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Flow Injection Techniques of Method Development for Flame Atomic-absorption Spectrometry

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The flow injection introduction of samples that would be difficult by conventional nebulisation owing to dissolved solid content, viscosity or quenching effects on flame reactions is demonstrated. The various ways of achieving sample dilution by control of volume injected, tube dimensions and flow-rate are discussed and a manifold described for producing solutions for calibration purposes and diluting off-range samples. The important characteristics of the nebuliser and instrument for flow injection work are evaluated. A simple manifold for investigating interference effects is described and its use illustrated for some well known effects. The possibilities of achieving pre-treatment by solvent extraction and extension to include indirect methods are discussed and the role of flow injection procedures in the method development for, and the extension of the range of application of, flame atomic-absorption spectrometry is critically evaluated.

Keywords: Atomic-absorption spectrometry; flow injection analysis; sample pre-treatment; nebuliser effects; solvent extraction

When an instrumental method has been selected for evaluation as the final stage in an analytical procedure,¹ there are a number of experiments to be performed. For flame atomic-absorption spectrometry (AAS) these may include a study of interferences (from other sample components, and pre-treatment procedures), precision, accuracy, detection limit, sample throughput, amount of sample needed, cost of reagents and safety aspects. In this paper the possible role of flow injection techniques for conducting some of these evaluating experiments will be described and discussed. Various methods of sample and standard dilution are demonstrated including the use of a stream splitting manifold, which allows dilution of the sample without decreasing the sampling frequency. A simple and rapid method for evaluating interference effects is also described. There are a number of ways in which flow injection methods can extend the range of flame AAS to samples that could not be handled satisfactorily by conventional nebulisation, because of the high dissolved solids content, variable viscosity and so on. These, together with the possible extensions available through the use of solvent extraction procedures, which include pre-concentration, clean-up as well as forming an integral part of indirect procedures, are also discussed. Information on flow injection techniques is readily available² and the FIA - AAS combination has been reviewed.³

Experimental

Apparatus

Several atomic-absorption spectrometers were used in these experiments including a Hilger and Watts Atomspek H 1170, a Shandon Southern A3300 and a Baird Atomic A 3400. For the first two instruments, results were recorded using Philips PM 8521 and Tekman TE 200 chart recorders, respectively. Results from the third instrument were recorded with both a Tarkan 600 chart recorder and/or a Baird Atomic Datacomp computing integrator.

Flow injection manifolds consisted of peristaltic pumps (Gilson Minipuls 2 or Ismatec mini S), injection valves (Altex Type 201-25, Rheodyne Type 5020 and P.S. Analytical T-series rotary injection valves), stream switching valves (Rheodyne Type 5011), end fittings and connectors (Altex type, supplied by Anachem) and PTFE tubing of approximately 0.6, 1.14 and 1.58 mm i.d. (various suppliers including Radiospares). Confluence points, phase separators and stream splitters were all home-made from either PTFE or glass. The P.S. Analytical

valve pneumatic actuator was used, which operates at a pressure below that required by the atomic-absorption instrument and thus a convenient air supply to operate the valve was obtained by "teeing" into the line from the compressor.

Reagents were stock metal solutions of 1000 p.p.m. (BDH Chemicals Ltd.) or were made by the appropriate dilutions of AnalR grade reagents.

Procedure

Solutions difficult to handle by conventional nebulisation

High dissolved solids. A single line manifold was used [(see Fig. 1(a)] with 10 cm of tubing between the injection valve and nebuliser. A series of solutions of 1 p.p.m. of magnesium containing up to 34% sodium chloride were introduced into the instrument via the 200- μ l loop of the injection valve. The effect of aspirating some of the solutions continuously was investigated.

Variable viscosity. Again a single line manifold was used and solutions of 1 p.p.m. of magnesium containing up to 50% V/V glycerol were introduced via the injection valve. Two different volumes were used, 30 and 200 μ l. The absorbances of the solutions under conventional nebulisation conditions were also recorded.

Use of organic solvents. Solutions of lead dithizonate in tetrachloromethane were prepared from aqueous solutions covering the concentration range 0–0.1 p.p.m. according to the procedure described by Donovan and Feeley.⁴ An aqueous carrier stream was used and 70- μ l volumes of the organic solution were injected. The fuel to oxidant ratio was increased to avoid extinguishing the flame.

