Chapter 5

Sensor Injection

5.1 What is a Sensor?

The term "sensor" is one which invokes a myriad of images, not the least of which have their origins in science fiction. The term is not always used where it is strictly appropriate, but rather to leverage some advantage from these images. Frequently, it simply implies small and compact. Ideally, it should be characterized by unattended operation. Though the ideal of unattended operation is constantly strived for, it is seldom achieved. Rather than debate the validity of any particular definition, we will adopt a pragmatic approach and adopt a definition which will give some clarity to this investigation.

We will distinguish between physical and chemical sensors[1]. A further characterization will distinguish between the measurement of physical attributes and chemical concentration. Then a matrix can be used to characterize all sensors (see Table X) on the basis of what the sensor measures and the principle it employs to carry out the measurement. Physical sensors rely on some physical phenomenon to produce a response which can be related to a physical or chemical parameter. Chemical sensors

on the other hand, depend on a chemical reaction to generate a signal that can be related to a physical or chemical parameter.

Table X

Characterization of sensors

Physical Sensors	Chemical Sensors
Physical parameters e.g. Thermometer	Physical parameters e.g. Chemisorption humidity sensor[1] p66
Physical Sensors Chemical composition e.g. Evanescent wave chemical sensor[1] p241	Chemical Sensors Chemical composition e.g. Oxidase-based glucose sensor[1] p210

Physical sensors are well established and widely used in many areas. Many present plant control systems are strongly, and even exclusively, dependant on physical sensors, e.g. temperature, flow rate, and pressure. We will focus our attention on sensors which yield information on chemical composition and, having identified the category of physical sensors, will pay no further attention to it.

There is no consensus on a precise definition for chemical sensors (as apposed to a detectors). Therefore, in this investigation, a sensor will be defined as a detector where the chemistry of measurement is contained within the sensing unit. For example,

under this definition, a photometer is a detector, an optrode where the chromogenic reagent is immobilized on a suitable sensing device, would be termed a sensor. This definition does not warrant further discussion and simply serves to give the reader a term of reference when considering the use of flow-based analysis as a sample presentation tool for sensors. Principles established in this investigation will, in the main, be applicable to all sensors which satisfy this definition and are used for the monitoring of liquid streams.

Despite some classical examples of most reliable chemical sensors such as the glass electrode for pH measurement (developed in 1930), chemical sensors have frequently been plagued with untold failures. Flow-based analysis, notably SIA, could improve this situation in the future.

5.2 PRESENT STATE OF THE ART

Before we look to the future though, a brief tour of the history of chemical sensor development is appropriate. Seiyama[1], notes that Jonson developed one of the first sensors (based on catalytic combustion) in 1923. The next significant advancement occurred when Wagner developed the theory of electromotive force (emf) of a solid electrolyte cell in 1957. This opened the door for the proliferation of electrochemical sensors of various shapes, designs, and electrochemical principles. These include ion selective electrodes, oxide semiconductor type gas sensors, and ion-selective field-effect-transistors (ISFETS). In the ensuing years, electrochemical sensors dominated

the field almost exclusively until superior optical fibres and supporting hardware came out of the communication industry.

Early chemical sensors drew on the sensitivity, and selectivity of electrochemical reactions. Such reactions were directly compatible with the emerging fields of micro electronics and the first chemically-sensitive field-effect-transistors (CHEMFETS) were first described more than two decades ago. Since then many papers and a few reviews[2,3] have followed. Many of the early problems have been addressed by moving as many of the manufacturing steps to the wafer level as possible. Some problem still exist and not all manufacturing steps can be carried out at wafer level. The Pacific Northwest Laboratory in the USA has made some significant steps in manufacturing reliable ISFETS. In fact in a plenary paper at the Signals and Sensors Symposium held in Dublin in 1992, Domansky *et al*[4] described how they are able to make multiple sensing ISFETS which are stable for up to 2 months. These workers believe that CHEMFETS are now ready for commercialization and blame the lack of commercially available CHEMFETS on inadequate marketing rather than technical problems. The solution is available, all that is required, according to these researchers, is a suitable problem. In contrast to criticisms pertaining to the life time of sensors, these workers report certain pH sensitive devices which have a life time of years, membrane ISFETS last a couple of months, but enzyme FETS still seldom last more than a few days.

While electrochemistry characterized many early developments and continues to enjoy research funding, there is a recent interest in the utilization of optical methods for

sensors[5]. Surface acoustic waves (SAW) and sensors which make use of optical fibres are the subject of numerous studies. A recent review[6] highlights the advantages and disadvantages of optical chemical sensors. These are summarized in Table XI.

