Atomic Spectrometry and Flow Injection Analysis: A Synergic Combination

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SUMMARY

The combination of flow-injection techniques with atomic spectrometry (flame atomic absorption and emission spectrometry and inductively-coupled plasma/atomic emission spectrometry) is reviewed, with particular reference to the more recent contributions. The considerable growth in the number of directly coupled pre-concentration and matrix isolation methods is noted, together with the increasing number of reports of indirect methods for metals, inorganic anions and even drug molecules. Many developments are motivated by a desire to increase the performance of the spectrometry over that obtained with conventional methods of sample introduction. Conflicting statements concerning the possible benefits of reduced uptake rate, of air compensation and of peak-area measurement are examined critically. The conflicting requirements of obtaining freedom from stable-compound interferences coupled with good detection limits are discussed, as are means of obtaining the best detection limits. Modifications to nebuliser and spray-chamber design are suggested for maximising peak height (to obtain good detection limits) and for working with reduced uptake rates (to reduce stable-compound interferences in flame-based spectrometries). The single well-stirred tank model is used to model nebuliser response and results are presented for the flow-injection behaviour of a Philips Scientific SP9 instrument under conditions of low flow rate which show reasonable agreement with the model. With this instrument, the best detection limits are obtained on the basis of peak-height measurements at the flow rate producing maximum signal-to-noise ratio.

In a review article which appeared in the proceedings of the first Flow Analysis Conference, held in 1979, Ruzicka and Hansen [1] cited only one reference to the use of flow injection techniques with atomic spectrometry. Thus Bergamin and co-workers [2] can claim the first publication to contain the words flow injection analysis (f.i.a.), atomic absorption spectrometry (a.a.s.) and flame atomic emission spectrometry (a.e.s.) in the title. In a summary of the relevant a.a.s. literature in early 1983 [3] some sixteen papers were cited, though by this time about four papers describing aspects of the combination of inductively-coupled plasma/atomic emission spectrometry (i.c.p./a.e.s.) and f.i.a. had appeared. The first in this latter category was a contribution from Ito et al. [4].

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Reviewing the literature in 1985, Tyson [5] commented that at the time of writing (late 1984) the total literature in the field amounted to some thirty papers on f.i./a.a.s. and cited about ten concerned with f.i./i.c.p./a.e.s. By September 1985, Ruzicka [6] was able to comment that the f.i./a.s. combination was the fastest growing group of applications in the field of spectroscopy and in the review of f.i.a. [7] that appeared in the proceedings of the third Flow Analysis conference, held in 1985, the literature had grown to 65 papers on a.a.s., three on flame a.e.s., 18 on i.c.p./a.e.s. and one on atomic fluorescence spectrometry (a.f.s.) [8], making a total of 87.

The most recent comprehensive coverage of the literature, the second edition of Ruzicka and Hansen’s book [9], surveys the world literature up to the end of 1986 and lists just over 1400 references of which 166 concern f.i./a.s. (123 a.a.s., 5 flame a.e.s., 37 i.c.p./a.e.s., one a.f.s. and one i.c.p./mass spectrometry [10]). At that stage, the use of atomic spectrometry with flow-injection techniques made up almost 12% of the world literature on f.i.a., though it has probably slipped back a little recently as proportionately fewer papers were published in this area in 1987 than in 1986, which saw a remarkable expansion in the f.i./a.s. literature. Separate reviews of the f.i./i.c.p. combination have also appeared [11–13].

If the definition of f.i.a. advocated by Ruzicka and Hansen [9] is adopted, namely “Information-gathering from a concentration gradient formed from an injected well-defined zone of a fluid, dispersed into a continuous unsegmented stream of a carrier”, it seems appropriate in the present context to include the literature concerning the direct coupling of liquid chromatography (l.c.) and atomic spectrometry. This literature has recently been reviewed by Ebdon et al. [14] who cite a total of 72 references including 24 to l.c./electrothermal atomisation a.a.s., a combination which has yet to feature in the “non-chromatographic” f.i./a.s. literature.

That there is much common ground between the combinations of chromatography and flow injection with atomic spectrometry is illustrated in several recent publications dealing with the interface between the solution-handling components of the instrument and the atom reservoir [10,15]. This common ground is likely to be a fruitful area of research, because the need for interfaces between the liquid-handling domain and the atom cell, capable of giving performances comparable to “conventional” interfaces, is becoming more widely recognised as interest grows in the possible benefits offered by the use of flow-injection techniques of sample handling.

Sample pretreatment and matrix removal
As with many developments in analytical science, the underlying theme discernible in the application of flow-injection techniques to atomic spectrometry is enhancement of the performance of the overall analytical method. As the performance of many analytical methods is limited by the performance of the
instrument involved, the motivation behind some of the work described in the literature is the desire to increase the performance of the atomic spectrometer in question. However, many analytical methods based on atomic spectrometry involve sample pretreatment and thus much of the work reported concerns the conversion of sample pretreatment procedures to flow-injection formats. These pretreatments, in turn, are designed to overcome some of the limitations of the instrumentation, such as inadequate detection limits or inaccuracies caused by matrix interference effects.

