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Item Type	article;article
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Download date	2024-09-23 06:56:35
Link to Item	https://hdl.handle.net/20.500.14394/6497

Flow Injection Sample Introduction for Atomic-absorption Spectrometry: Applications of a Simplified Model for Dispersion

Keywords: *Atomic-absorption spectrometry; flow injection; sample introduction; dispersion model*

In this paper a simple model is proposed to account for the absorbance - time curves obtained when a flow injection analysis (FIA) system is used for introducing samples into a flame atomic-absorption spectrometer. Three different uses of the FI system are described, based on limited dispersion (the analogue of discrete nebulisation), medium dispersion (standard addition method) and high dispersion (production of concentration - time profiles for calibration purposes). It is suggested that the way of looking at a flow injection system described here with particular reference to atomic-absorption spectrometry could be applied to a whole range of other FIA systems and, furthermore, FI sample introduction has more to offer than just reproducible passage of sample to instrument.

It is well known that the dispersion of a sample plug in a continuously flowing carrier stream depends on (1) the carrier tube dimensions (diameter and length), (2) the flow-rate and (3) the volume of the sample plug; also, as the quantitative parameter used is nearly always peak height, considerable efforts have been devoted to obtaining equations relating C_p/C_m , the ratio of the concentration at the peak maximum to that injected, to the above parameters.^{1,2} The value of the equations seems to be limited, as most publications in which FIA is used appear to adopt an approach to achieving the appropriate dispersion, residence time, etc., based on the guidelines set out in reference 1.

Basic Model

The dispersion effects due to injection, carrier tubing, etc., and detector are considered to be due to a single well stirred mixing chamber of volume V , i.e., this hypothetical tank is the only part of the system that produces a concentration gradient. If a volume V_i of concentration C_2 is injected into a carrier stream of concentration C_1 flowing with a velocity u then the peak maximum, C_p , occurs after time $t_m = V_i/u$ and the appropriate equations to describe the resulting concentration - time behaviour are

$$C = C_2 - (C_2 - C_1)\exp(-ut/V) \text{ for } t < t_m \quad \dots \quad \dots \quad \dots \quad (1)$$

$$C_p = C_2 - (C_2 - C_1)\exp(-V_i/V) \text{ for } t = t_m \quad \dots \quad \dots \quad \dots \quad (2)$$

$$C = C_1 - (C_1 - C_p)\exp[-u(t-t_m)/V] \text{ for } t > t_m \quad \dots \quad \dots \quad \dots \quad (3)$$

where C is the concentration at time t .

If C_1 is zero and $C_2 = C_m$, i.e., the normal flow injection condition, then equation (2) reduces to

$$C_p = C_m [1 - \exp(-V_i/V)] \quad \dots \quad \dots \quad \dots \quad \dots \quad (4)$$

Dispersion, D , is conveniently quantified¹ as C_m/C_p and thus in this model the dispersion is given by the reciprocal of $1 - \exp(-V_i/V)$. The value of V has to be determined experimentally (as described below) for any particular set-up, but once this has been done, dispersion as a function of volume injected can be easily calculated, as can the time taken to reach the peak maximum and the time for the concentration to fall to a given fraction of the maximum value. With an atomic-absorption spectrometer as detector, it was found best to operate at a flow-rate compatible with maximum sensitivity of the nebuliser response (about $4\text{--}5 \text{ ml min}^{-1}$) and to vary the dimensions of the tubing between injector and nebuliser in order to change the value of V .

If standards are injected into the continuously flowing sample stream then this system provides the analogue of the standard addition method. At the "peak" maximum, equation (2) applies, where C_1 is the unknown concentration of the sample and C_2 is the concentration of the standard. The maximum change in concentration, $\Delta C = C_p - C_1$, is thus given by

$$\Delta C = (C_2 - C_1)[1 - \exp(-V_i/V)] \quad \dots \quad \dots \quad \dots \quad \dots \quad (5)$$

and thus a plot of ΔC versus C_2 would intercept the C_2 axis at C_1 (i.e., when $\Delta C = 0$, $C_2 = C_1$). If it is assumed that an interference in the sample acts on the standards in the same way, then a plot of ΔA (maximum change in absorbance) versus C_2 will intercept the C_2 axis at C_1 . If the further, but not necessary, assumption is made that absorbance is a linear function of concentration, then the plot of ΔA versus C_2 would be a straight line.