Table XI

Strengths and weaknesses of optical chemical sensors

Advantages	Disadvantages
• Electronically passive	• Interference from ambient light
• Immune to electromagnetic interference	• Photodegradation or leaching of the optically active component
• Easily miniaturized	• Frequent recalibration required
• Corrosion resistant	• Limited dynamic range
• Suited to chemical (organic and inorganic) and biological analytes	• Slow response because sample and detector are in different phases
• Suited to remote sensing	• Limited life time
• Intrinsically safe	
• Small in size	

The advantages have proved to be so attractive that the disadvantages have all been overcome to a greater or lesser extent. Furthermore, all of the disadvantages can be addressed if some form of sample manipulation is employed. At a recent meeting

addressing the use of chemical sensors in the field of biotechnology[7], there was strong agreement on the fact that (bio)sensors can really only be used in practice if they are coupled with a suitable sample presentation system. This is particularly so if some of the problems related to stability, life-time, and convenient calibration are to be addressed.

Recent advances in micromachining, and electronics have been widely employed by researchers and continue to produce more reliable sensors. Advances in the life sciences (e.g. biotechnology) as well as new materials are also making significant contributions to the field of sensors. However, even though much research funding has been allocated to the development and study of chemical sensors, it may convincingly be argued that overall, sensors are not yet economically viable or practically implementable. Nevertheless, the potential rewards are massive, and so research funding continues to be allocated to this broad field of endeavour.

Optical fibres and associated optical chemical sensors have induced somewhat of a renaissance in optical methods. Interest covers the full spectrum of optical techniques; absorption, luminescence (including phosphorescence and chemiluminescence), and reflectance. Dramatic advance in performance and quality of light sources (lasers and light emitting diodes), optical fibres, amplifiers, and photodetectors have promoted rapid progress. These robust solid state components have enabled the development of solid state measuring equipment such as photometers based on a LED[8] and a versatile, robust,

and miniature fluorometer. When the chemistry of measurement is immobilized in these detectors, novel and powerful sensors result.

Work continues in making various sensors more reliable and robust. Chemometricians research the use of neural networks for pattern recognition[9] using the output from arrays of sensors. Materials scientists investigate new materials for use both as substrates and chemically active components. Eventually all of these elements must be incorporated to yield a true sensor array with all the attributes of our own olfactory system.

Until this is achieved, the coupling of sensors to appropriate sample manipulation systems clearly represents a workable intermediate and provides a means of employing optical and electrochemical sensors in the short to medium term. In so doing, a better understanding of the principles of application will be gained and may open the door to widespread acceptance of these powerful little devices.

The editorial board of Chemical Sensor Technology, vol 1[1] is of the opinion that fundamental research being carried out at present will really only reach commercialization in the next century. This will not prevent utilization of available sensors in current applications. Flow-based sample presentation systems could provide the required intermediate successes.

5.3 The use of Sensors for Process monitoring

As the value of process inventories increases with the scale of new plants and the cost of reagents and the value of products, there is a growing requirement to maintain strict statistical control of plant conditions through out the production process. The need for this control has been further expanded by the need for continuous environmental monitoring.

Present control systems generally seek to maintain a particular set point for critical process components. Control strategies of the future can be expected to become adaptive so that upset conditions or variations in the feed materials or required products are dynamically controlled during production. Obviously under such conditions it will be unacceptable to wait for results to come back from a remote laboratory. Even present control systems are dependant on rapid and frequent results. Also, monitoring only physical parameters such as temperature, flow rate, and pressures, while most important, is inadequate.

This problem is being addressed through the development and implementation of process analyzers. Many progressive chemical and pharmaceutical companies have sophisticated and well developed distributed process analyzer systems as well as the supporting research, and maintenance facilities to ensure their continued development. A frequent criticisms levelled at present process analyzers is that they are somewhat unreliable and too maintenance intensive. Unattended operation, as is experienced when

using certain physical sensors, is constantly held up as the standard to aspire to. Future chemical sensors stand a chance of reaching these lofty ideals.

Earlier the weaknesses of optical sensors were enumerated. Some of these may be expanded to describe the limitations of sensors in general:

- short life times - this may be addressed by making use of convenient disposable devices. Also if costs can be contained, a high degree of redundancy can be built into a sensor array and thereby enhance life time.
- inaccurate - because present sensors are often not stable, regular recalibration is needed. It is difficult if not impossible to calibrate sensors *in situ* without some form of sample (and calibrant) presentation system. Sensors are often poisoned by harsh process concomittants.
- poor reproducibility - this is also related to the lack of stability in present sensors and a wide variety of operating conditions.
- poor selectivity - as data processing power is increased and the concept of an array of sparingly selective electrodes is expanded, this problem may be resolved.
- response time of sensors to changing conditions is bedeviled by the need to achieve equilibrium across phase boundaries.

Before sensors are accepted on any significant scale, these problems will have to be adequately addressed. While for the long term, fundamental research is being directed at these shortcomings, in the short term, sample presentations schemes based on flow-analysis can go a long way to minimizing these problems.