Two of the commonest pretreatment procedures involve liquid–liquid extraction and accumulation on a solid reagent. Several different designs of manifold for each of these procedures have been reported. Initial work with liquid–liquid extraction systems used the injection valve as the interface between the extraction manifold and the spectrometer, the sample being pumped continuously into the system [16]. The main aim was to obtain greater sensitivity than for normal nebulisation into a flame atomic absorption spectrometer and the authors therefore argued that it was necessary to keep the flow rate to the instrument at the normal nebulisation rate (about 4 ml min$^{-1}$ for the instrument in question); thus to achieve a factor of $n$ increase in concentration in the organic phase, a sample flow rate of $4n$ ml min$^{-1}$ was required. It was pointed out that practical problems limited $n$ to about 4 for a directly coupled flow-injection/atomic absorption system. By passing the organic eluent through the injection valve of a simple single-line system, sensitivity increases of between 15 and 20 times were achieved.

A directly coupled system has been reported [17] not so much for preconcentration purposes but for the removal of interferences. The determination of zinc in iron, which suffers from a spectral overlap of the zinc line at 213.856 nm by a weakly absorbing iron line at 213.859 nm, was achieved by selective extraction of the zinc. The slight mismatch in flow between the manifold and the spectrometer was balanced by a compensating flow of organic solvent. The use of water for this purpose was found to reduce the sensitivity whereas air, which has been reported to be beneficial [18], decreased the precision.

Accumulation on an immobilised or solid reagent is proving an increasingly popular procedure, especially for sample preparation for i.c.p. work. Plasma spectrometry does not suffer from chemical interferences (such as stable compound formation or ionisation) to nearly the same extent as flame-based techniques but is more prone to spectral interferences and suffers from inadequate sensitivity for a number of anion-forming elements such as P, S and B and some commonly determined heavy elements such as lead. The design features of one of the earliest reported manifolds [19], used for the determination of heavy metals in sea-water, by flame a.a.s. would seem to be the most sensible. In this, a large volume of sample was passed through a small column of reagent and the unretained sample components were pumped to waste. The column was then back-flushed with a suitable eluent and the eluted metals were trans-
ported to the spectrometer. However, many of the more recently reported manifolds are constructed so that the unretained sample components pass through the nebuliser of the spectrometer. This may not cause difficulties for samples which contain a low level of dissolved solids, such as lake or boiler-feed waters, but there is a danger of nebuliser/burner (flame a.a.s.) or nebuliser/injector tip (i.c.p.) blockage if samples contain high levels of dissolved solids. To some extent, the latter problems can be offset for i.c.p. spectrometry by the use of nebulisers designed to operate with high solid contents and wide-bore injector tips.

The columns used have contained a variety of immobilised chelating functions, including Chelex-100 [20], Muromac A-1 [21], quinolin-8-ol on controlled-pore glass [22], poly(dithiocarbamate) [11,23] and poly(phenyl urea)/poly(ethylenediaminediacetic acid) [24] as well as Amberlite IRA-400 [25] and alumina [26].

The most recent technique for preconcentration and matrix removal to be adapted to the on-line format is that of precipitation [27]. The method, as described, did not contain an injection valve as such, though a transient signal was produced for the determination of lead by precipitation with ammonia, retention on a stainless-steel chromatographic filter and redissolution in nitric acid. Concentration factors of up to 700 were obtained for sample volumes of up to 250 ml. It is thought that this procedure could be readily adapted for the flow-injection manifold suggested by Bysouth et al. [28] for immobilised reagent collection, thereby avoiding the problem alluded to earlier, i.e., passing sample matrix components through the nebuliser and atom cell.

There are several reports of flow-injection manifolds for hydride generation [29] and cold-vapour mercury determinations [30]. But it should be noted that some of the original “conventional” designs of generation apparatus [31] are conceptually indistinguishable from a flow-injection version.

On-line dilution and calibration

Flow-injection techniques for calibration purposes, the majority of which concern applications to atomic spectrometry have recently been reviewed [32] and it is apparent that, since the last review of f.i./a.s. [5], there have been several developments in the use of manifolds for on-line dilution and calibration. A variable dispersion coefficient (6-40) manifold based on six flow lines of different dimensions connected in parallel between two six-way switching valves [33] was used for calibration and extended-range determinations of nickel, calcium and chromium up to 180, 75 and 180 mg l\(^{-1}\), respectively. A network manifold [34] which used the minimum between two overlapping peaks produced by splitting and asynchronous merging of the carrier stream was used to produce dispersion coefficients (dilution factors), of up to 77 in the determination of magnesium up to 100 mg l\(^{-1}\), two orders of magnitude above the top of the conventional working range. Calibration by the introduc-
tion of a variable volume of standard solution into the manifold by the valve-
less “controlled-dispersion” technique has been applied in the determination
of magnesium in clinical samples [35] and a microcomputer-controlled system
for extended range calibrations based on peak-width measurements has been
evaluated [36].

