part of a peak represent, in effect, different dispersions, the possibility of generating a concentration - time profile suitable for calibration purposes has been proposed⁴⁻⁶ and is also currently being investigated.⁸ The initial experiments have used a small glass vessel as a continuously stirred mixing chamber. Passage of a sharp concentration boundary through such a mixing chamber produces an exponential gradient according to the following equation:

$$C = C_m[1 - \exp(-ut/V)] \quad \dots \dots \dots (5)$$

where C is concentration at time t , C_m is the concentration at the high concentration side of the boundary (the other concentration being zero), u is the volume flow-rate and V is the volume of the mixing chamber. If the concentration boundary is in the opposite sense the exponential decrease in concentration follows the equation

$$C = C_m \exp(-ut/V) \quad \dots \dots \dots (6)$$

This method is analogous to that proposed by Horvai *et al.*⁹ for the calibration of ion-selective electrodes.

Experimental

Apparatus

For the studies of the standard additions method a Shandon Southern A3300 atomic-absorption spectrometer was used together with a Gilson Minipuls 2 peristaltic pump, an Altex, Model 201-25, eight-port injection valve (with two external loops) and 0.58 mm i.d. tubing as the basis of the flow injection manifold. For the concentration profile study, a Perkin-Elmer 290B atomic-absorption spectrometer was used together with two home-made constant-head vessels and a Rheodyne, Type 5011, six-position rotary valve as the flow injection manifold. The mixing chamber was a small enclosed cylinder with the inlet located radially on a base diameter and the outlet axially at the top. The solution was stirred with a magnetic stirrer. The arrangement is shown schematically in Fig. 1. Air - acetylene flames were used throughout with both instruments.

Reagents

Chromium and magnesium standards. These were prepared by dilution of 1000 p.p.m. stock solutions (BDH Chemicals Ltd.).

Iron(III) solution. This was prepared by dissolution of high-purity iron granules (BCS 149/3) according to the method of Nall *et al.*¹⁰

Procedure

For the standard additions studies, the effect of varying the volume injected and tube length on the sample dispersion was first investigated using the conventional mode of separation (*i.e.*, injecting the "sample" into a water carrier stream). With the apparatus used in these studies the injection-loop volume was varied from 13 to 500 μ l and the connecting tube lengths from 3 to 200 cm. A dispersion of 4 was used in the standard additions experiments described here. Substitution of appropriate values into equation (4) enabled a suitable concentration of iron to be calculated. Iron was added to the samples if necessary to increase the concentration to this level. The sample solution¹⁰ was used as the carrier stream and the standards were injected in turn. A graph of change in absorbance, ΔA , *versus* concentration of standard, C^s , was plotted and the value of the sample concentration found from the intercept on the C^s axis.

Fig. 1. Schematic diagram of flow injection - atomic-absorption apparatus for calibration based on use of concentration gradient generator. A and B are constant head vessels containing water and a concentrated solution of the element to be determined; C is the rotary valve allowing rapid switching between one solution and the other; D is the mixing chamber; E is the atomic-absorption spectrometer; and F is the chart recorder.

For the exponential dilution flask calibration method, the instrument output was recorded continuously as the solution aspirated was switched from 0 to 2.5 p.p.m. of magnesium. Solutions for analysis were introduced at the same flow-rate and the time corresponding to the steady-state absorbance was obtained from the chart recording; this was then converted into a concentration using equation (5). The over-all procedure is shown schematically in Fig. 2.

Fig. 2. Use of concentration gradient for calibration. (a) Concentration of the solution entering the mixing chamber is switched rapidly from zero to C_m ; (b) an exponential concentration gradient is introduced to the nebuliser and corresponding absorbance - time graph is recorded; (c) an unknown solution is introduced at the same flow-rate and the steady-state absorbance A^x obtained; (d) from the absorbance - time graph the corresponding time, t^x , is found. Finally this is converted into a concentration by substitution in equation (5), the values of C_m , u and V being known.

Results and Discussion

The variation of dispersion as a function of volume injected and tube length is shown in Fig. 3 for selected values of these parameters. Construction of such graphs enables appropriate values to be chosen so as to achieve a desired dispersion. It is suggested that wider use of such graphs would be valuable in comparing flow injection systems.