5.4 SENSORS AND FLOW-BASED ANALYSIS

Flow-based sample manipulation systems (such as FIA and SIA) are well suited to acting as a versatile sample presentation system. All that is required is for the sensor to be incorporated in a suitable flow cell. This approach offers several powerful options when applying sensors for process monitoring and control:

- Frequent calibration is conveniently achieved by simply presenting the sensor with appropriate calibration standards.
- The sensing surface can be rejuvenated by periodically (or continuously) flowing a suitable reagent solution through the flow cell containing the sensor.
- The integrity of the sensor can be tested by monitoring a baseline and periodically sequencing a check sample.
- Because the sensor is exposed to the harsh sample for a fraction of the time and then only to a small volume, sensor life time can be expected to improve.
- The sample is presented to the detector in a controlled and reproducible manner thus improving the precision of measurement.
- Reproducible sample handling procedures obviate the need for equilibrium conditions.

Experiments were carried out to demonstrate the ability of SIA to behave as an efficient sample presentation system for sensors. A potentiometric sensor developed at Mintek for the determination of cyanide[10] is used as typical sensor. Principles demonstrated for this sensor can be applied to other sensors as well. In particular because of their

present short stable life times, it is expected that many biochemical sensors will benefit most from this approach to sensor utilization.

5.5 EXPERIMENTAL

5.5.1 *Carrier stream*

The carrier stream, which has been described before[10], acts as an ionic strength buffer and manifold cleaning solution.

Calibration solutions were prepared freshly on a weekly basis and are stored in dark coloured bottles to minimize photodegradation of the cyanide. A range of calibrants were generated by serial dilution of a stock solution prepared by dissolving sodium cyanide in a 0.1 $mol.dm^{-3}$ caustic solution.

5.5.2 *Instrumentation*

The SIA manifold used in this investigation is given in Figure 24a. An Alitea C-4V peristaltic pump (Alitea USA, Medina, WA) is coupled to a Valco ECSD10-P multiposition selection valve (Valco, Houston, TX) using teflon tubing with an i.d. of 0.8 mm. Figure 24b represents the equivalent FIA manifold and illustrates the relative simplicity of SIA manifolds and strong relationship between FIA and SIA.

The cyanide sensor comprises an ion selective electrode of the first type and a single junction Thalamid-type reference electrode. This reference electrode was selected because of its independence to cyanide concentration. No significance can be attributed to the absolute voltages given in the diagrams because of the dynamic nature of the measurement process and the signal handling electronics employed in conjunction with the electrode assembly.

The electrodes are mounted in an optimized flow cell (see Figure 25) to provide excellent sensitivity and minimal dead volume. The FlowTEK package described in chapter 2 was used for device control and data acquisition. A typical method flow programme is given in Table XII. (The pump was halted while the valve position was advanced.)

Table XII

Method flow programme for cyanide determination

Time, sec	Pump	Valve Port
0	Off	1 (Home position)
2	Reverse	1, 2, 3, or 4*
5	Off	5
7	Forward	5
45	Off	

* The different ports were fed by bottles containing the calibration solutions. In the simulated plant experiment, Port 1 was fed by the simulated plant vessel.

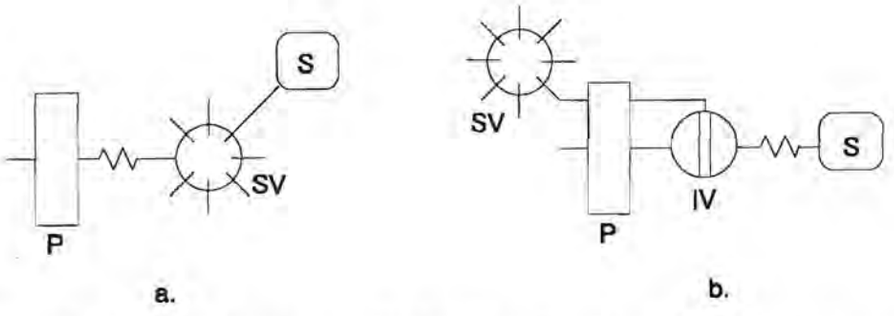

Figure 24: a. Sequential-injection manifold and b. equivalent flow-injection manifold for the determination of cyanide, P - pump, SV - selection valve, IV - injection valve, S - cyanide sensor in flow cell

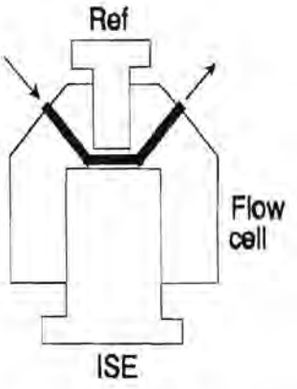

Figure 25: Cyanide ion selective electrode (ISE) mounted opposite a reference (Ref) electrode in a flow cell. Arrows indicate the flow path.

