Chapter 6

Summary

6.1 AUTOMATED DATA ACQUISITION AND DEVICE CONTROL

FIA has made significant advances since its definition in 1975. Many of these advances can be attributed to the sheer ingenuity of investigators. In recent years though, that ingenuity has been able to draw on the power of micro processor-base device control and data acquisition packages. In commercial software systems, the emphasis has been on striving for greater degrees of automation. To this end, present commercial systems are configured automatically when a particular manifold cartridge is inserted into the instrument. Of course such convenience carries a hefty price tag and are severely limiting to the researcher. The researcher requires the same powerful device control and data acquisition facilities but with the flexibility to make frequent changes to device events and conveniently acquire and compare results from one experiment to the next.

With the invention of SIA, it soon became obvious that accurate computer control of device events was mandatory. Volume is determined by time or pump cycles rather than physical injection loops, as is the case for FIA. It was therefore vitally important to ensure repeatable control of devices. Also, early indications were that computer-

aided device control and data acquisition could open up new fields of endeavour for all flow-based research, (eg. stopped-flow experiments could only be investigated meaningfully when the timing of devices could be accurately controlled).

These considerations prompted the development of a software package aimed specifically at the researcher. The guiding principles applied in the development of this package were as follows:

- It should provide useful diagnostic information to permit speedy method development and convenient evaluation of research findings.
- It should be flexible and allow a high degree of user-configurability.
- The device control method development option should be convenient and intuitive.
- Data should be stored in a format that would allow data manipulation in third party packages.

These objective have been realized in a user-friendly package called FlowTEK™. Use of the program for existing FIA applications has resulted in superior data. The package generates and stores information-rich response profiles and peak parameters (peak height, peak area, peak time, and peak width at a particular height). In the research environment, it has led to more productive use of researcher time. The tedious and often repetitive operation of the experiment is handled by the computer, thus freeing the researcher for more stimulating and productive activity.

In the present investigation, the package was used extensively, specifically to:

- acquire important data for studying the effect of various parameters on analyzer performance,
- investigate the suitability of SIA for trace enrichment and separation,
- explore the potential of sensor injection methodologies, and
- control all device events necessary to carry out these experiments.

In the research environment, the package was found to go beyond merely acting as a convenient tool, to even highlighting new areas of endeavour: peak shape is an under utilized source of information in flow-based analysis.

6.2 SYSTEM CONFIGURATION

The initial work carried out on SIA demonstrated its potential. Those early manifolds were far from optimized and yet they still pointed to the viability of the technique. To gain wide acceptance though, a clearer understanding of the controlling influences that impact on important parameters such as sensitivity and repeatability was required. The present study built on the excellent work being carried out at the University of Washington (UW) in the laboratories of Ruzicka and Christian. Important guide lines were established to assist in the design of SIA manifolds. Of course, these guidelines must be interpreted in the light of the application at hand; it may not always be desirable to maximize sensitivity.

Factors that were considered at the UW were:

- the interdependence of various tube volumes, particularly when a syringe pump is used,
- sample and reagent volumes, and
- the effect of flow-reversal as a means of ensuring zone penetration and good mixing between sample and reagents.

In the present investigation, attention turned to manifold design principles, *viz.*:

- the effect of tube diameter,
- the effect of reactor geometry,
- the implications of varying pump speed, and
- the order of sample and reagent selection.

An interesting consideration that comes from this study is that double-injection FIA has a lot in common with SIA. Both begin with a stack of well defined sample and reagent zones which must penetrate one another in order to ensure that the desired chemical reactions take place. This suggests that principles established for SIA are directly applicable to double-injection FIA.

At the conclusion of this study it was possible to specify the optimum manifold configuration to achieve good precision and maximum mutual penetration of the various zones.