There have been several developments in the use of the standard-additions
method. The reverse flow-injection method (in which the standards are in-
jected into the sample carrier stream) [37] has been adapted by Israel and
Barnes [38] for the determination of silicon in phosphoric acid by i.c.p./a.e.s.
and this version has been used by Fang et al. [39] for the determination of
barium and chromium in river sediment and coal fly ash. A merging-stream
version of the conventional standard-additions method has been described by
Araujo et al. [40], from the same group which described the flow-injection
version of the generalised standard-additions method [41]. An elegant ap-
proach, in which the sample zone is sandwiched between the blank (in front)
and a standard (at the rear), has been proposed by Fang et al. [42]. The ratio
of the instrument responses at points corresponding to a known dispersion
coefficient on the front and rear of the sample zone is taken as the quantita-
tive analytical parameter and substituted into an equation which relates it to the
concentration of standard, the sample concentration and the dispersion
coefficient.

Speciation

There have been few developments in flow-injection-based speciation stud-
ies recently [43-45], though it should be borne in mind that most of the ap-
plications of coupled liquid chromatography/atomic spectrometry alluded to
earlier are speciation studies. However, various indirect methods have been
reported, particularly by Valcarcel et al. Methods have been described for cy-
anide [46], nitrate and nitrite [47], perchlorate [48], chloride and iodide
[49,50], oxalate [51] and sulphonamides [52] as well as methods for aluminium
[53], uranium [54] and cerium and lanthanum [55]. This latter category
of indirect determination of metals is based on intermetallic effects with ele-
ments such as iron which is the species monitored.

Analysis of real samples

A major growth area in the f.i./a.s. literature is the number of reports of
analyses of real samples. Many of these reports illustrate the advantages of the
combination for handling solutions that would be difficult by conventional
procedures. These advantages include the ability to tolerate high levels of dis-
solved solids or variable viscosities, to work with non-aqueous solvents, and to
use small volumes of sample solution. Thus many of the reports concern the
analysis of clinical materials, environmental samples (soils, rocks, plant ma-
terial and waters), foods and petroleum products. A summary of the relevant
literature is given in Table 1.
**TABLE 1**

Analysis of real samples by flow injection/atomic spectrometry*

<table>
<thead>
<tr>
<th>Sample</th>
<th>Elements</th>
<th>Technique</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Serum</td>
<td>Zn</td>
<td>a.a.s.</td>
<td>56</td>
</tr>
<tr>
<td>Serum</td>
<td>Co, Mn</td>
<td>a.a.s.</td>
<td>57</td>
</tr>
<tr>
<td>Serum</td>
<td>K, Mg, Mn, Fe, Cu</td>
<td>a.a.s.</td>
<td>58</td>
</tr>
<tr>
<td>Whole blood</td>
<td>Cu, Zn</td>
<td>a.a.s.</td>
<td>59</td>
</tr>
<tr>
<td>Urine</td>
<td>Pb</td>
<td>a.a.s.</td>
<td>60</td>
</tr>
<tr>
<td>Hair</td>
<td>Pb</td>
<td>a.a.s.</td>
<td>61</td>
</tr>
<tr>
<td>Cerebrospinal fluid</td>
<td>Na, K, Ca, Mg, Fe</td>
<td>a.a.s.</td>
<td>62</td>
</tr>
<tr>
<td>Parotid saliva</td>
<td>Cu, Zn, Fe</td>
<td>a.a.s.</td>
<td>63</td>
</tr>
<tr>
<td>River sediment</td>
<td>Ba, Cr</td>
<td>a.a.s.</td>
<td>39</td>
</tr>
<tr>
<td>Soil and plants</td>
<td>Hg</td>
<td>c.v.a.a.s. b</td>
<td>30</td>
</tr>
<tr>
<td>Environmental silicates</td>
<td>Se</td>
<td>h.g./a.a.s. c</td>
<td>64, 65</td>
</tr>
<tr>
<td>Galvanising solutions</td>
<td>Zn</td>
<td>a.a.s.</td>
<td>66</td>
</tr>
<tr>
<td>Steel</td>
<td>P</td>
<td>i.c.p./a.e.s.</td>
<td>68</td>
</tr>
<tr>
<td>Steel</td>
<td>Cr</td>
<td>a.a.s.</td>
<td>69</td>
</tr>
<tr>
<td>Gasoline</td>
<td>Pb</td>
<td>a.a.s.</td>
<td>70</td>
</tr>
<tr>
<td>Used oil</td>
<td>Ag, Al, Ba, Ca, Cr, Cu, Fe, Mg, Mo, Na, P, Pb, Si, Sn, Zn</td>
<td>i.c.p./a.e.s.</td>
<td>71</td>
</tr>
<tr>
<td>Glycerine</td>
<td>As</td>
<td>h.g. c</td>
<td>i.c.p./a.e.s.</td>
</tr>
<tr>
<td>Foodstuffs</td>
<td>Pb, Cd</td>
<td>a.a.s.</td>
<td>72</td>
</tr>
<tr>
<td>Powdered milk</td>
<td>Fe, Cu</td>
<td>a.a.s.</td>
<td>73</td>
</tr>
<tr>
<td>Waters tap and run-off</td>
<td>Ba, Be, Cd, Ca, Co, Cu, Pb, Mg, Mn, Ni, Zn</td>
<td>i.c.p./a.e.s.</td>
<td>20</td>
</tr>
<tr>
<td>various</td>
<td>S</td>
<td>i.c.p./a.e.s.</td>
<td>26</td>
</tr>
<tr>
<td>tap</td>
<td>Pb</td>
<td>a.a.s.</td>
<td>27, 28, 74</td>
</tr>
</tbody>
</table>

*Unless otherwise stated, flame a.a.s. is used. bCold-vapour a.a.s. cHydride generation.