5.5.3 *Experimental Procedure*

The purpose of this suite of experiments is to demonstrate the power of SIA to enhance the utilization of sensors. This was achieved by carrying out the following experiments:

- adapt the existing flow-injection methodology used for the determination of cyanide to a sequential-injection manifold.
- investigate the impact of various manifold variables on sensitivity and precision.
- optimize the operational conditions.
- determine the analytical figures of merit which pertain.
- apply the sequential-injection analyzer to a simulated plant situation to demonstrate its usefulness for plant monitoring and control.
- consider SIA as a useful tool for sensor testing.

5.6 RESULTS AND DISCUSSION

5.6.1 *From FIA to SIA*

Considerable work has been carried out in the laboratory at Mintek to develop the method for the determination of cyanide using potentiometric detection[10]. This work has gone as far as to be tested and applied in the laboratory, on the pilot plant, and even in the process environment. In the latter, it has been used to control the addition of cyanide in a gold extraction process. The method has been found to be reliable and yields an accurate and precise result. It was for this application that the sensor used in this investigation was developed.

The process of migrating the methodology from the FIA platform to the SIA platform was a trivial one. The optimum sample size determined below corresponds to the optimum sample loop size. Flow-rates are directly comparable. Reaction coil lengths can also be transferred directly. The carrier stream was also adopted without changes.

5.6.2 *System Optimization*

The peristaltic pump was found to provide a more stable flow than the sinusoidal flow pump used for the studies described in chapter 3. This is clearly illustrated by comparing the precision attainable in a SIA manifold using the sinusoidal flow pump to that obtained when a peristaltic pump is used. A 120 $mg.dm^{-3}$ cyanide solution was

analyzed 20 times in two different manifolds that had been optimized. Firstly, the manifold was assembled with a sinusoidal flow syringe pump. Secondly, the syringe pump was replaced with a peristaltic pump. Appropriate changes were made to the flow programme. As far as possible, other operating conditions were matched. When the sinusoidal-flow pump was used, the relative standard deviation (s_r) was 0.032. The relative standard deviation (s_r), for the system which uses a peristaltic pump, was found to be 0.019. In addition, the fact that the peristaltic pump is a flow through pump and therefore does not first need to be loaded with wash solution also makes operation more convenient, and less time consuming. Consequently, the peristaltic pump was used as the stream propulsion device for the rest of the investigation.

Having selected the linear flow peristaltic pump, the impact of pump speed was investigated. Although there is an increase in sensitivity for pump settings greater than 300, under such conditions, precision suffered and carrier stream consumption was increased. The poorer precision may be attributed to the increased inertia of the pump and elasticity in the manifold which is accentuated at higher pump speeds. Any variability in starting and stopping the pump translates into discrepancies in the overall flow programme and therefore the sample volume. It is also likely (although not a pre-requisite) that at slower pump speeds, it is possible to get closer to equilibrium conditions. For all subsequent experiments, a pump speed of 300 which translates into a flow rate of 1 $cm^3.min^{-1}$ was used.

In FIA, sample volume is determined by the size of the sample loop on the injection valve (refer Figure 24b). In SIA, sample volume is determined by the duration of pumping with the sample port selected in the selection valve. Table XIII gives the times used, the calculated sample volume with a flow rate of 1.0 cm^3. min^{-1}, and the measured response from the sensor.

Table XIII

Sample Times and resultant Volumes

Sample Time, sec	Volume, mm^3	Response, V
1.0	16.7	1.01
2.0	33.3	1.62
3.0	50.0	1.69
4.0	66.7	1.74
5.0	83.3	1.86
10.0	166.7	2.03

The profiles (for sample volumes corresponding to 1, 3, and 10 sec) obtained under similar conditions are given in Figure 26. There is, as may be expected, an increase in peak height from small to large sample volumes. It is also interesting to take note of the peak shape for each sample. For sample volumes larger than 50 mm^3 (3 sec), the peak looses its familiar shape. This observation is easily explained. Given the

manifold used (notably the short reaction coil between the selection valve and the flow cell), for larger sample volumes, there is a region in the middle of the sample bolus where carrier solution has not penetrated. The concentration of the sample in these regions is therefore the same as in the original sample. Normally we would expect the signal to plateau under these conditions. The continued increase in signal despite no change in concentration can be attributed to the electrode slowly achieving an equilibrium state.

[As an aside, it is important to note that particularly when measuring plant solutions of varying ionic strength this situation is undesirable as the ionic strength buffer used as the carrier does not impact on that portion of the sample that is giving rise to the measured signal.]