6.3 SORBENT EXTRACTION USING SIA

Separation science had its origin at the very instant of creation. Even primitive man practised the art in the isolation of dies. Analytical techniques which now fall under the umbrella of separation science number more than 30. It therefore seems appropriate to ensure that SIA is capable of carrying out separations. Sorbent extraction was selected because of the versatility it offers and the large repository of known chemistries that it can draw on.

Various manifold configurations and flow programmes were evaluated. A manifold which provides excellent results was assembled. Good calibration curves were attained at various levels of enrichment. The repeatability of the system was demonstrated. Other performance criteria all point to a viable approach to trace enrichment.

A key attribute of the final manifold is its simplicity. This is an important consideration for applications in the process environment. Furthermore, the proposed method satisfies all of the requirements set for sorbent extraction in FIA, *viz.*:

- rapid and quantitative partition,
- rapid and complete elution, and
- an extensive selection of off-the-shelf complexing reagents.

Swopping from the aqueous sample solution to the organic stripping solution is easily achieved by simply selecting a different port in the selection valve. Whereas for

manual solvent extraction, manipulation of the organic phase is troublesome frequently requiring the handling of emulsions, in sorbent extraction using SIA, these manipulations are carried out by the apparatus under computer control. In principle the attainable level of enrichment should exceed that of manual methods because of the small volume of organic phase that is required. Proper choice of the stripping solvent ensures that the enriched analyte is stripped into a small volume of organic solvent. In classical solvent extraction, the ratio of organic to aqueous phase is physically limited to that which can be reliably handled in the separation funnel.

Having demonstrated the feasibility and usefulness of SIA for trace enrichment and separation using sorbent extraction, the way is open to apply it to particular applications. Reference to existing chemistries of separation will also reduce the development cycle. In the process environment, the potential of being able to carry out complex sample manipulations, such as trace enrichment, in an automated fashion using SIA, is most exciting.

6.4 SENSOR INJECTION

There is a strong long-term drive to provide plant personnel with reliable devices that can provide critical information on the chemical composition of feed materials, process streams, and effluent streams. The need for robustness, and low maintenance requirements without detracting from the demand for accuracy and precision continues to point to an array of sparingly selective sensors scattered in a distributed fashion

through out a process. This is now attainable with sensors that measure physical phenomenon but not yet realistically attainable for chemical sensors. For this to be realized, particularly in the short term, some form of sample manipulation is required.

SIA has proved to be equal to the task. When the sensor is incorporated into a suitable flow cell, the following benefits accrue:

- recalibration is conveniently and easily accommodated,
- *in situ* rejuvenation of the sensor is feasible,
- the sensor is only exposed to the potentially harsh sample solution for a short time, for the rest of the time, the sensor is exposed to wash solution, and
- various pre-measurement manipulations can be carried out in the manifold.

If we accept the definition of a chemical sensor as being a transducer where the chemistry of measurement is incorporated in the detection device, we can envisage sensor arrays incorporated in sequential-injection manifolds. Such devices will provide a level of redundancy that can be used to improve robustness and reliability. Such a system brings us closer to a low maintenance and versatile means of monitoring key process components.

6.5 WILL SIA REPLACE FIA?

It is unlikely that SIA in its present form will replace or supersede FIA. Few sample manipulation techniques match FIA in flexibility. The only requirement for successful

implementation in FIA is a repeatable (though not constant) flow pattern. This has resulted in the enthusiastic acceptance of FIA in service laboratories and has revitalized interest in classical wet chemistry.

In SIA careful planning and method design is required. Attention must be given to ensuring that zones are contained within the reaction coil and that device events are carefully synchronized. This requires closer attention during the method development phase. Nevertheless, once a method has been developed, SIA tirelessly and slavishly repeats the device sequence which generates the desired analytical results.

SIA does have several key advantages over other flow-based techniques:

- Manifolds are simple and robust, typically comprising a single line manifold with three devices: a pump, selection valve, and detector.
- The selection valve doubles as an injection valve and sample stream selector thus reducing the number of devices required.
- Carrier and reagent usage is kept to an absolute minimum.
- Widely differing applications all use the same flow manifold. In this investigation, there was no material difference in the optimized manifold used to study the impact of instrumental parameters, sorbent extraction using SIA, and sensor injection. At most there was a detector change or inclusion of the sorbent extraction cartridge.