Fig. 3. Variation of dispersion, D , measured as the ratio of steady-state absorbance to peak absorbance with tube length, L , and volume injected, V_1 . Volume injected: A, 13; B, 50; and C, 200 μ l. Tube length: 1, 200; 2, 100; and 3, 3 cm.

It was found that in the determination of chromium in the presence of iron, a constant depression in the chromium absorbance was observed when the iron to chromium mass ratio, $R_{I/a}$, exceeded 30. The top standard in the calibration sequence was 20 p.p.m., hence for a sample containing 10 p.p.m. of chromium, the concentration of iron required on the carrier stream to ensure successful application of the standard additions method was calculated from equation (4) to be 500 p.p.m. The results for the analysis of some BCS steels are shown in Table I. Although the analysis reported here and that reported previously⁵ (the determination of calcium in iron ore) may be artificial applications of the standard additions

TABLE I
ANALYSIS OF STANDARD STEELS BY FLOW INJECTION
STANDARD ADDITIONS METHOD

Sample	Certificate value of chromium, %	Chromium found, %
BCS 220/2	5.12	5.13 $\pm$ 0.02
BCS 241/2	5.35	5.34 $\pm$ 0.02
BCS 261/1	17.3	17.4 $\pm$ 0.1

method in atomic absorption, in that the various interference effects can generally be overcome by the use of a dinitrogen oxide - acetylene flame, they serve to illustrate the principle of the flow injection analogue of the standard additions method. This has advantages over the conventional method in that the necessary volumetric manipulations are reduced and the result is obtained by interpolation, a more accurate procedure than the normal extrapolative procedure. It should perhaps be pointed out that, in any format, the standard additions method will not work unless there is a constant depression plateau [*i.e.*, a graph of absorbance (or other analytical parameter) for a fixed concentration of analyte *versus* concentration of interferent levels off to a measurable value above a certain interferent concentration]. This fact is often omitted in text-book explanations of the method.

The results of the calibration based on the exponential concentration gradient mixing chamber are shown in Table II. The accuracy of the method depends on the accuracy of

TABLE II
CALIBRATION FOR MAGNESIUM BY EXPONENTIAL CONCENTRATION
GRADIENT FORMATION

Actual concentration, p.p.m.	..	0.125	0.250	0.500	1.00	1.50	2.00
Concentration found, p.p.m.	..	0.128	0.255	0.520	1.04	1.55	2.07

the flow-rate and, of course, on maintaining this constant. With the constant-head vessels used in these experiments it was found that the flow precision was about 1.5% relative standard deviation. The rate of stirring is also important, as at lower rates the mixing chamber behaves as though its volume were less than the measured volume. There is an additional possibility of error in deciding where the zero time point is; however, with the values of the parameters in equation (5) used in these experiments ($C_m = 2.5$ p.p.m., $u = 5.04$ ml min⁻¹ and $V = 7.18$ ml) the recorded absorbance - time graph covered a period of about 200 s and hence this error becomes important only at lower concentrations. This method has a number of advantages over the conventional method of constructing a calibration graph through a limited number of points. The calibration function is continuous and therefore no curve-fitting procedures are necessary; further, no assumptions need be made about the nature of the absorbance - concentration relationship. A single concentrated standard is used that again reduces the volumetric manipulation necessary and, as the procedure is rapid, re-calibration over the same or a new concentration range takes a minimum of time. Further, the use of a microcomputer to store the graph and perform the calculations should be a straightforward procedure.

Conclusions

In addition to the rapid, precise transport of small sample volumes to an atomic-absorption spectrometer it has been demonstrated that flow injection based sample-introduction procedures, involving relatively simple and inexpensive apparatus, offer a number of possibilities for the manipulation of sample and reagent concentrations through control of the appropriate dispersion. This opens up new possibilities for calibration procedures that have the potential for considerably reducing the volumetric manipulation necessary for the corresponding conventional procedure, hence considerably reducing the time spent on dilution of samples, addition of reagents and preparation of calibration solutions, etc. This could be an important consideration for the present generation of atomic-absorption spectrometers that incorporate automated sample introduction and data handling facilities. It is unlikely at this stage that all the possibilities of flow injection for calibration procedures have been exhausted¹¹ as there are several ways in which dispersion may be varied and reproducible concentration gradients produced.

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