As is the case for FIA, equilibrium conditions are not a requirement for SIA. The only requirement is a reproducible environment. From Table XIII it is clear that there is not much benefit gained from increasing the sample volume beyond 50 mm^3. Also, at high levels, it takes longer to re-establish the baseline (see Figure 26). A slight decrease in repeatability was also observed for larger sample volumes.

The excessive signal tailing observed in response profiles for the cyanide sensor is a function of the sensor response characteristics. Once the ions in the selective membrane have been disturbed by the passage of cyanide through the flow cell, it takes time for them to re-orientate themselves to conditions devoid of cyanide.

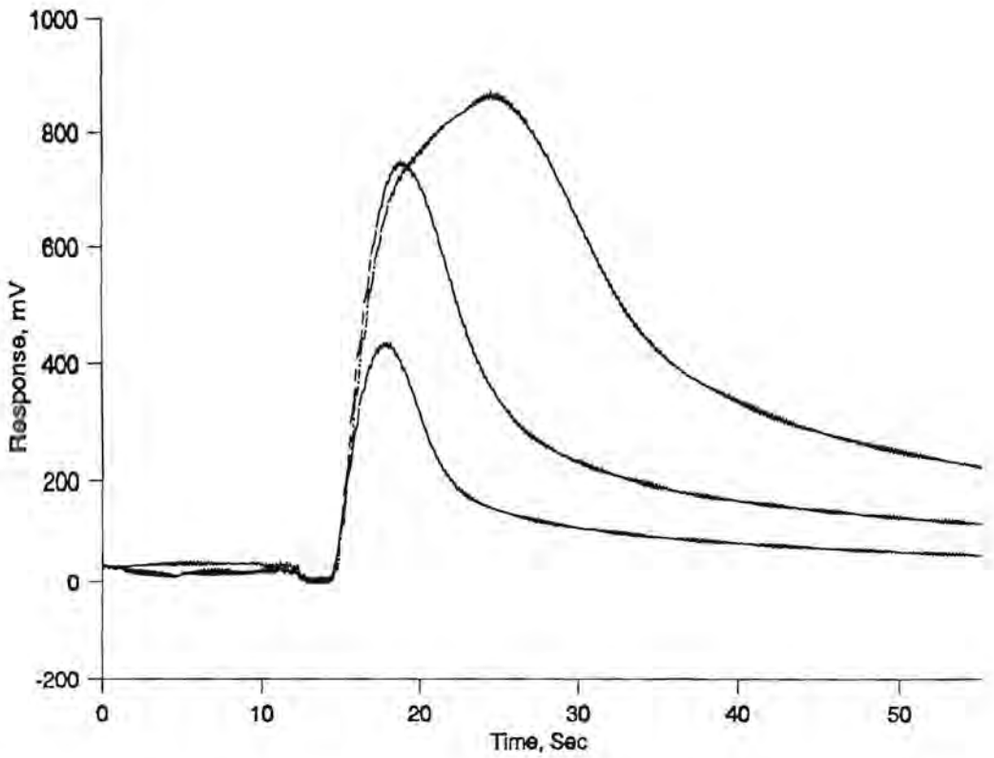

Figure 26: Response profiles for different volumes of sample. Volumes as per Table XIII corresponding to sample times of 1, 3, and 10 seconds.

It has been suggested that this tailing can be minimized by adding a small amount of cyanide to the carrier stream[11]. Experiments were carried out to ascertain the impact of doping the carrier stream with small amounts of cyanide. The comparison of the response profile for a solution containing 196 $mg.dm^{-3}$ of cyanide injected into a carrier without cyanide and one containing 10 $mg.dm^{-3}$ of cyanide is given in Figure 27. [The baseline of the two profiles were overlaid to assist comparison of the two profiles.] The cyanide in the carrier did not simply raise the baseline to achieve the desired reduction in tailing. Rather, the only effect that it had was to reduce the attainable sensitivity. A similar tail profile was achieved with a notable reduction in attainable sensitivity. This experiment brings into question the practice of doping the carrier stream with cyanide to reduce tailing. The only advantage of this practice would be to

yield a stable baseline. In SIA, even this advantage falls away because a shoulder on the leading edge of the profile develops when there is cyanide in the carrier stream. [The higher shoulder in the diagram is for the lower peak obtained with cyanide in the carrier. In some experiments, particularly when the solution in contact with the sensor had been stationary for a day or more, this shoulder was more pronounced]. This shoulder can be attributed to the fact that the solution in the flow cell is stationary while the sample is loaded and thus a temporary equilibrium is established during the sample loading period. This equilibrium is disturbed the moment flow commences through the flow cell. The disturbance of this equilibrium conditions gives rise to a shoulder at the start of the next profile. This temporary equilibrium is independent of flow when there is no cyanide present in the carrier stream.