Sample pre-treatment

Dilution. With the single line manifold the effects of changing the basic parameters of volume injected and tube dimensions (both length up to 220 cm and i.d. 0.58, 1.14 and 1.58 mm) were investigated. The effect of whether the connecting tubing was straight or coiled (radius of coil 0.5–1.0 cm) was studied, as was the effect of flow-rate for both continuous nebulisation and injection of an 82- μ l volume. Using the manifold shown in Fig. 1(b), the effect of diluting the sample with a stream of diluent merging at a confluence point was studied. In order to maintain the flow-rate to the nebuliser constant, the stream was split as described by Zagatto *et al.*⁵ [Fig. 1(c)]. The Atomspek H 1170 instrument was used for these studies with 20 p.p.m. of calcium for the

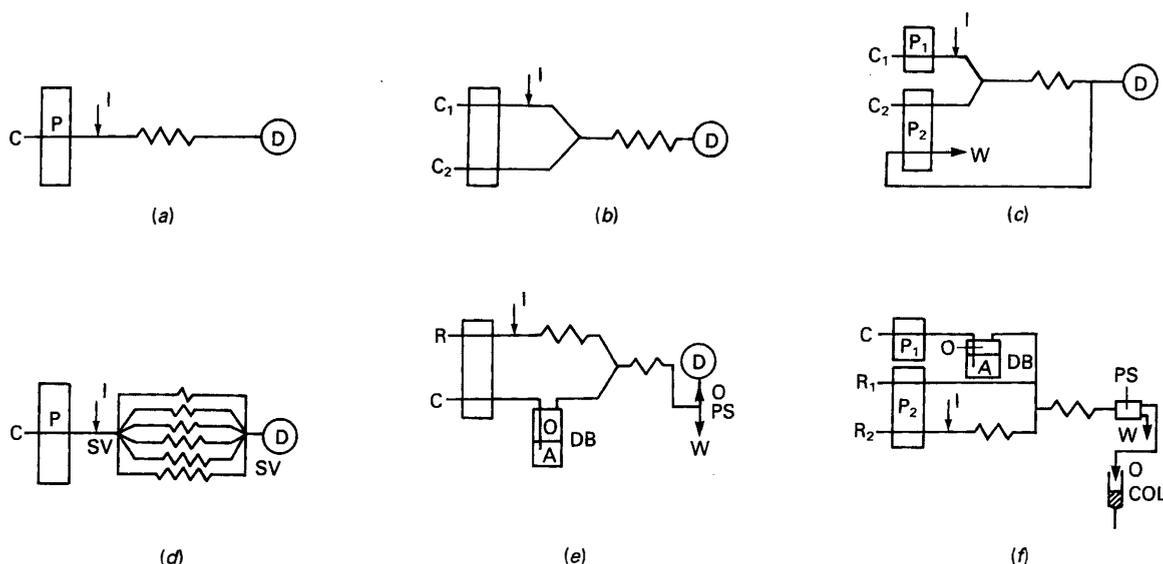


Fig. 1. Schematic diagrams of the flow injection manifolds. A, Aqueous phase; C, carrier stream; COL, small column of anhydrous sodium sulphate; D, atomic-absorption spectrometer; DB, displacement bottle for delivering organic solvents; I, injection valve; O, organic phase; P, peristaltic pump; PS, phase separator; R, reagent carrier stream; SV, 6-way switching valve; W, waste. Detailed descriptions of the manifolds (a)–(f) are given in the text

flow-rate studies and 40 p.p.m. of calcium for the merging stream experiment. In the former there was 2280 mm of 0.6 mm i.d. tubing between the injection valve and nebuliser and in the second, 120 mm of tubing connecting the valve to the confluence point with a coil of 2000 mm between confluence and split points. The “base-line to base-line” peak widths were also measured.

A variable dilution manifold was constructed by inserting two six-way stream switching valves in the manifold with different lengths of 1.58 mm i.d. tubing connecting the various positions on each valve [Fig. 1(d)]. The dilution obtained on switching the same volume, 65 μ l, down each of the lines was measured. The manifold was used to analyse a solution whose concentration was above the normal range for the instrument.

