# ADDENDUM A

# ADDENDUM A

## Method construction

Sequential injection analysis is dependant on precisely timed operations which took place in a preprogrammed sequence. These programming was done using the FlowTEK [1, 2] program, developed by Marshall [3]. The method used for the determination of seven metal ions in one sample (described in Chapter 10) is used to explain the construction of methods and procedures in FlowTEK.

The analytical cycle used in the determination consisted of the following operations: the sequential introduction of an air bubble, the extractant, the sample and a second air bubble, the extraction step itself, detection of the formed products and rinsing of the manifold.

A Hewlett Packard 8543 diode array spectrophotometer was use as detector and for data acquisition and manipulation. The FlowTEK program was used to control the different devices. (A device is defined as an analytical instrument or component which must be controlled by the software package. These devices must be compatible with TTL or switch control signals [2].) FlowTEK was also used to send a signal to the diode array after the product was stopped in the flow-through cell. The signal from FlowTEK was recognised by a macro (UMACINIT.MAC) written especially for this application. Three different signals could be recognised by the diode array spectrophotometer, *viz.* BLANK, STANDARD and SAMPLE. Since there was no program or device option in FlowTEK to send these signals, it was first necessary to define this device.

It was needed to use two pairs of outputs, one which combined the BLANK and STANDARD signal as well as one which combined the SAMPLE and a STOP signal. Both pairs of outputs were placed in a single method rather than two, this was necessary because, when changing one pair the other pair must not be changed as

well. This is accomplished only when both pairs of outputs are in the same method. It was also needed to initialise the digital outputs (from the interface) to the inactive state. This was done by selecting the **Startup** option on the *method* menu. The value **240** was entered there. The value was obtain from the fact that the digital outputs of ports **5**, **6**, **7** and **8** of the interface were al set to **1** (16 + 32 + 64 + 128 = 240). This meant that the end of the pulse (when defining the device) should be set to **11** (by typing **3** at the end of the configuring device process). The method was saved (using the option **File** on the *method* menu and typing **S** for save). It was needed to exit FlowTEK and restarted it to initialise the new dev.cfg (device configuration file).

To define the device, the option **Config devices** on the *method* menu was chosen. The questions or commands which followed were answered as follow:

| | | |
|---|---|---|
| *Enter device defn number:* | **8** | |
| *Enter device name:* | **BS** | (BLANK and STANDARD) |
| *Enter number of device actions:* | **2** | |
| *Enter action narration for action 1:* | **BLANK** | |
| *Enter digital output for action BLANK:* | **1** | |
| *Enter hotkey for BLANK:* | **B** | |
| *Enter action narration for action 2:* | **STAND** | |
| *Enter digital output for action STAND:* | **2** | |
| *Enter hotkey for STAND:* | **S** | |
| *Enter pulse length (0 for continuous):* | **0.5** | |
| *Enter digital output for pulse:* | **3** | (The end of the pulse is given as 11 on the *notepad* page - see Fig. 2) |

| | | |
|---|---|---|
| *Enter device defn number:* | **9** | |
| *Enter device name:* | **SS** | (SAMPLE and STOP) |
| *Enter number of device actions:* | **2** | |
| *Enter action narration for action 1:* | **SAMPL** | |
| *Enter digital output for action SAMPLE:* | **1** | |

| | |
|---|---|
| *Enter hotkey for SAMPLE:* | **S** |
| *Enter action narration for action 2:* | **STOP** |
| *Enter digital output for action STOP:* | **2** |
| *Enter hotkey for STOP:* | **Z** |
| *Enter pulse length (0 for continuous):* | **0.5** |
| *Enter digital output for pulse:* | **3** |

The device descriptions can be viewed under the *notepad* menu (Fig. 1). The first six device definitions are supplied with the software package. There are six more devices than can be user specified. Number 8 and 9 were used for the diode array spectrophotometer. The letter **N** must be typed to view the second page of the device configurations (Fig. 2). For sequential injection analysis the device configuration data of the Gilson pump (GP) and the selection valve (SV) are used (see Fig. 1).

