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Flow-injection atomic spectrometry: a new analytical technique

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Abstract

Much of the recent research in analytical atomic spectrometry has been concerned with problems of a practical nature. In particular, the inaccuracies arising from a variety of matrix effects and the limitations of sample introduction systems have provided a considerable driving force for recent developments in the various techniques. The philosophy of attempting to eliminate, or compensate for, interferences by procedures implemented at the atomization stage has had success for electrothermal atomization atomic absorption spectrometry but has proved of limited utility for other techniques. Despite considerable efforts, solid-sample introduction is still best done by procedures whose initial stage is dissolution. There is a steady growth in the flow-injection atomic spectrometric literature and a survey of the ca. 50 publications in 1990 shows that much of the interest is now centered on coupling preconcentration and matrix removal procedures with atomic spectrometry, although there is still work concerned with the basic characteristics of flow injection introduction, such as the reduction in sample loading, on-line dilution for calibration purposes and the ability to handle small sample volumes, being published. The role of the flow-injection valve as an interface between flow systems is highlighted. This interface allows independent optimization of the various flow systems coupled in this fashion. Several possible applications of recirculating closed-loop manifolds are described. These include the serial dilution of a stock standard for calibration purposes and to establish a working detection limit. This is illustrated by the dilution of a 2.45 mg l^{-1} solution of magnesium by a factor of 2.20 per injection. This procedure established a detection limit for the instrument involved of between 4.2 and 5.2 ng ml^{-1} . The on-line acid leaching of calcium from charcoal is shown to be sufficiently precise for the basis of a rapid screening procedure and the determination of copper in matrices containing up to 50 g l^{-1} silver is made possible by the on-line precipitation of the matrix as the chloride in a circulating loop containing a filter column of nylon fibres. The additional possibilities afforded by these designs of manifold and the great variety of manifolds described in the literature suggest that flow-injection atomic spectrometry may be emerging as an analytical methodology analogous to the variety of procedures encompassed by terms such as liquid chromatography in the vocabulary of the analytical methodology for molecular species.

Keywords: Atomic absorption spectrometry; Flow system; Calcium; Copper; Closed-loop manifolds

Analytical atomic spectrometry is a field in which there is sustained research activity. As the regular review literature [1–4] reveals, much of this interest is in the development of procedures, for the determination of analytes in real sample matrices, which are free from interference effects. The development of accurate analyses, with

precisions small enough to make the results useful in the context of the particular analytical problem, has been a long term research theme in this area, and may be traced back more than 25 years [5]. The problem areas may be summarized as “matrix effects” and “sample introduction”, although these are not mutually exclusive design-

nations, as a number of sample introduction limitations are imposed by the nature of the sample matrix.

CURRENT RESEARCH IN SAMPLE PRETREATMENT FOR ATOMIC SPECTROMETRY

Much of the recent research involving instrumental developments has been concerned with removing or compensating for interferences arising from the presence of large excesses of matrix components in the atom cell. For example, the technique of electrothermal atomization atomic absorption spectrometry (ETAAS) has been considerably improved in recent years by the development of delayed atomisation cuvettes (such as those using the L'vov platform), transversely heated cuvettes, the use of rapid heating rates, of chemical modifiers and of efficient background correction [6]. The general philosophy that may be discerned in such developments is one of minimum sample pretreatment coupled with as much modification of the sub-sampled material in the atomizer as is required either immediately prior to or during the atomization process. Other atomic spectrometric techniques in common use, such as flame atomic absorption spectrometry (FAAS), inductively coupled plasma optical emission spectrometry (ICP-OES), and those less widely available, such as inductively coupled plasma mass spectrometry (ICP-MS), have not been nearly so successful as ETAAS in the development of this approach. To some extent this may be a contributory factor to the reduced popularity of techniques such as direct current plasma optical emission spectrometry (DCP-OES) and microwave-induced plasma optical emission spectrometry (MIP-OES). For these two techniques, it could be argued that the problems arose from the limitations of sample introduction. It is difficult to introduce material into the DCP (it tends to pass round the sides) and the MIP has an extremely limited solvent load capability, to such an extent that only samples presented in the vapor phase are successfully measured.