**Fundamental studies**

It should be noted that it is, in general, not possible to consider an atomic absorption or i.c.p. detector as a special type of flow-through solution spectrophotometer. In the latter case, it is usually valid to assume that the contribution to the overall dispersion from the flow patterns in the detector is small, provided that the detector volume is sufficiently small, and that if physical dispersion is monitored by the absorbance/time profile produced for a species for which Beer's law is valid, it is possible to relate the absorbance/time profile directly to a concentration/time profile produced by the injection process and hydrodynamic regimes in the manifold. Such relationships are not valid for the former types of detector because the nebuliser and spray chamber contribute
significantly to the peak shape obtained. Thus, even for situations where a linear relationship between instrumental response and analyte concentration is obtained, it is not possible to relate response profiles directly to concentration profiles in the flow manifold. Thus, as a first stage in attempting to deconvolute the influence of the nebuliser and spray chamber on the peak shape, attempts have been made to account for the shape of the absorbance/time curve produced as a result of physical processes associated with nebulisation and transport in the spray chamber [75,76]. Both of these approaches are based on modelling the instrument response to the introduction of a discrete volume close to the nebuliser, so that the manifold dispersion coefficient is unity. The first approach is based on modifications to the single, well-stirred tank model originally proposed by Tyson [37]. The parallel-tanks model is discussed for modelling the shape of the rise curve for infinite volume injection and an extended single-tank model is used to describe the variation of peak height and width with volume injected and flow rate. In this extended model, the single tank is considered to have two inlets (for sample and for diluent) and two outlets (one to waste and the other to the detector). The second approach [76] is based on the axially dispersed plug flow model coupled with a relationship between absorbance and flow rate obtained from a consideration of (a) the mass balance of the nebuliser, spray chamber and flame and (b) an experimentally derived relationship between nebulisation efficiency and flow rate. Both models fit the results presented quite well but the limitations of plug injection are apparent. The models assume that all elements of the injected fluid are subjected to the same dispersion effects, but this assumption is true only for time-injection, where controlled timing over the valve return ensures that the rear of the sample plug is not dispersed by mixing with the carrier stream while passing through the length of the injection loop.

Operating conditions

Opinions are divided on the best operating conditions for flow injection/atomic absorption spectrometry. Brown and Ruzicka [77] concluded that in the f.i.a./a.a.s. combination, the pumping rate into the nebuliser should always be greater than the aspiration rate of the nebuliser in order to achieve optimum performance, whereas Garcia et al. [78] commented that flow injection at low aspiration rates is definitely a step in the right direction. They qualified this conclusion by stating that low aspiration rates led to poorer precision but presented results to show that flow injection with a bleed is more convenient than the use of a re-circulating nebuliser when the amount of sample available is limited. Even greater benefits for the use of air compensation have been claimed. Garcia et al. [79] concluded that air compensation was advantageous because the increased nebulisation efficiency improved the sensitivity and selectivity
and the reproducibility obtained for both peak height and peak area was comparable to that given by conventional a.a.s. In contrast, Sweileh and Cantwell [17] found that the use of air as a compensating fluid yielded a variable baseline and poor reproducibility. In one of the earliest papers on f.i./a.a.s., Wolf and Stewart [80] measured the total integrated signal from a sample introduced at a relatively low flow rate rather than the instantaneous maximum signal from a sample introduced at higher flows, and reported detection limits of 4 ng for copper and 3 ng for zinc; comparable detection limits for steady-state signals were 50 ng for copper and 10 ng for zinc. Different authors from the same laboratory concluded [81], however, that the signal/noise ratios for peak height and peak area in f.i./a.a.s. approached but never exceeded the ratios for conventional nebulisation. These conflicting statements make it difficult to construct a coherent picture of the fundamental aspects of flow injection/atomic absorption spectrometry; and some misconceptions about nebuliser function appear to exist. However, some general comments can be made which may help to rationalise these apparently conflicting findings.

**Nebuliser performance.** Firstly, it should be noted that there is no such thing as the “natural aspiration rate of the nebuliser”, as a number of papers either imply or state explicitly. Under a particular set of operating conditions (position of the capillary tip, oxidant pressure), a nebuliser develops a certain suction (i.e., it behaves as though the pressure in the spray chamber were less than the pressure outside). Obviously, this is not true macroscopically as the flame gases would not emerge from the burner slot, but it is true microscopically at the nebuliser tip where the detachment of the oxidant stream from the outside of the nebuliser capillary creates a region of low pressure. This microscopic region of low pressure is not the only mechanism by which solution is drawn into the spray chamber. There appears to be a frictional drag on the thread of liquid emerging from the nebuliser tip; it has been shown unambiguously for a number of concentric nebulisers that the suction depends not only on whether there is a column of liquid present but also on the flow rate of the liquid column [82]. As the flow rate increases, the nebuliser suction decreases. Overall, the effect is that the nebuliser will draw solution into the spray chamber at a rate which depends on the restrictions on the external flow, i.e., on the length and diameter of any tubing and the hydrostatic head over which liquid has to be raised.