**Next Page Hard Copy RED Print MET Print PDR Print Quit**

```
Board : PC30-B
Experiment time :    154.0
Zoom min time :      0.0
Zoom max time :      154.0
Start acquisition : 150.0
I/O port for GP :    1
I/O port for SV :    3
I/O port for BS :    5
I/O port for SS :    7
Save profile : Yes
Abridged profile : Yes
Regression on Height
Detector displ : Paged
Inject mode : Auto
Startup :   (0)
Rescale Y-axis : Fixed
Min : 0.00    Max :10.00

F1 : Displ Analog input
F2 : Displ Digital input
F3 : 010000000000 (2)
F4 : 110000000000 (3)
F5 : 000000000000 (0)
F6 : 000100000000 (8)
F7 : 001100000000 (12)
F8 : 000000000000 (0)
F9 : 000000000000 (0)
F10 : Directory
```

| Detector | 1 | 2 | 3 | 4 |
|---|---|---|---|---|
| A/D channel | 1 | | | |
| Transformation | None | | | |
| Auto Zero | None | | | |
| AZ time | 0.0 | | | |
| AZ offset | 0.000 | | | |
| Min Integ Lim | 150.0 | | | |
| Max Integ Lim | 154.0 | | | |
| Width Height | 0.000 | | | |
| Peak Time | @ Pk max | | | |

```
Path :                          c:\flowtek\PHD\EXTRAC\
Main Procedure file :           MULTIEXT.PDR
Method file :                   MULTIEXT.MET
Reduced data file :             3AUG.RED
Experiment Profile Root :       3AUG
Calibration file :              DEFAULT.CAL
```

| Name | AP | GP | IV | SV | AS | SW |
|---|---|---|---|---|---|---|
| Action | FWD<br>REV<br>OFF | FWD<br>REV<br>OFF | INJ<br>LOAD | ADV<br>HOME | NEXT | TRUE<br>FALSE |
| Hotkey | F<br>R<br>O | F<br>R<br>O | I<br>L | A<br>H | N | T<br>F |
| Output | 01 (1)<br>10 (2)<br>00 (0) | 10 (2)<br>11 (3)<br>00 (0) | 01 (1)<br>10 (2) | 10 (2)<br>01 (1)<br>00 (0) | 1 (1)<br>0 (0) | 1 (1)<br>0 (0) |
| Pulse | 0.00 | 0.00 | 0.00 | 0.30 | 5.00 | 0.00 |

**Fig. 1** Schematic representation of the FlowTEK notepad screen (page 1 for device descriptions).

| | | | | | | |
|---|---|---|---|---|---|---|
| Name | SP | BS | SS | 0 | 0 | 0 |
| Action | 2<br>REV<br>OFF | BLANK<br>STAND | SAMPL<br>STOP | | | |
| Hotkey | F<br>R<br>O | B<br>S | S<br>Z | | | |
| Output | 0 (0)<br>1 (1)<br>0 (0) | 01 (1)<br>10 (2)<br>11 (3) | 01 (1)<br>10 (2)<br>11 (3) | | | |
| Pulse | 0.00 | 0.50 | 0.50 | 0.00 | 0.00 | 0.00 |

**Fig. 2** Schematic representation of the FlowTEK notepad screen (page 2 for device descriptions).

For the extraction method four different devices were used, *viz.* the Gilson pump (GP), the selection valve (SV) and the two newly configured devices (BS and SS). These four devices were selected using the option **Type** (of) **device** on the *method* menu. The questions or commands which followed were answered as follow:

| | | |
|---|---|---|
| *Enter number of devices:* | **4** | |
| *Enter type device 1:* | **GP** | |
| *Enter digital point for GP:* | **1** | (This represent the first position the device occupy on the interface board) |
| *Enter type device 2:* | **SV** | |
| *Enter digital point for SV:* | **3** | |
| *Enter type device 3:* | **BS** | |
| *Enter digital point for BS:* | **5** | |
| *Enter type device 4:* | **SS** | |
| *Enter digital point for SS:* | **7** | |

