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Flow Injection Techniques in Atomic Absorption Spectrometry

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In this paper the combination of a flow injection sample introduction system with an atomic-absorption spectrometer is described, in which low, medium and high dispersion of the sample in the carrier stream have been utilised. A simple model of the dispersion is proposed to account for the absorbance - time behaviour observed and for the results of preliminary experiments, in which sample solution is continuously pumped.

Apparatus

The carrier was pumped by a Gilson minipuls peristaltic pump via an Anachem 2 × 4 port slider injection valve to the nebuliser of either a Pye Unicam SP90 or a Shandon Southern A3300 atomic-absorption spectrometer. The absorbance was recorded as a function of time.

Preliminary Experiments

The effect of pumping a solution continuously into the spectrometer nebuliser, rather than allowing the nebuliser to operate naturally (*i.e.*, by aspiration under the action of the oxidant flow) is shown in Fig. 1, curve A. This shows that although the absorbance increases as the flow-rate is increased, the efficiency of the nebuliser (in terms of introducing sample solution into the flame) passes through a maximum. This is also demonstrated by the fact that the peak absorbance obtained when a 200-μl sample plug was injected via a distilled water carrier stream, under low dispersion conditions (valve very close to nebuliser), also

passes through a maximum [Fig. 1, curve (*B*)], which it will be noted, does not coincide with the nebuliser's natural flow-rate.

Low Dispersion

Basic model

When a step change in concentration is made at the nebuliser then, because of the nature of the response of the nebuliser and the response times of the instrument and recorder, an exponential increase in absorbance with time is observed. This continues until a plateau is reached and as the concentration is stepped back to zero, the absorbance decreases exponentially to zero. As the volume of the concentration step decreases so the length of the plateau decreases, until eventually the maximum steady-state value is no longer reached and a peak with a sharp maximum is obtained instead (the flow-injection condition).

If a step concentration change from C_1 to C_2 is made immediately prior to a mixing chamber of volume V in a stream flowing with velocity u (what chemical engineers call a continuously stirred tank reactor, see for example reference 1) then the resulting concentration (C) - time (t) profile, is given by the following equation:

$$C = C_2 - (C_2 - C_1)\exp(-ut/V) \quad \ldots \quad (1)$$

When C_1 is zero this reduces to

$$C = C_2 [1 - \exp(-ut/V)] \quad \ldots \quad (2)$$

and when C_2 is zero the equation becomes

$$C = C_1\exp(-ut/V) \quad \ldots \quad (3)$$

The combined effect of the action of the nebuliser and the instrument and recorder response time is the same as though the response were instantaneous, and a mixing chamber of volume V were introduced into the flow system. If it is assumed that absorbance is a linear function of concentration, then the absorbance - time graphs can be conveniently analysed by re-arranging the absorbance forms of equations (2) and (3) to give $t = V/u[\ln A/(A_m - A)]$ and $t = V/u(\ln A_m/A)$, where A is the absorbance at time t and A_m is the maximum absorbance, so that a volume, V, is obtained if the flow-rate u is known.

For the low dispersion flow injection experiment the analysis of the curve is simpler. If a volume, V_i, is injected into the flowing stream then the time for the absorbance maximum to be reached will be V_i/u; substituting in the absorbance form of equation (2) gives $A_p/A_m = 1 - \exp(-V_i/V)$ (where A_p is the peak absorbance and A_m is the steady-state value). Therefore the value of V can be calculated very easily. The term A_p/A_m is the reciprocal of the dispersion of a flow-injection system as defined by Růžička (see for example reference 2). If the value of V is established for a set of conditions, the effect of the sample volume can be readily predicted, as can the ratio A_p/A_m.

Experimental and results

The injection valve was located as close to the nebuliser as possible and 100-μl volumes of calcium solutions were injected into a stream of distilled water, flowing at 0.0822 ml s^{-1}. For a step change in concentration, the Shandon Southern instrument gave an absorbance - time profile that corresponded to a hypothetical mixing chamber volume of 43 μl. Thus for a 100-μl injection volume the value of A_p/A_m is calculated to be 0.90 (*i.e.*, a dispersion of 1.1). The experimentally determined value obtained was 0.92 $\pm$ 0.02, for a series of calcium solutions containing 3–15 p.p.m. of calcium. The flow-rate can be calculated from the time taken to reach the absorbance maximum and the volume injected. This enables the time taken for the absorbance to fall to a specified fraction of the maximum value to be calculated. In this case, the absorbance will have dropped to 1% of the maximum in a further 2.4 s.

Low-dispersion injection is the flow-injection analogue of discrete nebulisation and the precision obtained in this study (on peak heights) of 1% relative standard deviation, compares favourably with other studies.[3–6]

Medium Dispersion

This mode of operation was used to provide the flow injection analogue of the standard additions method. The sample was pumped continuously into the nebuliser and discrete volumes of standards were injected into the sample stream.

Basic model

The expected concentration - time behaviour is given by equation (1), where C_1 is the concentration of the sample, and C_2 is the concentration of the standard. At the peak maximum $t = V_1/u$ so that equation (1) becomes

$$C_p = C_2 - (C_2 - C_1)\exp(-V_1/V) \quad .. \quad .. \quad .. \quad (4)$$

where C_p is the concentration at the peak maximum. The difference between the concentration at the peak maximum and the concentration of the sample stream is given by $C_p - C_1$ $(= \Delta C)$ and an expression for this is obtained by subtracting C_1 from both sides of equation (4) as follows

$$\Delta C = (C_2 - C_1)\,[1 - \exp(-V_1/V)] \quad .. \quad .. \quad .. \quad (5)$$

If it is assumed that absorbance is proportional to concentration then, from the absorbance form of equation (5), when $\Delta A = 0$, $C_2 = C_1$.