Secondly, it should be noted that operating conditions which produce high sensitivity will not necessarily produce good detection limits and will almost certainly produce chemical or physical depression from other matrix components. The reason for this is that high sensitivity can be produced by changing the drop-size distribution to give a greater range of drop sizes and transporting this greater range of drop sizes into the flame. If the solution contains only a few mg l\(^{-1}\) of dissolved solids, then the only effect of the larger drops will be to produce a slight cooling of the flame, which may not be significant for an
easily atomised element, and to increase the atomisation noise as a larger spread of droplets produces a greater fluctuation in the rate of appearance of atoms in the flame. This drop-size distribution is controlled by a number of design features and operating parameters of the nebuliser and spray chamber [83], among the most critical of which is the position of the nebuliser capillary in the venturi throat. One manufacturer indicates that a relative movement here of as little as 0.1 mm changes the suction from zero to maximum [83]. For this reason, many instrument manufacturers design the nebuliser so that this parameter cannot readily be changed after being set, in production, to a position which corresponds to an optimum between high sensitivity, low detection limits and freedom from stable-compound interferences or occlusion effects. The emphasis given to each of these three performance requirements depends on the particular manufacturer's viewpoint and thus different instruments will have different performance characteristics. Thus, it may well be possible to obtain greater sensitivity from an instrument than that obtainable with the manufacturer's recommended operating conditions for the nebuliser by, for example, applying increased external pressure to the sample delivery system to increase the flow rate to the nebuliser [77]. Similarly, it may be that if reduced external pressure is applied and the flow rate is reduced so that the nebuliser is run under starvation conditions, a decrease in precision is obtained, which may [78] or may not [17] be offset by the use of air compensation. This will be critically dependent on the particular nebuliser design and on whether it is possible to re-optimise the operating conditions for operation under starvation conditions. If the position of the capillary in the venturi throat is fixed or cannot be moved precisely over small distances, it may not be possible to achieve optimum conditions at low flow rates.

Thirdly, although it is not possible to generalise about nebuliser performance from all aspects of the performance of one particular nebuliser, there are several generally applicable performance characteristics. As the flow rate is increased from zero, the sensitivity (as monitored by the absorbance for a fixed concentration) follows the general curve shape shown in Fig. 1. After passing through a maximum, or possibly a plateau region, the sensitivity falls because the nebuliser ceases to function at high flow rates when the only mechanism for droplet production is impaction on the various surfaces encountered by the liquid jet. The particular flow rates at which this maximum region occur depend on the particular nebuliser design and on the operating conditions. In general, the flow-injection curve will differ from the steady-state (or infinite-volume) curve because at high flow rates the transient peak may not be captured by the recording electronics of the instrument (see Fig. 1), and again the flow rate corresponding to the maximum depends on the particular nebuliser. It is also possible to generalise to the extent that it is widely agreed that, as flow rate is increased from zero, the nebulisation efficiency (i.e., the fraction of solution transported to the flame) falls steadily from 100% to around 10%
in the steady-state maximum region. This fall in nebulisation efficiency is accompanied by a shift in drop-size distribution to larger droplets and thus the extent of stable-compound interferences (as typified by the effect of phosphate on calcium in the air/acetylene flame) increases. It would also seem possible to find agreement between the results reported by some workers on the use of flow-injection peak-area measurements to the extent that, as conditions are changed to reduced external pressure and as flow rate is reduced, the peak area initially increases and a range of flow rates can be found for which the precision of peak-area measurements is better than the precision of peak-height measurements.

*Peak area and detection limits.* Whether this means that better detection limits will be obtained for peak-area measurements and what happens to peak area as the flow rate approaches zero is uncertain. However, some simple predictions can be made. Regardless of its precise mathematical definition, the detection limit is reached in reality when the signal cannot be distinguished from the random fluctuations of the baseline response to the blank. Obviously, if the instrument cannot distinguish a peak height above the baseline, it cannot distinguish a peak area, so that a detection limit based on peak area cannot be better than one based on peak height. Thus if the relative standard deviations for peak area and peak height are plotted as a function of flow rate, an increase in both these functions should be observed at sufficiently low flow rates. The shapes of these curves (see Fig. 2) should be such that either they come together at the detection limit or the detection limit for peak area is reached first. So far, few experimental data are available at sufficiently low flow rates to establish the real nature of these plots. That the curves are different in regions of flow rate that are accessible with flow-injection apparatus suggests that for routine operation it would be beneficial to identify the flow rate and measurement mode for which the relative standard deviation is below a desired value.