The screen is now divided into four panels, each containing a straight line in the middle of the panel. The position of these lines represent the 'OFF' position of each device. Programming of each device are now allowed. Device events are entered by choosing the option **Insert** in the *method* menu. It is important to switch on **NUM LOCK** when

using the **Insert** or **Delete** options. The programming for the different operations needed were done as follows:

**Insert**

| | | |
|---|---|---|
| *Device number:* | **2** | (selection valve) |
| *Enter time of event:* | **0** | |
| *Hotkey (A H):* | **H** | (Select HOME position - connected to the first air inlet) |

**Insert**

| | | |
|---|---|---|
| *Device number:* | **1** | (Gilson pump) |
| *Enter time of event:* | **4** | |
| *Hotkey (F R O):* | **R** | (Switch pump on in the reverse direction) |

**Insert**

| | | |
|---|---|---|
| *Device number:* | **1** | (Gilson pump) |
| *Enter time of event:* | **4.5** | |
| *Hotkey (F R O):* | **O** | (Switch pump off) |

**Insert**

| | | |
|---|---|---|
| *Device number:* | **2** | (selection valve) |
| *Enter time of event:* | **5.5** | |
| *Hotkey (A H):* | **A** | (Select second port - extractant solution) |

**Insert**

| | | |
|---|---|---|
| *Device number:* | **1** | (Gilson pump) |
| *Enter time of event:* | **6.5** | |
| *Hotkey (F R O):* | **R** | (Switch pump on in the reverse direction) |

**Insert**

| | | |
|---|---|---|
| *Device number:* | **1** | (Gilson pump) |
| *Enter time of event:* | **10.5** | |
| *Hotkey (F R O):* | **O** | (Switch pump off) |

**Insert**

| | | |
|---|---|---|
| *Device number:* | **2** | (Selection valve) |
| *Enter time of event:* | **11.5** | |

| | | |
|---|---|---|
| *Hotkey (A H):* | **A** | (Select third port - standard or sample solution) |
| **Insert** | | |
| *Device number:* | **1** | (Gilson pump) |
| *Enter time of event:* | **12.5** | |
| *Hotkey (F R O):* | **R** | (Switch pump on in the reverse direction) |
| **Insert** | | |
| *Device number:* | **1** | (Gilson pump) |
| *Enter time of event:* | **16.5** | |
| *Hotkey (F R O):* | **O** | (Switch pump off) |
| **Insert** | | |
| *Device number:* | **2** | (Selection valve) |
| *Enter time of event:* | **17.5** | |
| *Hotkey (A H):* | **A** | (Select fourth port - second air inlet) |
| **Insert** | | |
| *Device number:* | **1** | (Gilson pump) |
| *Enter time of event:* | **18.5** | |
| *Hotkey (F R O):* | **R** | (Switch pump on in the reverse direction) |
| **Insert** | | |
| *Device number:* | **1** | (Gilson pump) |
| *Enter time of event:* | **19** | |
| *Hotkey (F R O):* | **O** | (Switch pump off) |
| **Insert** | | |
| *Device number:* | **2** | (Selection valve) |
| *Enter time of event:* | **20** | |
| *Hotkey (A H):* | **A** | (Select fifth port - holding coil) |
| **Insert** | | |
| *Device number:* | **1** | (Gilson pump) |
| *Enter time of event:* | **21** | |
| *Hotkey (F R O):* | **R** | (Switch pump on in the reverse direction) |

**Insert**

| | | |
|---|---|---|
| *Device number:* | **1** | (Gilson pump) |
| *Enter time of event:* | **26** | |
| *Hotkey (F R O):* | **F** | (Switch pump on in the forward direction) |