Investigation of interference effects

The manifold shown in Fig. 1(b) was used to investigate the effect of various potential interferences on the determination of calcium. A continuous stream of calcium solution was pumped along C_2 and merged with a water stream, C_1 . The potential interferent was injected at I into the water carrier. The concentration of calcium thus remains the same throughout the experiment whereas the injected material's concentration increases then decreases in a manner dictated by the dispersion effects of the manifold. The interferences included phosphate, aluminium, lanthanum and some organic solvents. The effect of temperature was assessed by comparing the signals obtained with conventional nebulisation as a function of temperature with those obtained by pumping the solutions at a constant rate [Fig. 1(b) with no injection]. The single line carrier tubing was immersed in a hot water-bath.

Sample pre-treatment by solvent extraction

The injection of organic extracts obtained by conventional extraction in a separating funnel (lead dithizonate in tetrachloromethane) has been described above. In this work a 50 : 1 aqueous to organic phase volume ratio was used. A manifold, constructed to perform solvent extractions, is shown in Fig. 1(e). The solvent, isobutyl methyl ketone (IBMK), was displaced from a glass bottle by water. The confluence between the organic phase and the aqueous phase [1% *m/V* ammonium tetramethylenedithiocarbamate (ammonium pyrrolidinedithiocarbamate, APDC)] was a glass Y-connector

and the phase separator was a glass T-connector. Copper was used as the test element. Volumes of 50 μ l and 1 ml were injected.

Indirect methods

Solutions of 12-molybdophosphate in butyl acetate prepared from aqueous phosphate solutions according to the method of Hurford and Boltz⁶ were injected (200 μ l) into an aqueous carrier solution in a single line manifold [Fig. 1(a)]. Both peak heights and peak areas were measured. The flow-rate was optimised for maximum signal to noise ratio. The procedure was extended by attempting to design a manifold for the formation and extraction of the heteropoly species. This is shown in Fig. 1(f). The phase separator used was a controlled porosity PTFE membrane similar to that described by Nord and Karlberg.⁷ The resulting organic extract was dried by passing through a small column of anhydrous sodium sulphate and 200 μ l were injected into a single line manifold as for the conventional extraction procedure.

Results and Discussion

Dissolved Solids

The effect of high dissolved solids can be seen in Fig. 2(a). No difficulty was experienced with even the most concentrated solution with regards to burner blockage. With conventional nebulisation the maximum amount that could be tolerated was 5% provided that the solution was not nebulised for longer than the minimum time necessary to take a measurement. The increase in signal for the sodium chloride alone is due to either scatter or magnesium atomic absorption (10% *m/V* AnalaR sodium chloride could contain up to 2 p.p.m.) and it would be expected that the genuine magnesium signal would be enhanced by ionisation suppression and depressed by incomplete volatilisation from the larger salt clots formed in the flame at higher salt concentrations. These effects were not investigated further as the main objective of the experiment, to demonstrate that very high levels of dissolved solids could be tolerated without burner blockage, had been achieved. The results would suggest that for analysis of real samples under these conditions the standards would have to be matrix matched, if they could be prepared free from contamination by the analyte element. If not, the standard additions method