Although the ability to accept gaseous sample materials is a useful feature, particularly for ap-

plications to gas or supercritical fluid chromatographic detection [7], it is a feature common to all atomization devices and is clearly of limited utility in general, as most sample materials are solids. Despite strenuous efforts by a number of research groups to develop alternative methods of introducing solid samples into atom cells [8], there is still no generally applicable alternative to a procedure which commences with dissolution. Conversion of a representative sub-sample of a solid material into free atoms at atmospheric pressure in a routine laboratory environment is a feat of considerable chemical ingenuity requiring a large amount of energy to break the various chemical bonds. In general, atomic spectrometers are constructed so that the material that is introduced into the high-temperature atomizer is sufficiently finely divided that during the residence in the atomizer a representative population of free atoms is generated.

Small particles may be produced from solid samples by the coupling of mechanical or heat energy. Materials may be ground and/or bombarded with energetic particles (as is used in arc/spark ablation [9]). After grinding, material may be mobilized directly in a carrier gas stream (as is the case in a swirl cup [10]) or may be wetted to form a slurry which is then handled as though it were a homogeneous solution. Heat energy may be supplied by electrical heating of a substrate (as in electrothermal vaporization, ETV [11]) or from a laser (laser ablation, LA [12]). However, the most successful procedure involves harnessing the favorable free-energy change in a dissolution reaction to produce, in general, ions in solution. Molecular species are usually broken down or vaporized by the dissolution reaction. Although this may be a potential source of error (if analyte-containing molecules are lost), it is usually a beneficial feature of the dissolution in that unwanted matrix components can be removed. For flame- and ICP-based techniques, the next step is usually the fragmentation of the bulk solution into fine droplets by the transfer of energy from an appropriate source. The most widely used type of energy is the kinetic energy of a high-velocity gas stream, although other types of energy, such as ultrasound, are also used. Follow-

ing nebulization [13], the droplets are fractioned by a spray chamber [14] and only the smallest are transferred to the atomizer. The droplet size distribution is such that only a few percent of the total material introduced is transferred usefully to the atomizer.

Clearly there is scope for considerable improvement in the efficiency of this process and few research groups in analytical atomic spectrometry have been able to resist the challenge. The improvements in aerosol generation and transport as a result of their efforts have been disappointingly small. Nonetheless, the generation and transport of aerosols provide a particularly versatile means of interfacing samples and instruments and considerable use is made of this approach in analytical chemistry [15].

There is, therefore, interest in improving the characteristics of analytical methodology in which sample dissolution is required. At present, particular attention is being paid to the possibilities of closed-vessel procedures involving direct internal heating of the solvent in contact with the solid sample by microwaves [16]. Despite having advantages over "conventional" open-vessel/hot-plate procedures, microwave digestions are still slow and labor intensive. Typically, it takes ca. 1 h from insertion of the limited number of vessels into the oven into the transfer of the contents into a calibrated flask.

FLOW-INJECTION ATOMIC SPECTROMETRY

Many of the basic characteristics of flow-injection procedures are attractive for incorporation into methodology involving atomic spectrometric measurement. Flow-injection techniques have the potential for full automation, use small amounts of sample and reagent and provide a contamination-free sample handling environment.

Since 1979, when the first atomic spectrometric publications with the words "flow injection" in the title appeared, there has been a steady growth in interest (as evidenced by the number of publications). This interest accelerated after 1982 and the general trend would still seem to be upwards. The growth of the FI atomic spectrometric (FI-

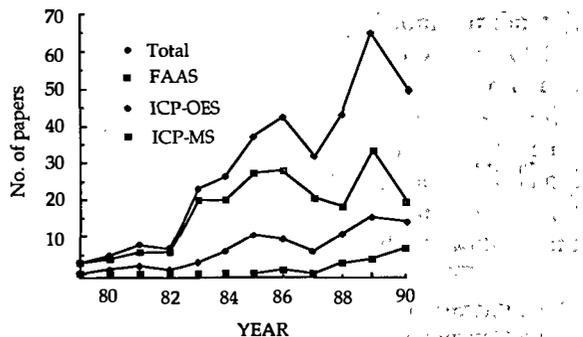


Fig. 1. Growth of the flow-injection atomic spectrometric literature from 1979 to 1990. The total numbers of papers may not be equal to the sum of the three categories indicated owing to a small number of papers concerned with graphite furnace atomic absorption spectrometry, d.c. plasma optical emission spectrometry, inductively coupled plasma atomic fluorescence spectrometry, etc.