**Insert**

| | | |
|---|---|---|
| *Device number:* | **1** | (Gilson pump) |
| *Enter time of event:* | **31** | |
| *Hotkey (F R O):* | **O** | (Switch pump off) |

**Insert**

| | | |
|---|---|---|
| *Device number:* | **2** | (Selection valve) |
| *Enter time of event:* | **32** | |
| *Hotkey (A H):* | **A** | (Select sixth port - detector) |

**Insert**

| | | |
|---|---|---|
| *Device number:* | **1** | (Gilson pump) |
| *Enter time of event:* | **33** | |
| *Hotkey (F R O):* | **F** | (Switch pump on in the forward direction) |

**Insert**

| | | |
|---|---|---|
| *Device number:* | **1** | (Gilson pump) |
| *Enter time of event:* | **43** | |
| *Hotkey (F R O):* | **O** | (Switch pump off - waiting period) |

**Insert**

| | | |
|---|---|---|
| *Device number:* | **3** | (BLANK or STANDARD) |
| *Enter time of event:* | **93** | |
| *Hotkey (B S):* | **B or S** | (Depending on the solution in the flow-through cell at that moment a BLANK or a STANDARD signal is send to the diode array spectrophotometer for data acquisition.) |

***OR***

**Insert**

| | | |
|---|---|---|
| *Device number:* | **4** | (SAMPLE or STOP) |
| *Enter time of event:* | **93** | |
| *Hotkey (B S):* | **B or S** | (Sample solution must be present in the flow-through cell at that moment. A SAMPLE or STOP signal is send to the diode array spectrophotometer for data acquisition.) |

**Insert**

| | | |
|---|---|---|
| *Device number:* | **1** | (Gilson pump) |
| *Enter time of event:* | **103** | |
| *Hotkey (F R O):* | **F** | (Switch pump on in the forward direction) |

**Insert**

| | | |
|---|---|---|
| *Device number:* | **1** | (Gilson pump) |
| *Enter time of event:* | **153** | |
| *Hotkey (F R O):* | **O** | (Switch pump off - end of analytical cycle) |

To delete any existing event, the option **Delete** on the *method* menu must be used. The time of the event needed to be erased must be typed in when asked for it. The procedure to delete an event is the same as the procedure needed to insert an event.

To ensure that no redundant data will be stored, data acquisition could be started only a few moments after the valve was switched to select the detector line. This will result in the collection of only the peak profile and relevant data. To accomplish this the option **Expt time** on the *method* menu must be selected and the time to start data acquisition must be typed in. Because data acquisition and manipulation was performed using the software of the diode array spectrophotometer, this option was not use in the method constructed. The final method is represented schematically in Fig. 3.