Experimental and Results

Apparatus

Injection valves. (1) Six-port Rheodyne Type 5020; (2) eight-port Altex Type 201-25. A home-made flap valve³ was used in initial work but was found to give significantly poorer precision.

Pump. Gilson Minipuls 2 peristaltic pump. Use of the suction of the nebuliser alone, as has been reported recently,⁴ was found to be unsatisfactory, but the use of constant-head vessels provide a satisfactory, inexpensive alternative to peristaltic pumps.

Tubing and connectors. Anachem PTFE tubing, 0.58 mm i.d., and couplings.

Atomic-absorption spectrometers. Pye Unicam SP9, SP90A Series 2, Shandon Southern A3300 and Perkin-Elmer 290B.

Determination of Volume, V , of Hypothetical Mixing Chamber

The flow-rate was first determined either by timing the delivery of a fixed volume or by injection of a known volume and measuring, using a chart recorder, the time taken to reach the peak maximum from when the trace first deviated from the base line. This method is not particularly suitable with low values of V as the time involved may be less than 1 s. A step change in concentration from zero is then made so that the steady-state signal, A_m , is reached and the rising part of the curve is analysed according to the absorbance form of equation (1) with $C_1 = 0$, namely

$$A = A_m[1 - \exp(-ut/V)] \quad \dots \quad \dots \quad \dots \quad \dots \quad \dots \quad (6)$$

This equation can be rearranged to give

$$V = ut/\{\ln[A_m/(A_m - A)]\} \quad \dots \quad \dots \quad \dots \quad \dots \quad (7)$$

where A is the absorbance at time t . Thus, substitution of pairs of A , t values into equation (7) yields values of V ; suitable values of t may be chosen so that $A_m/(A_m - A)$ has convenient values or alternatively a plot of t versus $\ln[A_m/(A_m - A)]$ has a slope of V/u .

Limited Dispersion ($1 < D < 3$)

With the injection valve located close to the nebuliser and a flow-rate of $82 \mu\text{l s}^{-1}$, a value of $42 \mu\text{l}$ was found for V with the Shandon Southern instrument. Thus, injection of $100 \mu\text{l}$ of solution is expected to give a signal 0.908 of the maximum value (*i.e.*, the dispersion is 1.10). The value found for a series of calcium solutions was 1.09 ± 0.03 . It is expected that the peak maximum is achieved in 1.22 s and that the signal will have decreased to 1% of the peak value after a further 2.3 s and to 0.1% after 3.5 s.

The use of limited dispersion FI sample introduction provides the same benefits as discrete nebulisation with the additional features that effects due to sample viscosity are reduced and that the nebuliser is continuously washed with carrier stream. A precision of about 1% relative standard deviation was obtained.

The

Medium Dispersion ($3 < D < 10$)

The interference effects of phosphate and aluminium on calcium are well known and were used to test the applicability of the FI analogue of the standard addition method. With phosphate, which exerts a constant depressive effect above a certain phosphate to calcium ratio, the method works provided that the dispersion is greater than a certain critical value depending on the amount of phosphate present in the sample. The FI system must be designed so that when the standard is dispersed in the flowing sample stream the phosphate to calcium ratio never falls below the value required to give the constant depression. This is illustrated in Fig. 1. The system does

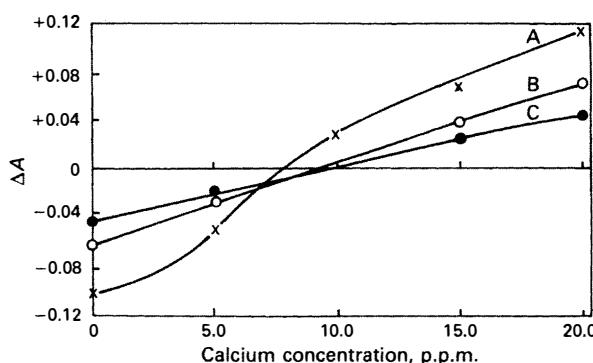


Fig. 1. Effect of dispersion on flow injection standard addition calibration for calcium in the presence of phosphate. Dispersion: A, 1.7; B, 2.6; and C, 3.4. Carrier stream, 10 p.p.m. of calcium plus 500 p.p.m. of phosphate.