AS) literature is shown in Fig. 1. It is difficult to provide accurate numbers because of the growing number of publications in foreign language journals which do not appear in the abstracts journals until a considerable time after publication. There are also problems associated with terminology associated with commercially produced systems. Owing to the exclusive nature of the licensing arrangements, only one manufacturer of FI equipment for use with atomic spectrometry (Perkin-Elmer) uses the description "flow-injection atomic spectrometry" [17]. Other manufacturers use terminology taken from chromatography [18].

Although FI-AS is a relatively small area of the total FI research activity, it has been reviewed on numerous occasions [19] and is the subject of a review book [20]. From these surveys it can be seen that, whereas the early interest was in the the use of FI techniques as a means of diluting and transporting samples, there has been a considerable development in the interfacing of sample pretreatment procedures with an atomic spectrometer using FI technology.

The scope of FI procedures may be illustrated by a consideration of the papers published in 1990. The breakdown of the 1990 literature by technique is shown in Fig. 2. Of these 53 papers, 2 are reviews [21,22], 8 are concerned with basic aspects of micro-volume sample introduction [23-

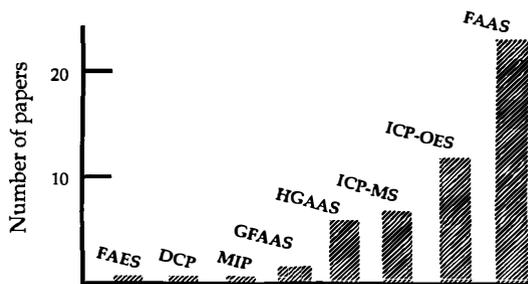


Fig. 2. Breakdown of the 1990 flow-injection atomic spectroscopic literature according to the major techniques used in the experiments described. At least one paper describes the use of two techniques. Abbreviations are as used in the text together with FAES, flame atomic emission spectrometry; DCP, direct current plasma; MIP, microwave induced plasma; HGAAS, hydride generation atomic absorption spectrometry; GFAAS, graphite furnace atomic absorption spectrometry.

30], 4 are concerned with calibration [31–34], 5 are concerned with speciation [35–39], 7 are adaptations of indirect methods [40–46] and the remaining 27 involve matrix removal and/or pre-concentration [17,18,47–71]. This last group may be subdivided according to the chemical basis for the procedure. These include precipitation [50], electrodeposition [51,52], liquid–liquid extraction [47–49], vapor generation [17,53–59] and solid-phase extraction [18,60–71]. It is not possible to provide a rigid categorization of these papers as several of them contain topics that could be considered in more than one category. For example, use is made of on-line dialysis for dilution and sample clean-up in two papers concerned with speciation [38,39]. Both flame AAS and ICP-OES were used [67] for the determination of aluminum in dialysis concentrates by FI-AS procedures involving solid-phase extraction.

For the systems in which sample pretreatment chemistry is performed, the flow-injection valve may be regarded as an interface between two flow systems. This is illustrated schematically in Fig. 3 for a six-port rotary “injection” valve. The loop of the injection valve may simply provide the mechanism of transfer of a discrete volume of liquid from system 1 to system 2, or the “loop” may be the location of key components and chemical reactions. In either instance, the valve allows the two flow systems to be optimized inde-

pendently of each other. For example, in the liquid–liquid extraction sample preparation system for graphite furnace atomic absorption spectrometry, Backstrom and Danielsson [47] used the FI valve to interface between the intermittent operation of the atomizer and the continuous extraction system. In the determination of lead in water, Bysouth et al. [62] used a chelating column mounted in the valve loop to retain the lead selectively. On switching the valve, the column was inserted into the carrier stream connected to the nebulizer of the flame atomic absorption spectrometer so that the up-stream injection of a discrete volume of acid released the lead from the column.