---

**Fig. 1.** Atomic absorption signal as a function of flow rate: (a) response for discrete volume introduction; (b) steady-state response.

**Fig. 2.** Hypothetical plots of relative standard deviation of the signal against flow rate: (a) peak height; (b) peak area.
for the longest concentration range [84]. Whether this would be a peak-area or peak-height mode and whether the flow rate used would come within the reduced external pressure region of operation, depends on the particular nebuliser and operating conditions. Results presented in the literature so far indicate that no generalisations on this point are possible.

One reason for the differences in precisions reported for peak area and peak height, may be the additional noise introduced by the mode of delivery. At low flow rates, peristaltic pump-roller fluctuations are readily observed as a regular oscillation of the steady-state signal. Such pulsations form a major source of noise in the system [85]. This may be one reason why compensation methods (solvent or air) are reported to improve precision. In one recent study [79] in which the carrier delivery was changed from a peristaltic pump to a pressurised air system, the peak-height precision was improved from being consistently worse than that of peak area to being consistently better. Thus, claims concerning the relative merits of peak areas and peak heights and reduced flow rates for improving detection limits may be based as much on the characteristics of the carrier stream delivery as on the characteristics of the nebuliser. There is obviously room for further work in this area and on the design of interfaces specifically for flow-injection introduction of samples to atomic spectrometers.

The remainder of this paper is concerned with an examination of the use of peak-area measurements in f.i.a. and of the performance of an atomic absorption spectrometer under conditions of reduced external pressure with peak-height and peak-area measurements both with and without air compensation.

**Peak area**

The basis of the single, well-stirred tank model, in which all dispersion effects are considered to be due to plug flow into a tank with only one inlet and outlet, and the concentration is detected at the outflow with no further dispersion, has been described in detail [86]; the equations for the rise curve, peak maximum, fall curve and peak width have been derived [87].

The result of physical dispersion is an exponentially shaped peak, as shown in Fig. 3. The area, \( B \), under the peak is the sum of the area under the curve from time \( t = 0 \) to \( t = t_p \), and the area under the curve from \( t = t_p \) to \( t = \infty \). This is most easily calculated if the time origin is shifted to the peak maximum for the fall curve, because the equation is then considerably simplified:

\[
B = \int_0^{t_p} C_m [1 - \exp (-Qt/V)] dt + \int_0^\infty C_p \exp (-Qt/V) dt
\]

where all symbols are defined in Table 2 and

\[
C_p = C_m [1 - \exp (-V_i/V)]
\]
\[ B = C_m \int_0^{t_p} dt - C_m \int_0^{t_p} \exp(-Qt/V)dt + C_p \int_0^\infty \exp(-Qt/V)dt \]

\[ = C_m [t]_0^{t_p} - C_m [\exp(-Qt/V)]_0^{t_p} + C_p [\exp(-Qt/V)]_0^{\infty} \]

\[ = C_m V_i/Q + (C_m V/Q) \exp(-V_i/V) - C_m V/Q + C_p V/Q \]

\[ = C_m V_i/Q + (C_m V/Q) \exp(-V_i/V) - C_m V/Q \]

\[ + C_m V/Q - (C_m V/Q) \exp(-V_i/V) \]

\[ = C_m V_i/Q \]

Thus the area under the peak is directly proportional to the injected concentration and to the volume injected and inversely proportional to the flow rate. The combination of concentration and volume injected makes peak area directly proportional to the amount of analyte injected. This can be contrasted with the situation for peak height (see Eqn. 1), which is exponentially related to the volume injected and the tank volume but is independent of the flow rate. The equation for peak width is

\[ \Delta t = (V/Q) \ln \left[ (C_m/C') - 1 \right] \exp(V_i/V) - 1 \]

i.e., the measured parameter, \( \Delta t \), is exponentially related to the volume injected and inversely proportional to flow rate, but the relationship with tank volume is not easily visualised. The dispersion coefficient, \( D \), is given by \( C_m/C_p \) and thus the ratio of peak area to peak height is given by \( DV_i/Q \).

**TABLE 2**

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>( A )</td>
<td>Absorbance</td>
</tr>
<tr>
<td>( B )</td>
<td>Area under peak</td>
</tr>
<tr>
<td>( C_p )</td>
<td>Concentration at which peak height is measured</td>
</tr>
<tr>
<td>( C' )</td>
<td>Concentration at which peak width is measured</td>
</tr>
<tr>
<td>( C_m )</td>
<td>Steady-state concentration</td>
</tr>
<tr>
<td>( D )</td>
<td>Dispersion coefficient for injected material</td>
</tr>
<tr>
<td>( Q )</td>
<td>Volumetric flow rate</td>
</tr>
<tr>
<td>( t )</td>
<td>Time</td>
</tr>
<tr>
<td>( t_p )</td>
<td>Time to reach peak maximum (( t_p = V_i/Q ))</td>
</tr>
<tr>
<td>( \Delta t )</td>
<td>Peak width at baseline</td>
</tr>
<tr>
<td>( V )</td>
<td>Volume of mixing chamber</td>
</tr>
<tr>
<td>( V_i )</td>
<td>Volume injected</td>
</tr>
</tbody>
</table>
EXPERIMENTAL