6.6 WHAT HAS SIA TAUGHT US?

In this investigation we have discovered that SIA can be applied to complex sample manipulation procedures such as trace enrichment, and that the usefulness of sensors is increased by incorporating them in a sequential-injection manifold. We have also developed a versatile device control and data acquisition package suited to research into flow-based methods of analysis such as FIA and SIA. Though most necessary and most valuable, these are not the most important finding of this investigation.

To date, flow-based analytical methodologies have been based on the physical determination of volumes. The injection valve with its sample loop is fundamental to FIA and all fields of instrumental chromatography. Even in segmented flow analyzers packets of sample and reagent are defined by the mechanical and physical introduction of bubbles.

In SIA, control is shifted from the mechanical to the temporal. Given a repeatable flow programme, volumes are determined by time. This means that we can do away with an injection valve or bubble introduction mechanism. While it is true that at present we must use a selection valve to sequence sample zones, this is only the beginning. In future this requirement will fall away as innovative stream selection options emerge. Looking to Nature we can expect membranes to play an important role in facilitating selection. Also it can be expected that electrical charge either coupled to membranes or in isolation will provide a means of selection. This suggests some exciting possibilities

for miniaturization and the combination of the sample manipulation manifold and the detector into a single unit. This is only conceivable because SIA has taught us that no nett flow is necessary for mixing to take place.

In the initial papers on SIA, the random walk model was used as a theoretical basis for SIA. It was this model that taught us that no nett flow is required for mixing (between sample and reagent) to take place, specifically at the molecular level. Flow is only useful for transporting components from one point in the manifold to the next. We were reminded that mixing at the molecular level takes place under the influence of entropy which is a random process. Mixing is fundamental to flow-based sample manipulation procedures.

The volumes employed in present flow-based systems are surely only appropriate because of the scale of manifold components., notable the tubing diameter and dimensions of detector flow cells. With these dimensions, the influence of longitudinal transport by laminar flow dominates the mixing process. As dimensions are reduced, the influence of the dispersion process will increase and the mixing of zones will largely come under the influence of entropy.

These observations suggest a research direction that will lead to the development of integrated flow-based sensors that have been miniaturized to the extent where manipulation close to the molecular level is attained but which exploit the advantages offered by flow-based sample manipulation.

Appendix A

Publications and Presentations

J.Ruzicka, G.D. Christian, and G.D. Marshall, Poster, CPAC sponsors meeting, Seattle, WA, Nov 1989

G.D. Marshall and J.F. van Staden, Anatech '92, Atlanta, Georgia, Apr 1992.

G.D. Marshall and J.F. van Staden, 3rd IUPAC symposium on Analytical Chemistry in the exploration, mining, and processing of materials, Sandton, South Africa, Aug 1992.

G.D. Marshall and J.F. van Staden, FIA Workshop, Sandton, South Africa, Feb 1994.

G.D. Marshall and J.F. van Staden, Analytica '94, Cape Town, Dec 1994.

J. Ruzicka, G.D. Marshall and G.D. Christian, *Anal. Chem.*, **62**, (1990), 1861.

J. Ruzicka and G.D. Marshall, *Anal. Chim. Acta*, **237**,(1990), 329.

G.D. Marshall and J.F. van Staden, *Anal. Instr.*, **20**(1), (1992), 79.

G.D. Marshall and J.F. van Staden, *Proc. Control and Quality*, **3**, (1992), 251.

G.D. Marshall and J.F. van Staden, *Submitted to Anal. Chim. Acta,* (1994).

G.D. Marshall, FlowTEK™ *1.1 Reference Manual,* Mintek, Randburg, (1992), 104pp.