In this paper, the possibilities of coupling recirculating, closed-loop sample pretreatment procedures with flame atomic spectrometry using flow injection valve interfaces are illustrated. Three procedures are described: the sequential dilution of a stock solution for the production of calibration standards and to estimate the detection limit, the determination of calcium in charcoal and the determination of copper in the presence of excess of silver. Although each of the manifolds used for these procedures is slightly different, the method of operation is the same. The recirculating loop is filled with carrier, a discrete volume of solution is injected and allowed to recirculate and finally a sub-sample of the loop contents is injected into a single-line carrier for transport to the instrument. This principle of operation is illustrated in Fig. 4.

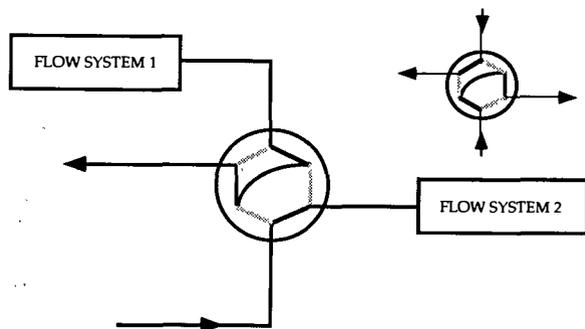


Fig. 3. Flow-injection valve interface. The inset shows the alternate position of the valve whereby the contents of the loop are inserted into flow system 2.

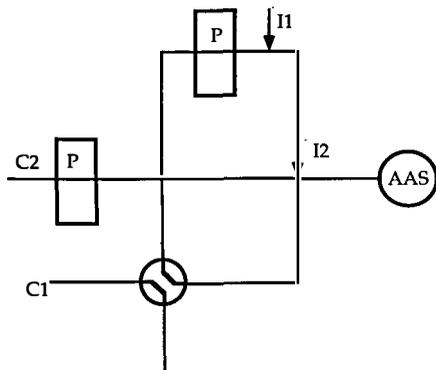


Fig. 4. Basic principle of the recirculating loop manifold. The loop is filled by carrier C1 on switching the distribution valve. Sample is injected into the loop at I1. After an appropriate time a sub-sample is injected into carrier C2 by the injection device I2.

Although a number of methods for the calibration of atomic spectrometers by the application of FI procedures have been described [72], none has yet appeared to be an attractive proposition for commercial development, possibly because of the instrumental complexity involved in some of the reported procedures require extensive software development or precise control over the timing of various operations, or both. There is still a need for a simple reliable procedure for calibration and dilution. The aim of the investigation is to examine the feasibility of a closed-loop procedure in which the dilution produced depends only on the volumes of loops involved and does not require precise timing of any operation.

The determination of calcium in charcoal would normally proceed via a dry ashing stage followed by acid dissolution. This procedure is lengthy and would not be satisfactory as a basis for rapid determination. The aim of the investigation was to evaluate the possibility of the development of a rapid flow-injection method for the characterization of charcoal according to the ratio of calcium carbonate to calcium oxide contents. As a first stage in the method development, a rapid method for obtaining an estimate of the total calcium is sought. The procedure will be developed further by the extension of the manifold to allow the determination of the carbon dioxide released from carbonate species (as-

sumed to be predominantly calcium carbonate). The amount of oxide present may be calculated by difference on the basis that the only two species present in any significant amounts are the oxide and carbonate. As it is desired to measure the ratio of the amounts of these species, it is not necessary to obtain complete leaching of the calcium, only that the oxide and carbonate are leached to the same extent.

Determinations by flame-based procedures in which high concentrations of silver-containing solutions are introduced to the spectrometer are problematical owing to the formation of solid silver acetylide in the spray chamber. This leads to blockage of both burner and nebulizer and is also a serious hazard as it may detonate if allowed to become dry. The aim of the studies was to investigate the possibilities of matrix removal by the precipitation of the silver and retention in an on-line filter.