Apparatus and reagents

A single-line manifold was used with the minimum length (20 cm) of tubing (0.5 mm i.d.) between the injection valve (8-port slider type) and the spectrometer (Philips SP9). A 53-µl injection volume was used. The carrier stream of distilled water was propelled by a variable-speed peristaltic pump (Ismatec MS-4 Reglo) fitted with pump tubing of internal diameter 0.89 mm. No pulse damping was used. The output from the spectrometer was monitored by a Philips SP9 computer and a Philips model 8251 chart recorder. The spectrometer was optimised for the determination of lead at 283 nm by adjusting the various operating parameters to obtain maximum sensitivity with conventional aspiration. The nebuliser capillary position was not adjusted because the capillary is locked into position before dispatch from the factory. In the conventional mode of operation, solution was aspirated at about 4 ml min$^{-1}$ through a 30-cm length of tubing (0.5 mm i.d.) over a hydrostatic head of between 5 and 15 cm.

For some experiments, the spray chamber impeller was removed and a glass inset (Fig. 4) was placed inside the spray chamber. All other operating parameters remained unaltered. For some experiments, air compensation was used by the introduction of freely aspirated air through a T-connector mounted just in front of the nebuliser. The carrier stream was introduced vertically upwards and turned through 90° as recommended by Garcia et al. [78].

Reagent-grade water from a LiquiPure RG system was used as the carrier stream. The test solution contained 10 mg l$^{-1}$ lead produced by serial dilution of a stock 1000 mg l$^{-1}$ solution (BDH SpectrosoL).

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Fig. 3. Exponential peak shape (plot of concentration against time) for the single, well-stirred tank model of peak shape in a flow-injection system.

Fig. 4. Schematic diagram of glass insert for spray chamber. A slot is cut at $a$ to allow positioning of the impact bead and a hole at $b$ allows the tangential inlet of acetylene. The aerosol emerges at $c$ immediately below the burner tube and droplets collected in the narrow part of the insert drain through a hole at $d$. 
Procedures
The flow rate was varied in seven stages down to the minimum deliverable without changing pump tubing. The flow rate was measured by connecting the pump tubing inlet to a 50-ml burette carrier stream reservoir and timing the delivery between appropriate graduations with a stopwatch. At each flow rate, the steady-state signal and the transient signal were obtained both with and without air compensation. Data for peak height and area and the respective relative standard deviations were read directly from the computer printout.

The rise time of the steady-state and the transient response was measured for normal aspiration (i.e., without the peristaltic pump) both with and without the insert in the spray chamber.

RESULTS AND DISCUSSION

Variation of signals with flow rate
The flow rates corresponding to the various pump settings together with the steady-state absorbances are given in Table 3 and plotted in Fig. 5A. The flow-injection results are shown in Table 4 and the results are plotted in Fig. 5B and C. The relative standard deviations are plotted in Fig. 6. The response in the conventional mode of operation was 0.54 A s for peak area (4-s integration) and 0.14 A for peak height; the relative standard deviations were 0.4 and 0.7%, respectively. For the flow-injection mode, air compensation reduces the peak-area sensitivity by between 4 and 20% (Fig. 5B) and degrades the precision at flow rates greater than 1.5 ml min$^{-1}$ but improves the precision at flow rates less than 1.1 ml min$^{-1}$ (Fig. 6A). When peak heights are measured, air compensation decreases the sensitivity by about 30% (Fig. 5C) but the precision is greatly improved (Fig. 6B).

For the range of flow rates investigated, peak height decreased and peak area

![Fig. 5. Plots of instrumental response against flow rate: (A) steady-state absorbance; (B) transient peak area; (C) transient peak height. (●) No air compensation, (○) air compensation.](image-url)
TABLE 3

Steady-state response as a function of flow rate

<table>
<thead>
<tr>
<th>Pump setting</th>
<th>Flow rate</th>
<th>Steady-state absorbance</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(ml min⁻¹)</td>
<td>(µl s⁻¹)</td>
</tr>
<tr>
<td>7</td>
<td>3.4</td>
<td>57</td>
</tr>
<tr>
<td>5</td>
<td>2.6</td>
<td>43</td>
</tr>
<tr>
<td>4</td>
<td>2.3</td>
<td>38</td>
</tr>
<tr>
<td>3</td>
<td>2.0</td>
<td>33</td>
</tr>
<tr>
<td>2</td>
<td>1.5</td>
<td>26</td>
</tr>
<tr>
<td>1</td>
<td>1.1</td>
<td>19</td>
</tr>
<tr>
<td>0</td>
<td>0.72</td>
<td>12</td>
</tr>
</tbody>
</table>