Equation (5) therefore, predicts that ΔA will be a linear function of C_2, which intercepts the concentration axis at C_1.

Experimental and results

The dispersion was increased by incorporating a 100-cm length of 0.76-mm bore tubing between the injection valve and the nebuliser. The sample volume injected was 200 μl. When distilled water was injected into a stream containing 10 p.p.m. of calcium, the absorbance - time profile corresponded to a mixing chamber volume of 182 μl, and the dispersion had increased to 1.5. For the injection of 5, 15 and 20 p.p.m. into the 10 p.p.m. stream (absorbance 0.56) the model predicts peak absorbances of 0.38, 0.74 and 0.92, respectively. The experimental values were 0.40, 0.71 and 0.85. Part of the discrepancy is due to the non-linearity of the absorbance - concentration relationship.

The standard addition calibrations obtained for (A) 5 p.p.m. of calcium, and (B) 5 p.p.m. of calcium in the presence of 200 p.p.m. of phosphate, are shown in Fig. 2.

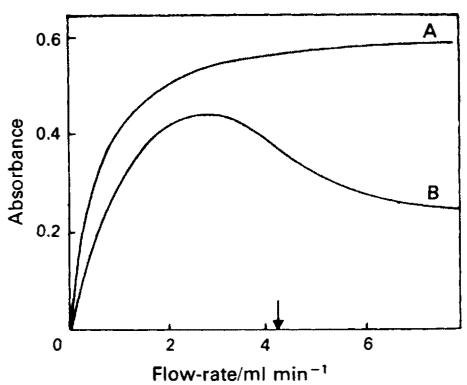

Fig. 1. Relationship between absorbance and flow-rate. (A), Solution continuously pumped into nebuliser and (B), 200 μl injected into carrier stream.

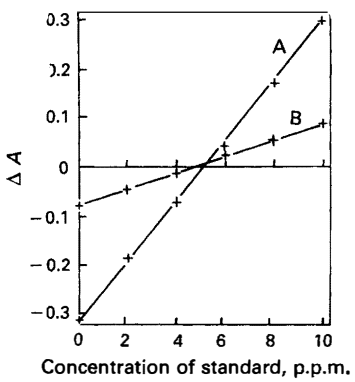

Fig. 2. Standard addition analysis of 5 p.p.m. of calcium. Plot of ΔA against concentration of standard. (A), 5 p.p.m. in distilled water and (B), 5 p.p.m. in 200 p p.m. of phosphate.

High Dispersion

Basic model

If a real mixing chamber is introduced into the flowing stream then a known concentration - time profile may be generated when a step change is made in the concentration. If this is from zero, then equation (2) applies, and if suitable values of V and C_2 are chosen the profiles generated may be almost linear. For example, with $V = 10$ ml, $C_2 = 50$ p.p.m. and $u = 4$ ml min^{-1}, the calibration over the first 33 s (0–10 p.p.m.) would give a correlation coefficient of 0.999 for a least-squares fit of the best straight line.

Experimental and results

A small glass chamber containing a magnetic stirrer was incorporated into the line between the injection valve and the nebuliser. The agreement between the actual and the predicted behaviours for a profile generated from a mixing chamber of volume 8.4 ml with $C_2 = 10$ p.p.m. of calcium and a flow-rate of 4.38 ml min^{-1}, is shown in Fig. 3. Results for the high dispersion case have been somewhat variable and it is felt that the single mixing chamber model may be an oversimplification in this case. However, it is suggested that the generation of curves of this type would be a useful way of calibrating the instrument, particularly if it were interfaced with a computer-based data handling facility.

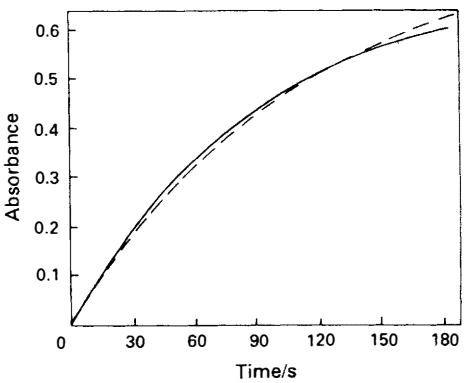

Fig. 3. Absorbance - time profiles generated by a mixing chamber. Continuous line, real behaviour; broken line, theoretical behaviour.

Conclusion

It has been demonstrated that the manipulation of the concentration of a sample by dispersion in a flowing carrier stream has potential as a sample introduction technique for atomic-absorption spectrometry. The experimental set up is simple and inexpensive. Low dispersion systems provide the analogue of discrete nebulisation with precision better than 1% relative standard deviation and a total peak base width of less than 5 s. Medium dispersion systems provide the analogue of the standard additions method and can give base widths of about 8 s. High dispersion systems provide known concentration - time profiles that may be useful for calibration purposes. In all instances the concentration - time behaviour observed can be modelled as the passage of concentration step changes through a single mixing chamber.

References

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