not work with aluminium as interferent as these is no constant depression plateau. As the aluminium to calcium ratio is increased the calcium signal eventually drops to zero. The interference was overcome by the addition of lanthanum to the sample stream. As well as acting as a releasing agent, the lanthanum enhances the signal due to its ionisation-suppressant action. This is illustrated in Fig. 2. The results for the analyses of some BCS iron ores are given in Table I. In all instances an air - acetylene flame was used.

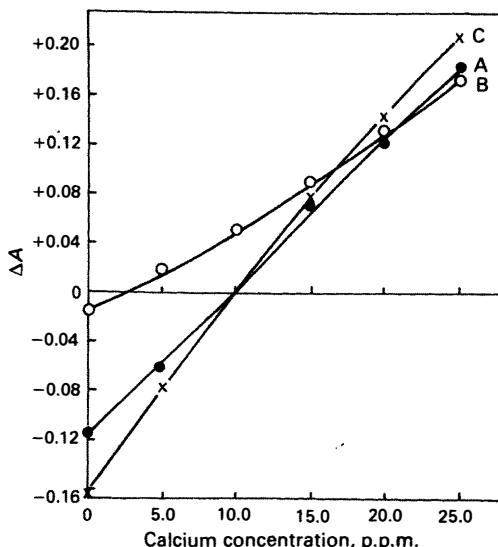


Fig. 2 Flow injection standard addition calibrations for calcium in the presence of aluminium. A, 10 p.p.m. of calcium; B, 10 p.p.m. of calcium plus 20 p.p.m. of aluminium; and C, 10 p.p.m. of calcium plus 20 p.p.m. of aluminium plus 0.25% *m/V* of lanthanum. Dispersion 4.5.

The FI standard addition method has the advantages over the conventional method of (a) using the same standard solutions for a number of samples, thus reducing considerably the amount of volumetric manipulation necessary, and (b) being an interpolative method, thus increasing the accuracy over the normal extrapolative method.

TABLE I
DETERMINATION OF CALCIUM IN SOME BCS IRON ORES BY THE
FLOW INJECTION STANDARD ADDITION METHOD

Sample	Calcium present, %	Calcium found, %
BCS 303 ..	14.0	14.2*
BCS 378 ..	4.70	4.67
BCS 302/1 ..	2.89	2.67

* Sulphosalicylic acid and strontium were used instead of lanthanum.

In recent work on the determination of chromium in steel, problems have been encountered with burner blockage on prolonged nebulisation of a sample stream containing a high salt concentration. It has been found that the method works in the alternative configuration in which a discrete volume of the sample solution is injected into the standards, used in turn as the carrier stream.

High Dispersion ($D > 10$)

A high dispersion was achieved by incorporating a small (approximately 10 ml) glass mixing chamber into the FI system. Passage of a step concentration change from zero to C_m produces the concentration - time profile given by equation (1) with the appropriate substitutions, namely

$$C = C_m[1 - \exp(-ut/V_m)] \quad \dots \quad \dots \quad \dots \quad \dots \quad \dots \quad (8)$$

where V_m is the volume of the mixing chamber.

If the corresponding absorbance - time response of the instrument is recorded, this curve may be used as a calibration as the time axis may be replaced by concentration according to equation (8). In practice, the absorbance of the sample is observed at the same flow-rate at which the calibration graph was generated, the time to which this corresponds found by interpolation and finally the concentration by calculation using equation (8) (this can be achieved rapidly with a programmable calculator). Preliminary studies have shown the method to be accurate to about 2%. The method has the advantages over the conventional working curve method of (a) generating a continuous response curve over the desired concentration range, (b) using only one standard solution, (c) allowing rapid re-calibration over a different concentration range and (d) producing a calibration amenable to handling directly by a bench-top computer.

One of us (A.B.I.) gratefully acknowledges financial support from the National University of Malaysia.

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Received August 13th, 1981

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