Closed-loop recirculating systems, whose application for flow analytical purposes predates FIA [73], have been used for a number of analytical purposes in flow-injection analysis [74]. Recently, continuous-flow recirculation manifolds have been used as part of the sample preparation procedure. The digestion of sewage sludge samples in a continuous-flow reactor in a microwave oven with return of the partially digested sample to the sample reservoir was described by Carbonell et al. [28]. The extraction of iron from dried, ground plant material in a recirculating closed-loop reactor with the aid of ultrasound with subsequent determination of the iron by solution spectrophotometry was described by Lazaro et al. [75]. In both of these methods, the solid sample reservoir forms part of the recirculating loop, but in the first procedure [28] a sub-sample was injected into a single-line manifold for transport to the flame atomic absorption spectrometer, whereas in the second [75] the entire recirculating loop formed the loop of the injection valve. On injection into a merging streams manifold, the sample was merged with a reagent stream and the product of the reaction detected spectrophotometrically.

In the procedures outlined in this paper, fluid is injected into the recirculating loop and after an

appropriate time interval a sub-sample of the fluid in the recirculating loop is injected into a carrier stream for transport to the instrument. For the calibration procedure, diluent is injected into the loop which contains a stock standard solution and a portion of the diluted standard solution produced after recirculation is injected into a single-line manifold and transported to the spectrometer. For the determination of calcium, a powdered sample in a packed bed located in the recirculating loop is first flushed with water until all the air has been removed. Acid is then injected into the recirculation loop and the calcium leached from the charcoal. A sub-sample of the calcium solution now circulating is injected into the manifold connected to the spectrometer. For the determination of copper in silver, the recirculation loop is filled with a solution of a precipitant and contains a filter device. On injection of a sample solution, the silver matrix is precipitated as a simple inorganic salt and retained on the filter. A sub-sample of the remaining components of the solution is now injected into the manifold connected to the spectrometer.

EXPERIMENTAL

Apparatus

Three atomic absorption spectrometers were used, Perkin-Elmer (Norwalk, CT) Models 2280, 1100B and 3100. All were used with air-acetylene flames according to the manufacturer's recommended operating conditions. The absorbance signals were monitored by either a chart recorder (Asea Brown Borai Model SE 120, supplied by Fisher Scientific, Pittsburgh, PA) or, with the Model 1100B spectrometer, a printer (Epson Model LQ-850, supplied by Perkin-Elmer). Connection of the flow-injection manifold to the nebulizer capillary was made by a friction fit. Manifolds were constructed from 0.5 or 0.8 mm i.d. PTFE tubing. Valves were either six-port rotary valves (Rheodyne Model 50, supplied by Alltech, South College, PA, or Model 1106, from Omnifit Atlantic Beach, NY), four-way slider valves (Altex Model 20, supplied by Alltech) or four-port distribution valves (Omnifit Model 1114). Peri-

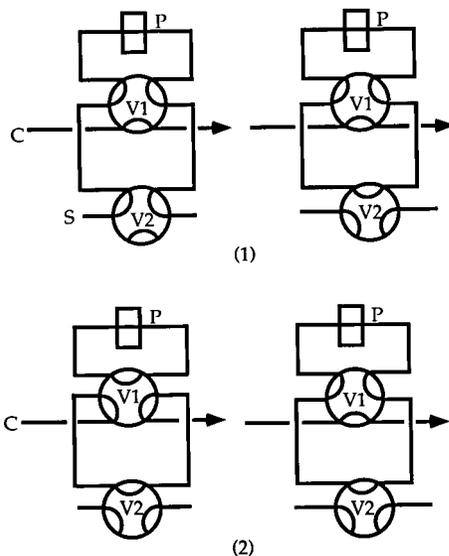


Fig. 5. Calibration circulating loop constructed from two six-port rotary valves. In (1) the loop is filled by S and valve V2 switched to close the loop. In (2) valve V1 is switched to inject part of the loop contents into carrier C. Returning the valve inserts carrier into the recirculation loop. Repeated actuation of V1 produces serial dilution of the original solution S.

static pumps (Ismatec Model MS-4 Reglo 8-100, supplied by Cole-Parmer, Chicago, IL) were used. Further details of the construction of the manifolds are given in Figs. 5-7.