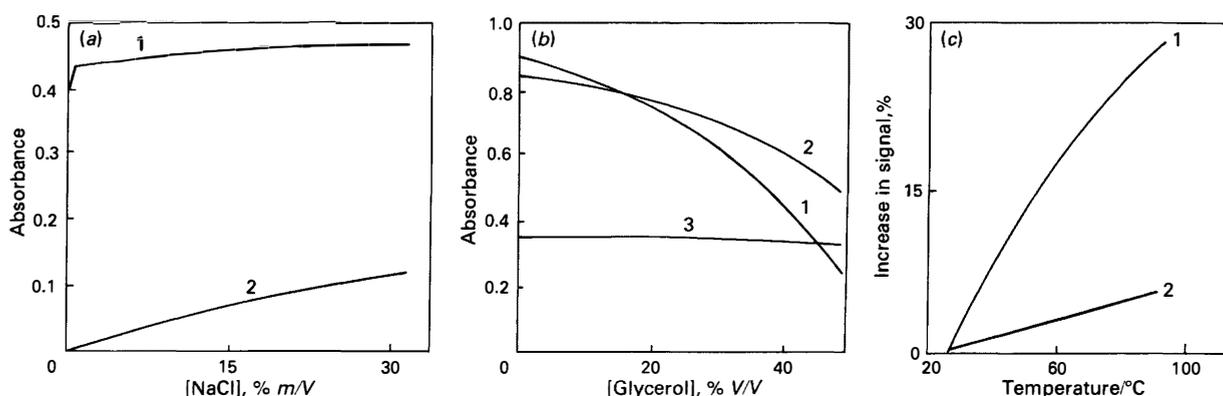


Fig. 2. (a) Variation of absorbance with sodium chloride concentration: 1, containing 1 p.p.m. of Mg; 2, blank. (b) Variation of absorbance with glycerol concentration: 1, steady state; 2, 200- μ l injection; 3, 30- μ l injection. (c) Percentage increase in absorbance as a function of temperature: 1, normal aspiration; 2, pumped aspiration

would have to be used. The flow injection analogues of the latter method described previously⁸ would not be suitable as this utilises injection of standards into the continuously flowing sample stream. Although the theoretical basis has yet to be worked out, it might be possible to inject the sample into the standards used in turn as the carrier stream.⁹ Another possibility is the injection of the sample at specific time intervals into a known concentration gradient, such as that produced by a well stirred mixing chamber.¹⁰

The ability to handle solutions with high dissolved solids means that flame AAS could be used in a situation for which the analyte concentrations would be below the detection limits at the dilutions necessary for conventional nebulisation. This has been demonstrated by Zhou *et al.*,¹¹ but their use of concentrations in solutions containing large masses of solids sometimes expressed in *m/m* units makes a comparison with solutions whose concentrations are expressed in the more common *m/V* units difficult.

Viscosity Effects

The effect of adding glycerol to the solutions can be seen in Fig. 2(b). Under the low dispersion conditions of this experiment there is still a marked effect for 200 μ l of solution. However, with 30- μ l injections, the decrease in signal is only 10% at 50% *V/V* glycerol and no effect at all is observed for concentrations below 20%. The effect of nebulising solutions at different temperatures is shown in Fig. 2(c) from which it can be seen that the use of a peristaltic pump to control the flow-rate results in a much smaller increase in the signal than when conventional aspiration is used. It is likely that if a hot solution is injected into a carrier at room temperature then this would have little effect on the signal and thus no special precautions would be needed in analysing hot solutions with reference to room temperature standards. As with the glycerol solutions, the effect will diminish as the dispersion of the system is increased and the viscosity difference between the sample zone and carrier is reduced. Viscosity effects in the analysis of clinical samples have been discussed by Rocks *et al.*¹²

Organic Solvents

The calibration obtained for lead at 217.0 nm had the following equation from a linear regression analysis of the results for 0, 0.01, 0.02, 0.05 and 0.10 p.p.m.: $A = 0.602C + 0.055$, where A is the absorbance and C is the lead concentration. At 283.3 nm the equation was $A = 0.287C + 0.013$; the correlation coefficients were 0.995 and 0.989, respectively. The relative standard deviation of the blank was 2.6% at 217.0 nm and 4.4% at the higher wavelength. The

improvements in detection limit and sensitivity are mainly due to the favourable extraction volume ratio that it is possible to achieve with this system. In addition to this advantage, chlorinated solvents are usually denser than water and separate readily to the bottom of a separating vessel. The residual aqueous phase prevents evaporative loss but the organic phase can be easily sucked out to fill the loop of the injection valve. It was found that volumes greater than 70 μ l extinguished the flame and that the fuel to oxidant ratio needed careful adjustment. Phosgene was not detected by use of a Draeger tube detector in the atmosphere near the instrument. The detection limit of this device is 0.05 p.p.m. and the TLV is 0.1 p.p.m.

After the initial transfer to the extraction vessel, the solvent is handled in a closed system and the liquid surface is not exposed to the laboratory atmosphere as it would be for the "conventional" micro-sampling procedure. The advantages to be gained by introducing organic solvents into flame atomic-absorption spectrometers have been comprehensively evaluated by Cresser,^{13,14} and although FIA techniques will not permit the continuous introduction of solvents such as tetrachloromethane, they could extend the range of solvents currently thought to be acceptable for laboratory use.