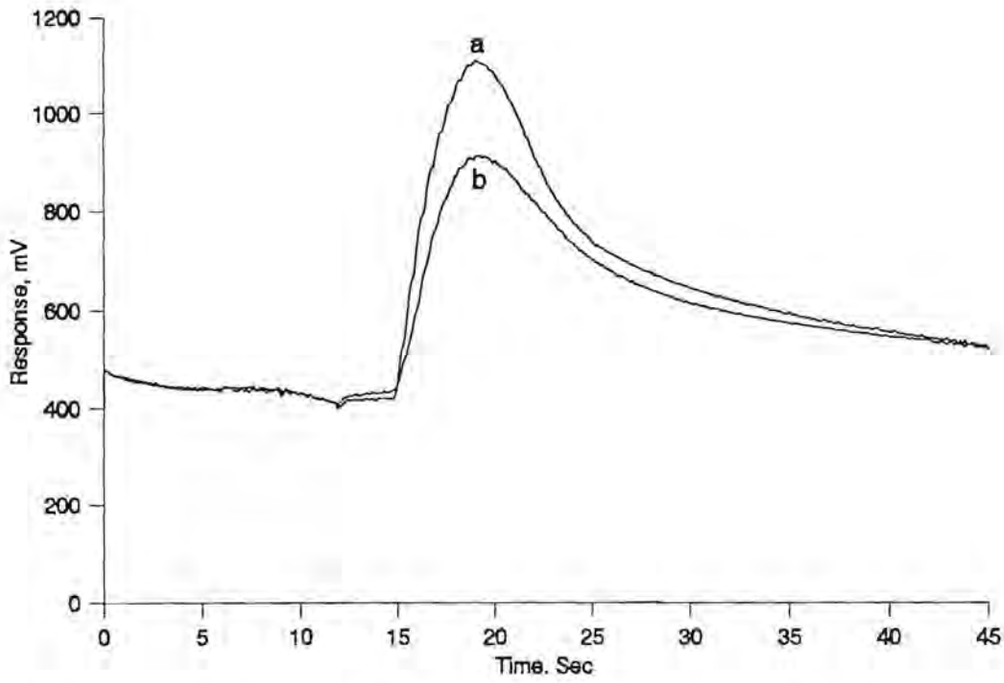

Figure 27: Influence of cyanide in the carrier stream. a) no cyanide b) 10 mg.dm^{-3} cyanide in the carrier stream.

5.6.3 *Analytical Figures of Merit*

Once an optimized system had been obtained, analytical figures of merit were determined. Figure 28 provides a trace of response profiles obtained when three standards were measured in triplicate and the second standard was measured 10 times. The precision of the peak height measurements is very good; the relative standard deviation (s_r) was determined for 10 measurements of a cyanide solution (192 mg.dm^{-3}) and found to be 0.016. Area measurements were less precise though still good enough for most purposes (s_r = 0.030). (No advantage could be gained by using peak area measurements). When peak height response was plotted against the natural logarithm of the concentration, a straight line was obtained (r^2 = 0.9997), with the following equation: $\text{Resp} = 1.620\ ln\ [CN^-] + 3.341.$

A sample throughput of 80 samples per hour is attainable.

5.6.4 *Use of SIA for sensor testing*

The concept of using flow-injection analysis as a diagnostic technique for the development and testing of sensors was proposed by Yerian *et al*[12]. These workers investigated the development and testing of an immobilized urease sensor. They pointed out that many papers on sensors seldom provide critical information on sensor performance, e.g. speed of response, reproducibility, sensitivity, selectivity, and lifetime. They then went on to demonstrate the power of flow-based analysis (specifically FIA) for monitoring sensor performance during the development phase and also once the