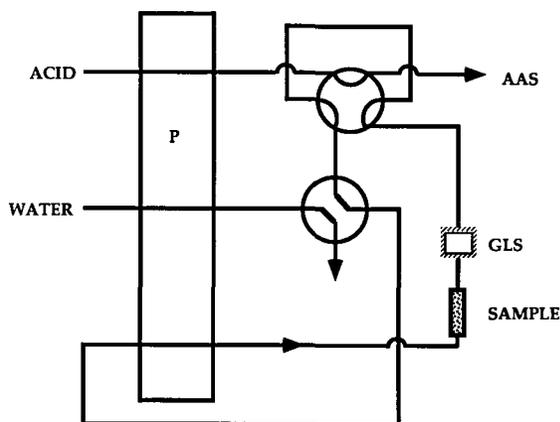


Fig. 6. Acid-leaching manifold. The loop is first filled with water from the distribution valve. Following removal of the residual air, acid from the carrier stream is injected and circulated. In preliminary experiments a gas-liquid separator, GLS, was used to remove bubbles from the stream. In later experiments this device was not necessary.

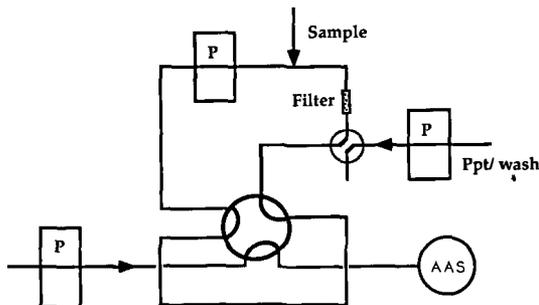


Fig. 7. Matrix removal manifold by precipitation. The loop is filled with precipitant via the distribution valve. On injection of the sample, the precipitate formed is retained on the filter column. A six-port rotary valve sub-samples into the carrier stream for the atomic absorption spectrometer.

Procedures

The volumes of the recirculation loops and of the injected portions of the loops were determined by filling with a concentrated standard solution and subsequent collection of the required loop contents in a calibrated flask, dilution to volume and analysis by flame atomic absorption spectrometry with conventional sample introduction and calibration.

Dilution manifold

The recirculating loop (see Fig. 5) was filled with the top standard in the sequence by the appropriate switching of valve V2. The first signal was produced by actuating valve V1, which inserted the contents of the connecting lines into the carrier stream connected to the spectrometer. On return of this valve to its initial position, the carrier fluid (distilled, deionized water) was injected into the recirculation loop. After a few minutes, during which the contents of the loop were diluted by the injected carrier fluid, the valve was actuated a second time, producing a second flow-injection peak. The procedure was repeated as required or until no further response was detected. A stock magnesium solution was prepared by dissolution of magnesium and dilution to give a top standard of 2.45 mg l^{-1} .

A set of five replicate calibrations was performed over several hours, from which the dilution factor per injection was calculated. The instrumental detection limit was obtained from the

results of repeated injection and dilution until no further response could be seen. As the dilution factor is known, the concentration injected on the n th injection may be readily calculated. Thus, if the n th injection is the first in the sequence for which no detectable response is obtained, the concentration of the solution corresponding to injection number $n-1$ may be taken as a measure of the instrumental detection limit.

Calcium leaching manifold

The sample material was ground and sieved so that the particle size was between 0.5 and 1.0 mm. A sub-sample of this material (ca. 40 mg) was packed into a low-pressure liquid chromatographic guard column cartridge (Upchurch Scientific, Oak Harbor, WA) and inserted into the manifold. The distribution valve (see Fig. 6) was turned to allow water to fill the recirculation loop and flush the residual air from the cartridge. Once the air had been removed, the loop was closed and the injection valve switched to insert a portion of the acid carrier stream [10% (v/v) hydrochloric acid] into the recirculation loop. After a 10-min recirculation, the injection valve was switched back, thereby injecting a portion of recirculating loop contents into the acid carrier. The system was calibrated by the injection of standards via the loop of the injection valve.