It is possible to devise FIA manifolds that will perform solvent extraction. The results obtained with the manifold shown in Fig. 1(e) over the range 0–10 p.p.m. of copper produced a calibration plot whose slope was 1.3 \times that of the corresponding aqueous phase calibration for the injection of 1000 μ l. Injection of 50 μ l produced a calibration of slope 0.5 \times that of the conventionally nebulised aqueous phase. Conventional extraction showed that the solvent effect on nebulisation and atomisation processes would cause an enhancement factor of 2. Nord and Karlberg have reported¹⁵ enhancement factors of 15–20 for a system based on the same chemistry using continuous uptake of sample solution with a phase volume ratio of 12.8 (as measured by the ratio of flow-rates). In the system reported here, the precision is about 1.5% relative standard deviation based on peak height with a base-line to base-line peak width of 15–20 s. Thus the procedure is extremely rapid compared with the conventional use of separating funnels and consumes about 0.6 ml of IBMK per analysis.

Although the enhancement obtainable is limited because the system disperses the sample zone as all FIA manifolds do, the technique could simply be used for separation of the analyte from interfering components of the sample in situations where a low analyte concentration is not encountered. Flow injection methods of solvent extraction do not appear to suffer some of the problems of earlier automated solvent extraction systems, which for example required mechanical agitation (10 mm amplitude at greater than 40 Hz).¹⁶ The

critical design features appear to be the device that produces segments of aqueous and organic phase and the flow-rates of these two phases. Separation is less critical in a single-stage extraction as quantitative recovery of the organic phase is only necessary if a back-extraction stage is to be included. The concentration of the analyte in the organic phase is independent of the percentage recovery. The continuous introduction of the organic phase into the instrument means that setting the base-line to zero automatically subtracts any contamination from trace amounts of the analyte in the chelating reagent, buffer solutions, etc.

The experiments with the manifold shown in Fig. 1(f) are preliminary in nature. So far, it has proved possible to determine phosphorus in the concentration range 10–50 p.p.m. in the injected sample solutions. It has been found that butyl acetate had, apparently, a depressive effect on the determination of Mo and thus a further development of the system would be the inclusion of a back-extraction stage. A considerable enhancement was observed using conventional procedures from the components of the ammonical buffer used for this extraction. As reported by Wolf and Stewart,¹⁷ it was found that precision based on flow injection peak height was poorer than that obtained with peak area measurement. The use of anhydrous sodium sulphate as a drying agent successfully reduced the blank level to below the detection limit of the instrument (about 0.5 p.p.m. of Mo) indicating that these values arise because of aqueous phase droplets (containing an excess of molybdate reagent) suspended in the organic phase rather than co-extracted isopolymolybdate.

Although the resultant flow-rate of organic phase is slow for obtaining the best performance from the nebuliser, there would be no difficulty in transferring portions of the extract into an electrothermal atomisation device. As with the copper extraction, the flow injection manifold for indirect phosphorus determination is extremely easy and rapid to use.

Sample Pre-treatment

Dilution

The extent to which the sample has been diluted at the peak maximum is normally referred to as the dispersion, D , and is measured by the ratio of the instrument response to an infinitely large volume (steady state) to the response at the peak for the injection of a finite volume of sample. The

variation of D with volume injected is shown in Fig. 3(a), with tube length and i.d. in Fig 3(b) (the effect of coiling is also shown) and with flow-rate in Fig. 3(c), which also shows how the steady-state signal and the flow injection peak height are both functions of flow-rate. The effect of diluting the sample at a confluence point is shown in Fig. 4(a), which shows the variation of peak height for the manifolds with and without a stream split. The peak widths obtained with these manifolds and also for the single line manifold are shown in Fig. 4(b).

Dispersion varies with the parameters of volume injected and tube dimensions in a manner similar to that predicted by Růžička and Hansen's rules.² The effect of the flow-rate is a result of the effect on peak height and steady-state values, as the flow-rate has a profound effect on the fundamental operation of the detector. As the flow-rate is increased from zero the nebulisation efficiency decreases; this is offset initially by the increasing rate of atom formation and so the net signal increases. Eventually, the decrease in nebulisation efficiency dominates and the signal passes through a maximum and then decreases. The shape of the signal *versus* flow-rate curve and the position of the maximum appear to be dependent on the particular design of the nebuliser, spray chamber and impact devices as well as operating parameters such as oxidant flow and position of the nebuliser capillary tip. Results with the instruments listed earlier suggest that the curve shape approximates to a parabola. In practice, there are difficulties with working at low flow-rates: the precision is significantly poorer and a low-frequency component due to pulsations from the peristaltic pump is easily identified, and the low pressure in the tubing results in either the solution de-gassing or the ingress of air at connectors (or both) distorting the peak shape.