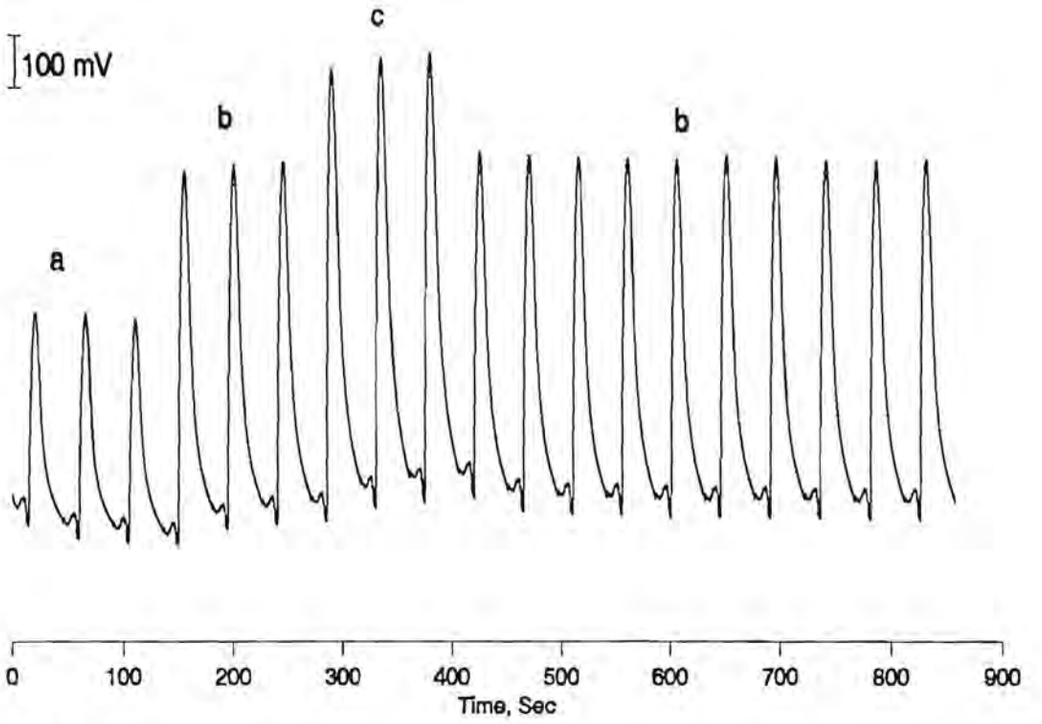

Figure 28: Response profiles obtained for the replicate injection of cyanide solutions with the following concentrations a) 96 $mg.dm^{-3}$, b) 192 $mg.dm^{-3}$, and c) 288 $mg.dm^{-3}$

sensor design had been finalized. With their proposed manifold, they were able to test one sensor at a time.

While these workers demonstrated the feasibility of flow-based analysis for the testing of sensors, they did not address the question of testing large numbers of sensors. In most cases, sensors are mass produced. Nevertheless, each sensor must be individually tested as failure rates of 30 per cent are not uncommon. SIA provides a convenient platform for a test rig. Consider the manifold depicted in Figure 29. A test solution is repeatedly drawn up via one of the ports of a multiposition selection valve. The test solution is dispensed sequentially to each of the sensor flow cells. The resultant response profiles are compared to predefined minimum standards, and faulty sensors are

quickly and conveniently identified. Using any of the convenient commercial connectors, or even a simple tubing sleave, flow cells are easily changed to allow rapid testing of large batches. Also, tests such as the comparison of different types of sensors, or sensor life time studies, as well as a host of other tests can conveniently be carried out using this test manifold.

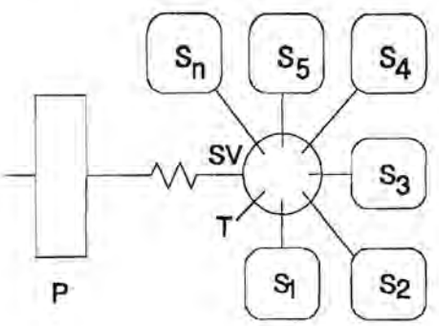

Figure 29: Sensor testing manifold. P - Pump, SV - Multi-position selection valve, T - Test solution, S_1 to S_n - Sensors to be tested.

5.6.5 *Process Monitoring*

The main area of application for sensors will be in the process environment. Process environments as different as hospital wards and chemical plants are envisaged. It is therefore important to demonstrate, at least in concept, that this mode of operation is feasible. To do this, a plant situation was simulated in the laboratory. A vessel was filled with a solution containing cyanide. The sequential-injection analyzer was programmed to sample and monitor the cyanide concentration in the simulated process vessel. Several random adjustments were made to the cyanide in the process vessel to simulate changing plant conditions. In particular after 620 measurements a spike of

concentrated (2.4 $g.dm^{-3}$) cyanide solution was added to the simulated process vessel and after 1480 measurements, the process solution was diluted with water. Every four hours the analyzer was automatically recalibrated.

The output from this experiment is given in Figure 30. The analyzer was able to track major and minor changes in cyanide concentration in the simulated process vessel. While this simple test certainly does not demonstrate the long term application of SIA in a process environment - a test period of at least a few months would be required for that - it does demonstrate the concept of process monitoring using sensors with a sequential-injection front end. The slope of calibration curves throughout the test period was constant. The intercept did however, vary. The effect of temperature on the reference potential and changing pumping characteristics is believed to be the reason for this. This is not a problem provided that the analyzer is calibrated frequently. The sequential-injection front end makes calibration a trivial exercise. The analyzer was found to run conveniently and was characterized by consistent performance, low sample consumption (± 1.2 dm^3 per day), and accurate analysis.