Silver matrix isolation manifold

The recirculating loop (see Fig. 7) was filled with 0.5 M hydrochloric acid by switching the distribution valve. The loop contained a filter column consisting of nylon fibres packed in a 50 mm \times 3 mm i.d. glass column (Omnifit Model 416320). After circulation for 4 min, the injection valve was switched to inject a sub-sample into the water carrier stream for transport to the spectrometer. The recovery of 10 mg l^{-1} of copper from solutions containing up to 50 g l^{-1} of silver was investigated.

Method development

For the dilution and calibration manifold several closed loops were constructed and used. The effect of flow-rate in the recirculating loop was investigated. Some preliminary experiments were

carried out in which the concentration of dye solutions injected into closed loops was followed as a function of time with a visible spectrometer. The possible benefits of the inclusion of a "split and confluence" (i.e., a two-line network) in the recirculating loop were examined. For the other two procedures initial experiments were done with single-line manifolds coupled directly to the spectrometer. For the determination of charcoal a number of experimental variables were studied, including the effects of the flow-rate, acid concentration and particle size. The effect of particle size in the closed-loop configuration was also studied and the need for a gas-liquid separator examined. For the precipitation manifold a variety of possible inorganic precipitants were examined, as was the efficacy of a number of filtration devices, including various membrane filters and packed columns.

RESULTS AND DISCUSSION

Dilution manifold

All the manifolds constructed were found to operate satisfactorily provided that the recirculating flow-rate was kept below about 10 ml min^{-1} . Above this flow rate, the recirculating fluid was observed to degas and, although most of the bubbles redissolved at locations of high pressure in the loop, a stream of bubbles gradually built up in the circulating loop. In order to obtain a reasonable number of calibration points across the usual, somewhat limited, working range of flame atomic absorption spectrometry, a target value for the dilution factor of between 2 and 2.5 was selected. For the manifold constructed according to this criterion, the volumes of the recirculating loop and of the injected loop were found to be 1636 and 891 μl , respectively. The additional non-significant figures are retained in these volumes, as it is the ratio of the total volume to that remaining (745 μl) which gives the dilution factor per injection of 2.20.

The ratio of successive peaks from the calibration experiments gave the values 2.18 ($n = 4$, $s = 0.04$), 2.20 ($n = 5$, $s = 0.09$), 2.18 ($n = 5$, $s = 0.05$), 2.16 ($n = 5$, $s = 0.06$) and 2.20 ($n = 6$, $s = 0.08$),

where n is the number of peak ratios taken and s is the standard deviation of the n ratios. Overall, a dilution factor of 2.19 ($n = 24$, $s = 0.06$) was obtained with a 95% confidence interval of ± 0.03 (2.16–2.22). A peak above the baseline noise was recorded for the eighth injection and a decrease in the baseline noise was observed for the ninth injection. As the initial concentration in the loop was 2.45 mg l^{-1} , it may be calculated, from the range of dilution factors covered by the confidence interval, that the eighth injection introduced a concentration of between 9.2 and 11 ng l^{-1} and the ninth injection introduced between 4.2 and 5.2 ng l^{-1} . Hence a realistic "detection" limit may be rapidly established for the particular manifold and injection valve without recourse to any statistical evaluation of the data either for the calibration or for the replicated introduction of a dilute solution. For the type of instrument used in this study, which gives a chart recorder output which is digitized, the latter method will give an over-optimistic estimate of the detection limit as the instrumental rounding of small signals to the nearest digit causes an almost noise-free "signal" to be produced at the chart recorder output.

For a series of standards re-analysed as unknowns, calibration of the instrument by the successive dilution method gave results that were indistinguishable from those obtained by conventional calibration in calibrated glassware and direct nebulization. It was observed that an injection could be made every 40 s, by which time it was presumed that the concentration of the fluid in the recirculating loop was spatially homogeneous. Thus data for an eight point calibration could be generated in less than 6 min, which represents a substantial saving in time over the conventional serial dilution. Off-range samples may also be rapidly diluted by repeated injection as every three injections represent, approximately, an order of magnitude decrease in concentration.