Most of the experiments described here were performed at flow-rates near that giving a maximum signal. The effect on the peak heights of merging the sample peak with a stream of diluent does not show the expected decrease in accordance with the increased dilution factor, calculated on the basis of flow-rates, coupled with a decrease due to increased total flow-rate. It is possible that the actual flow-rates did not correspond to those computed from the pump settings.

As predicted,³ the use of a stream split does not contribute to a decreasing peak height and may even be counter productive at high total flow-rates. The same was found with peak widths, which were observed to decrease steadily as the flow-rate increased, even though peak heights increased to a

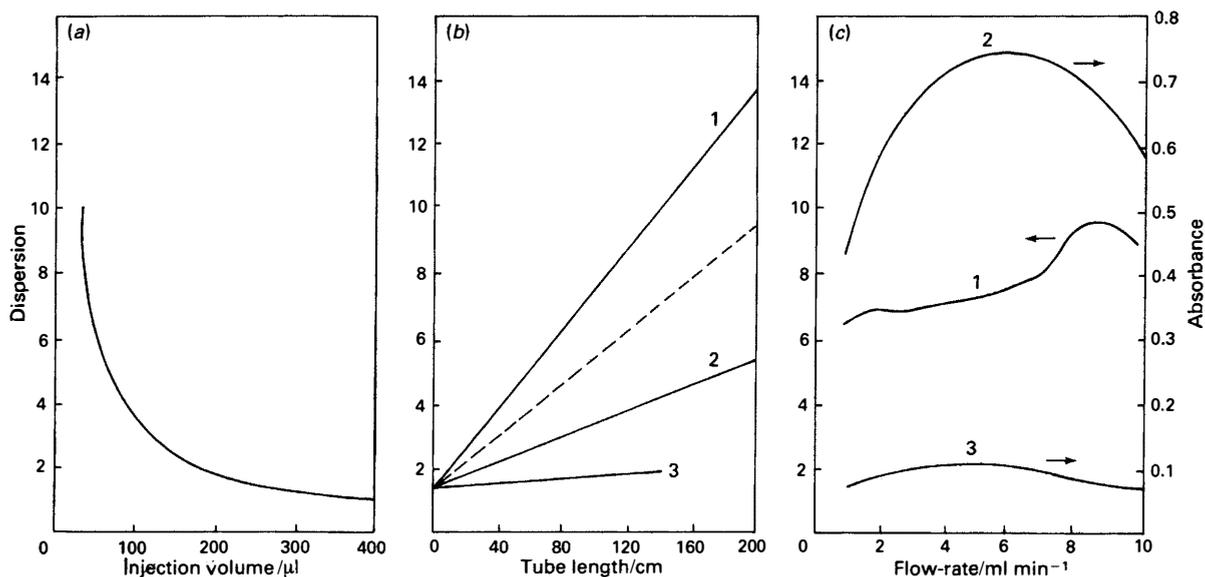


Fig. 3. (a) Variation of dispersion, D , with volume injected using 200 cm length tubing. (b) Variation of D with tube length: 1, 1.58 mm i.d. for (solid line) straight tube and (dashed line) coiled tube; 2, 1.18 mm i.d.; 3, 0.58 mm i.d. (c) 1, Variation of D with flow-rate; 2, variation of steady-state absorbance with flow-rate; and 3, variation of peak height (absorbance) with flow-rate

maximum and then decreased. This effect is what would be expected as the flow-rate increased, provided the increase in sensitivity initially obtained is not too great.