TABLE 4

Flow-injection responses as a function of flow rate

<table>
<thead>
<tr>
<th>Pump setting</th>
<th>Peak area (A s)</th>
<th>Peak height (A)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>No compensation</td>
<td>Air compensation</td>
</tr>
<tr>
<td>7</td>
<td>0.11 (6.2)</td>
<td>0.093 (18)</td>
</tr>
<tr>
<td>5</td>
<td>0.14 (4.6)</td>
<td>0.13 (17)</td>
</tr>
<tr>
<td>4</td>
<td>0.15 (2.3)</td>
<td>0.13 (11)</td>
</tr>
<tr>
<td>3</td>
<td>0.17 (4.6)</td>
<td>0.17 (7.6)</td>
</tr>
<tr>
<td>2</td>
<td>0.18 (4.1)</td>
<td>0.17 (6.0)</td>
</tr>
<tr>
<td>1</td>
<td>0.22 (7.0)</td>
<td>0.20 (3.2)</td>
</tr>
<tr>
<td>0</td>
<td>0.24 (7.0)</td>
<td>0.23 (8.9)</td>
</tr>
</tbody>
</table>

*Values given are the mean of 5 replicate injections; the percentage relative standard deviations are given in parentheses.

increased. This is what would be expected for peak area based on the model used, but the model predicts a 4.7-fold increase in peak area whereas only a 2.2-fold increase was observed because the response of the atomic absorption detector decreases with flow rate. If the decrease were linear, there would be no change in the peak area (assuming absorbance to be directly proportional to concentration) but, as Fig. 5A shows, the curves are slightly convex and thus any point on the curve is always above the line connecting a point of higher flow rate to the origin and so a decrease in flow rate favours an increase in area. This shape of curve appears to be common for nebuliser behaviour so that this observation is likely to be general. The suggestion that the detection limit for peak height cannot be better than that for peak area is supported by
the trends shown in these results; as the peak height decreases, the precision for the corresponding peak area degrades more rapidly, particularly when air compensation is used.

Implications for detection limit

The results indicate that for the best detection limits to be obtained from this particular instrument, used in the flow-injection mode, peak-height measurements should be used; the flow rate should be that at which the flow-injection response is maximal and without air compensation. The model indicates that one means of increasing the peak height is to increase the volume injected. Of course, when the injected volume is sufficiently large, a steady-state response is obtained; if there are no considerations of sample availability, pre-concentration or matrix removal, level of dissolved solids, etc., then flow injection has nothing to offer and the conventional mode should be used. However, if the sample properties are such that flow injection is desirable, then an alternative means of increasing the peak height is to reduce the volume of the mixing tank. Although several factors actually contribute to this "volume", the interior volume of the spray chamber must be the major contributor, thus the aim is to reduce this volume. Preliminary results with the glass insert showed a reduction in rise time to the steady-state signal from about 3.5 s to about 2.5 s and an increase in peak height of about 50% in the flow-injection mode. Further experiments are in progress to evaluate fully the possible benefits of this interface design.

Validity of the model

Dispersion coefficients were calculated by assuming a linear relationship between absorbance and concentration and the function $DV_i/Q$ and the ratio of peak area to height were calculated for each flow rate. The values are given in Table 5. It can be seen that there is reasonable agreement between the values (better for the situation without air compensation) and thus the single, well-
TABLE 5

Validity of the single well-stirred tank model

<table>
<thead>
<tr>
<th>Pump setting</th>
<th>$D$ (s)</th>
<th>Area/height (s)</th>
<th>$DV_i/Q$ (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>7</td>
<td>1.67</td>
<td>1.78</td>
<td>1.57</td>
</tr>
<tr>
<td>5</td>
<td>1.61</td>
<td>1.60</td>
<td>2.03</td>
</tr>
<tr>
<td>4</td>
<td>1.53</td>
<td>1.56</td>
<td>2.14</td>
</tr>
<tr>
<td>3</td>
<td>1.39</td>
<td>1.51</td>
<td>2.39</td>
</tr>
<tr>
<td>2</td>
<td>1.28</td>
<td>1.60</td>
<td>2.61</td>
</tr>
<tr>
<td>1</td>
<td>1.27</td>
<td>1.56</td>
<td>3.73</td>
</tr>
<tr>
<td>0</td>
<td>1.08</td>
<td>1.47</td>
<td>5.00</td>
</tr>
</tbody>
</table>

The single well-stirred tank model is confirmed as a useful basis for the description of the response characteristics of a nebuliser/spray chamber to a discrete input at constant flow rate.

Conclusions

There has been a considerable expansion in the use of flow-injection techniques in combination with atomic spectrometry in the period since 1985. The biggest growth areas have been in the use of on-line preconcentration and matrix removal, the development of indirect methods and the application to real samples. There is still confusion in the literature over the possible benefits of low flow rate, peak-area measurement and air or liquid compensation procedures. Much of this confusion is due to the individual nature of the performance characteristics of atomic absorption nebulisers and spray chambers and of the use of mathematically calculated detection limits rather than measurements of concentrations which approach the signal that cannot be distinguished from the random fluctuations of the blank response. Low flow rates are beneficial if it is desired to minimise stable-compound interferences, otherwise the aim should be to work at conditions optimized for signal-to-noise ratio and sample-volume requirements. The basic design criteria for a flow-injection/atomic spectrometry interface are to reduce the internal volume of the spray chamber, to increase the nebulisation efficiency and to reduce the noise.
REFERENCES