5.7 FUTURE WORK

The present sequential-injection hardware has been adapted from flow-injection equipment. As was the case for FIA in the early days, this has hampered the development and widespread acceptance of SIA. The extent of this incompatibility is particularly evident when comparing the dimensions of components used for sample

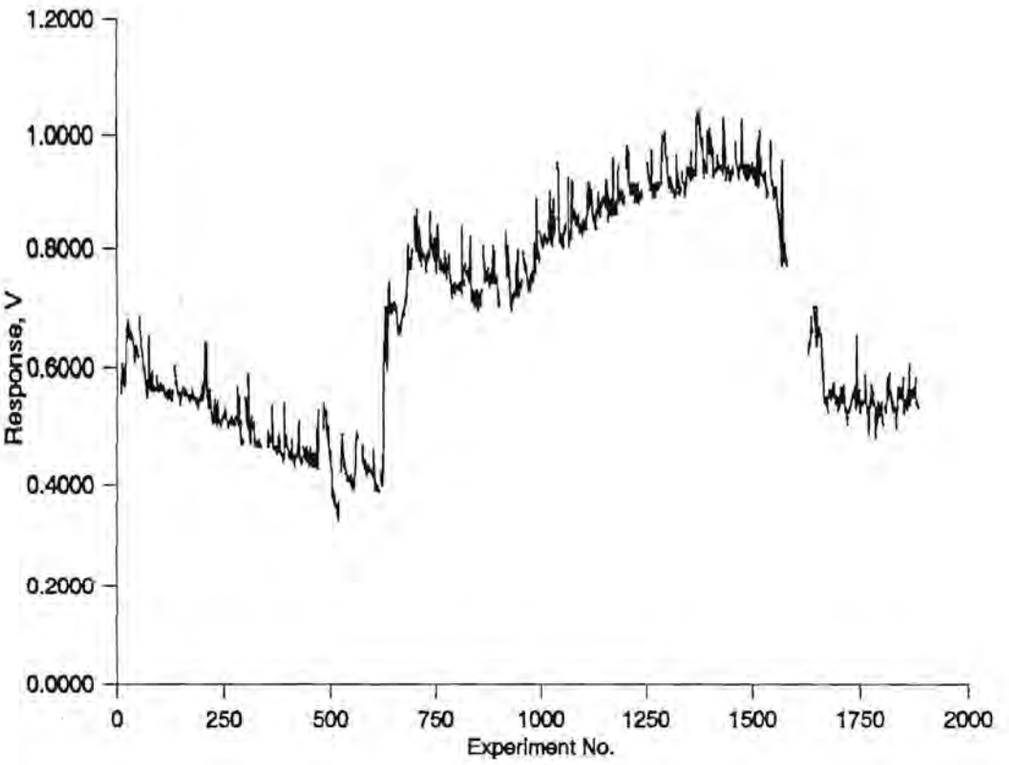

Figure 30: Cyanide monitoring using a sequential-injection analyzer in a simulated process environment.

presentation to the dimensions of typical sensors. Differences span three order of magnitude. Clearly there is much room for innovative research. Novel propulsion and stream selection methods will have to be developed. Miniaturized pumps and valves have been described though more as research curiosities than devices ready for commercialization. The same micro machining techniques used in the production of sensors could be used to prepare sample presentation front ends. Once integrated into compact packages, such devices will have tremendous potential as portable devices or *in-vitro* measurement systems.

5.8 REFERENCES

1. T. Seiyama, Chemical Sensor Technology, Vol. 1. Elsevier, Amsterdam, (1988).
2. L.A.R. Pioda, V. Stankova, and W. Simon. *Anal. Lett.*, **2**, (1969), 665.
3. W.E. Morf, The principles of ion-selective electrodes and of membrane transport, Elsevier, Amsterdam, (1981), 266.
4. K. Domansky, J. Janata, M. Jasowicz, and D. Petelenz, *Analyst*, **118**, (1993), 335.
5. J.N. Zemel, J.V. der Spiegel, T. Fare, and J.C. Young, Fundamentals and Applications of Chemical sensors, The American Chemical Society, (1986).
6. R. Narayanaswamy, *Analysts*, **118**, (1993), 317.
7. J. Ruzicka, Private communication, (1992).
8. G.D. Marshall, M.J.C. Taylor, D.E. Barnes, and S.J.S. Williams, *Process Control and Quality*, **2**, (1992), 249.
9. M.Hartnett, D. Diamond, P.G. Barker, *Analyst*, **118**, (1993), 347.
10. M.J.C. Taylor, D.E. Barnes, G.D. Marshall, D.R. Groot, S.J.S. Williams, *Process Control and Quality*, **3**, (1992), 173.
11. C. Pohlandt-Watson, *Mintek report M275*, Mintek, Randburg, South Africa, (1986).
12. T.D. Yerian, G.D. Christian, and J.Ruzicka, *Anal. Chim. Acta*, **204**, (1988), 7.