There is another factor operating in addition to the two mentioned above, and that is that at faster flow-rates the instrument amplifier and recorder time constants eventually

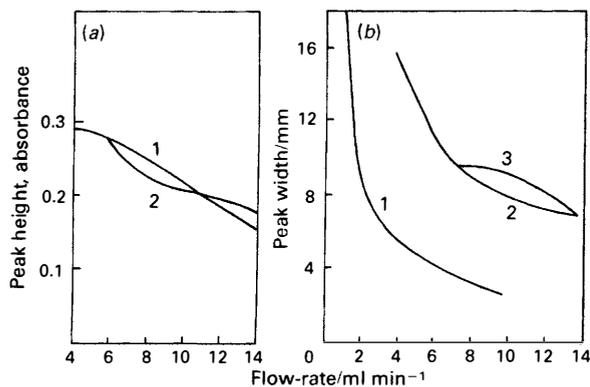


Fig. 4. (a) Variation of peak height with diluent flow-rate; sample carrier flow-rate constant at 4.0 ml min⁻¹: 1, no stream split [manifold 1(b)]; 2, stream split [Fig. 1(c)]. (b) Variation of peak width with flow-rate: 1, no diluent [Fig. 1(a)]; 2, with diluent but no split; 3, with diluent and split

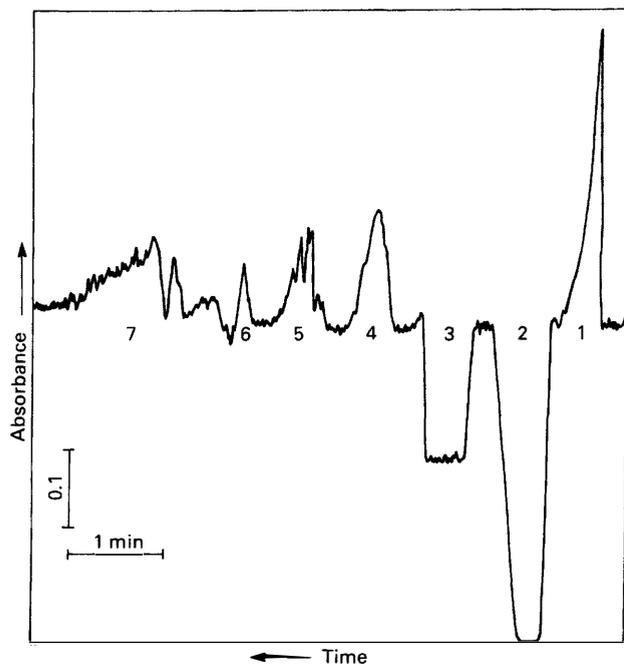


Fig. 5. Investigation of interference effects using manifold of Fig. 1(b), with C₂, calcium stream, C₁, water and interferent injected at 1. 1, 100 p.p.m. calcium; 2, 1000 p.p.m. aluminium; 3, 1000 p.p.m. phosphate; 4, ethanol; 5, IBMK; 6, 1000 p.p.m. potassium; and 7, 10% lanthanum

become significant compared with the duration of the signal and the decrease in sensitivity is due, in part, to the inability of the recording system to follow faithfully the transient signal shape. It should thus be borne in mind that it is possible to produce large values of D by utilising the various properties of the spectrometer discussed above that do not arise from a real dilution of the sample material. This is important if it is intended to calculate concentrations of reagents, etc., merged with or in the carrier stream as is required for performing standard additions or reagent addition or matching standards and samples.⁸ However, if all that is required is to reduce the instrument response for a given concentration then small volumes should be used at faster pumping rates. This produces the additional advantage that, compared with the use of longer and wider tubes as a means of reducing instrument response through genuine dilution, the peak widths are narrower and the sample throughput rate is increased. However, it is likely that under conditions in which instrumental time constants are significant, there will be increased curvature of the calibrations.

The genuine dilution obtained in the manifold through the use of tubing of different dimensions was used as the basis for the construction of a device for (a) producing calibration solutions from a single stock standard and (b) diluting off-range samples. The dispersions of the six lines are given in Table 1 together with the results for the analysis of a 100 p.p.m. solution of lead. The normal calibration range for the instrument used was 0–40 p.p.m.