The experiments with the dye and solution spectrophotometer showed that a significant reduction in the time required for complete homogenization of the concentration in the circulating loop could be obtained by the inclusion of a split

and confluence in which the lengths of the branches of the network were different. It is suggested that such a modification to the manifold produces, at the confluence point, concentration oscillations in the combining streams which are out of phase and which therefore tend to interfere destructively. A consideration of the need to damp concentration oscillations rapidly suggests that other hydrodynamic devices, such as mixing tanks, should also be investigated in this respect. Such studies are in progress.

Calcium leaching manifold

It was found possible to produce a calcium signal by the injection of acid into a single-line manifold connected directly to the spectrometer into which had been inserted of a packed reactor of charcoal. However, the signal was irreproducible and very dependent on particle size. In addition, the back-pressure introduced by the solid material substantially decreased the flow-rate to the spectrometer. This gave rise to calibration difficulties as it required that the instrument be calibrated under the same flow-rate conditions, which were irreproducible from one run to the next. The amount of calcium leached was found to be largely independent of the acid concentration.

In the recirculating mode, initial difficulties were experienced with finely ground charcoal samples as the pressure drop caused the solution to degas. Also, it appeared difficult to remove all the residual air from the reactor. A number of designs of gas-liquid separator were evaluated and, although a device based on a microporous tube was successful, it was not particularly robust and better results were obtained by increasing the particle size of the sample (i.e., not grinding to such an extent). However, it was clear that the amount of calcium leached was related closely to the particle size and, to increase the concentration in the loop, the total volume was kept to a minimum.

The total volume of the recirculation loop used was found to be 249 μl and that of the injection loop 109 μl . Hence the concentration of hydrochloric acid solution circulating was 4.4% (v/v). The recirculation flow-rate was 0.95 ml min^{-1}

and that of the carrier to the spectrometer 3.1 ml min^{-1} . For a series of six replicate determinations on the same charcoal sample, whose calcium content had been determined by the off-line dry-ashing procedure, to be $2.0 \pm 0.3\%$ (w/w), where the \pm term is the 95% confidence interval, a recovery of $7 \pm 1\%$ was obtained. The sample masses ranged between 37.2 and 40.5 mg. There was no correlation between the recovery and the sample mass. For the process for which this method is being designed, the precision is adequate. The second stage of the overall procedure, the determination of the carbon dioxide released on acidification of the carbonate species, is currently under development. Thus, from a knowledge of the total amount of calcium and of the amount of carbonate, the amount of oxide may be calculated.

Silver matrix isolation manifold

The volume of the recirculating loop was 4.0 ml, into which 1.5 ml of the silver sample solution was injected. It was found that 4 min were sufficient for the precipitated silver chloride to be collected in the filter column and the concentration of the solution in the recirculating loop to become uniform. A 2.5-ml sub-sample was injected into the single line manifold connected to the atomic spectrometer. A solution of ammonia (1 + 1) was found to remove the precipitate from the column efficiently. For a solution containing 10 mg l^{-1} of copper, the recovery was 97% in the presence of 50 g l^{-1} of silver [relative standard deviation (R.S.D.) 1%], but this performance degraded in the presence of 100 g l^{-1} silver to 95% (R.S.D. 15%).

Conclusions

The recirculating loop manifold provides a versatile reactor design for the implementation of a number of sample pretreatment procedures for analytical atomic spectrometry. In particular, this design of reactor allows the coupling of reactions whose rates would not be compatible with the direct coupling of a flow reactor to the spectrometer. When this reactor design is considered together with the considerable variety of manifold designs used for the sample pretreatments de-

scribed in the recent flow-injection atomic spectrometric literature, the flow injection-atomic spectrometry combination appears as an extremely versatile part of the overall analytical method. By analogy with techniques such as liquid chromatography, for which the term is considered to encompass a number of analytical procedures in which on-line sample pretreatment procedures may be coupled with molecular spectrometry in solution, it may be argued that FI-AS is emerging with similar status for analytical methods involving atomic spectrometry.

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