The method is reasonably rapid compared with conventional serial dilution as the maximum time for a peak to pass through the system completely was 90 s. However, the results in Table 1 give a misleading impression as to the accuracy of the method as there is an uncertainty in the value of D of about 1–2% and in the value of the concentrations corresponding to the peak of about the same, meaning that the uncertainty in the calculated result is between 1.4 and 2%. Some further experiments are in progress on this manifold, which have involved modification of the injection valve so that only 10 μ l are injected. This allows a value of D up to 70 to be obtained; however, the values obtained for the various lines apparently depend on concentration and these might be limitations to the values of D that can be achieved in this way.

Interference effects

The effect on the response for calcium of various potential interferences is shown in Fig. 5. The depressive effects of phosphate and aluminium are readily seen, as are the enhancing effects of various organic solvents, potassium and lanthanum. The peak shapes also reveal information about the interference effects. The peak for the injection of the 100 p.p.m. calcium solution shows the shape of the concentration gradient of the injected material. The peak for phosphate clearly shows that as the phosphate concentration increases, the depression increases until a critical phosphate to calcium concentration ratio is exceeded, after which there is no further depression and the signal levels off until the concentration of phosphate decreases to the critical value again, after which the signal increases to the original value. This behaviour may be

Table 1. Results for the variable dispersion device

Line No.	Tube length (1.58 mm i.d.)/mm	D	Peak concentration for 100 p.p.m. of Pb, p.p.m.	Calculated original concentration, p.p.m.
1	110	2.52	39.7	100.0
2	250	3.49	28.7	100.2
3	415	4.34	23.0	99.8
4	560	5.24	19.1	100.1
5	1115	7.53	13.3	100.1
6	2000	14.9	6.71	100.0

contrasted with that obtained for aluminium. Here, the extent of the depression increases continuously with aluminium concentration until a 100% depression is obtained. The implications for the possible use of the standard additions method for overcoming such interferences have already been discussed¹⁸ (phosphate type can be compensated for, aluminium type cannot). It can be seen that this FIA manifold allows assessment of interference effects very rapidly and greatly speeds up the collection of information about how the effect varies with operating parameters, etc. Provided the dispersion due to the manifold is large compared with the distortion of the peaks by the instrument, it should be possible to obtain data on percentage depression as a function of concentration ratio from the peak shape. The shape of the gradients for the injected material must be known and it looks, from the shape of the 100 p.p.m. Ca peak, as though the single well stirred tank model could be applied. Alternatively, a gradient-forming device such as a mixing chamber could be included in the manifold to give known exponential gradients. By analogy with FIA "titrations"² and other peak width methods¹⁹ it is expected that the width of the peaks is proportional to the concentration of interferent, though it is doubtful if this would ever prove to be the basis of a viable analytical method. The applications of the manifold for evaluating the effect of other sample components, e.g., acids used for dissolution, as part of a method development protocol are readily envisaged.

Sample pre-treatment by solvent extraction and the possible extension to indirect methods have already been discussed under the Organic Solvents.

Conclusions

Flow injection techniques have a number of advantages over conventional nebulisation for both extending the range of applicability of flame atomic-absorption methods and for use in method development experiments. The manifolds required are easily constructed from readily available commercial components and compared with the cost of the instrument or the operator's time are relatively inexpensive. Manifolds can be designed to deal with samples whose concentration is above the normal working range of the instrument and, through the use of solvent extraction preconcentration procedures, samples whose concentrations are below the normal working range. Such pre-concentration procedures, normally considered to be unsuitable for routine laboratory use, may be readily achieved by flow injection methods.

Indirect methods may also appear more attractive when the necessary chemical and maybe physical manipulation of the sample can be reduced to filling and injecting the contents of a sample loop. In this area as in others, flow injection methods are quicker, more precise and use less reagent. They are also applicable to situations in which only a limited amount of

sample is available. They do not have much more to offer in the analytical situation in which the sample can be sprayed directly and analysed against aqueous standards, apart from providing some quick methods of serially diluting the stock standard solution and their use may be inappropriate for situations in which the highest possible signal to noise ratio is required and to which pre-concentration methods cannot be applied. To judge by the number of papers that appear in the literature every year describing the analysis of real samples by flame AAS, most analytical situations for which flame AAS has been selected suffer from interference effects and require careful development and evaluation if the method is to give accurate results. There seems little doubt that the number and type of samples for analysis that might be tackled by flame AAS is going to increase and hence that the use of flow injection methods could be a major factor in the successful development of new methods.

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