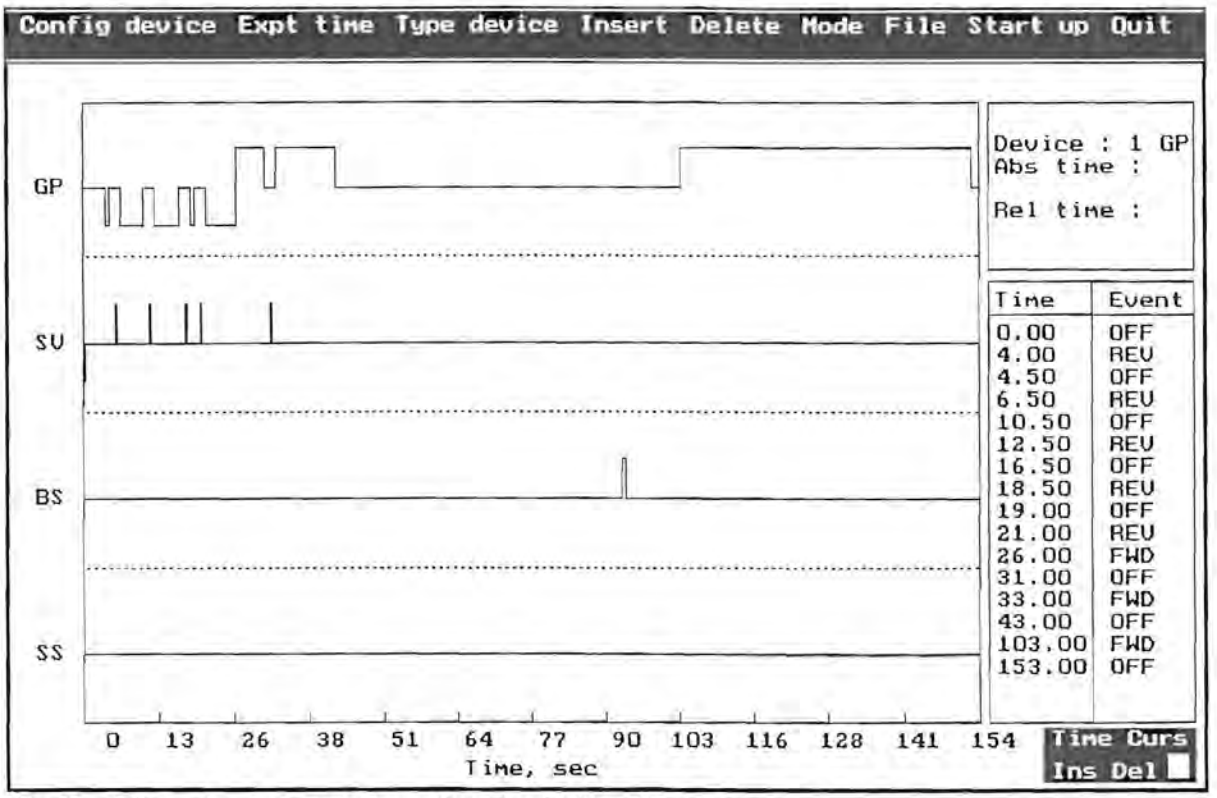


**Fig. 3** Schematic representation of the FlowTEK method screen.

After a method is constructed, the option **File** on the *method* menu is used to safe (**S**) the method under an appropriate name. The method file used for the multi-component extraction was saved as **multiext.met**. When the method must be repeated a fixed number of times it is best to write a *procedure* to carry out the repetitions. Five repetitions of the method were used during the final evaluation of the SIE system.

To create a *procedure*, the option **Repeated** on the *main* menu must be selected. The option **Build Proc** on the *repeated* menu is used to create a procedure. The procedure was named multiext.pdr. It was necessary to specify whether a method file (.met) or another procedure file (.pdr) was used in this application. The following commands or questions must be answered:

| | |
|---|---|
| *Enter main procedure:* | **C:\FLOWTEK\PHD\EXTRAC\MULTIEXT.PDR** |
| *Enter method or procedure file:* | **MULTIEXT.MET** |
| *Enter number of repetitions:* | **5** |

If more methods or procedures are to follow, the process must be repeated till all the methods together with their number of repetitions are listed. Otherwise **ESC** terminates the procedure definition. To use this main procedure file, the option **Main Proc** on the *method* menu must be chosen. The name of the main procedure file must then be typed in. The option **Red. Data file** on the *Repeated* menu selects a reduced data file for saving each experiments' peak parameter data and relative experiment identification information. The experiment number counter is reset to 1 when the reduced data file name is changed **or when the program was exited**. Every time the program is restarted a **new** reduced data file must be opened, otherwise the previous data would be lost. The option **Profile file** on the *Repeated* menu selects the file root name for storing the profile data. The file name extension gives the number of the experiment number. If no profile root is chosen, profile files are not saved.

To execute the *Main procedure* the option **Go!** on the *Repeated* menu must be chosen. The option **Once** on the *Main* menu is chosen if only one run is needed. The *Main procedure* can be aborted by pressing **ESC**.

## Simplified method

To construct a basic method for a simple application employing only sample and one (or more reagents) (Fig. 4) the following procedure is needed:

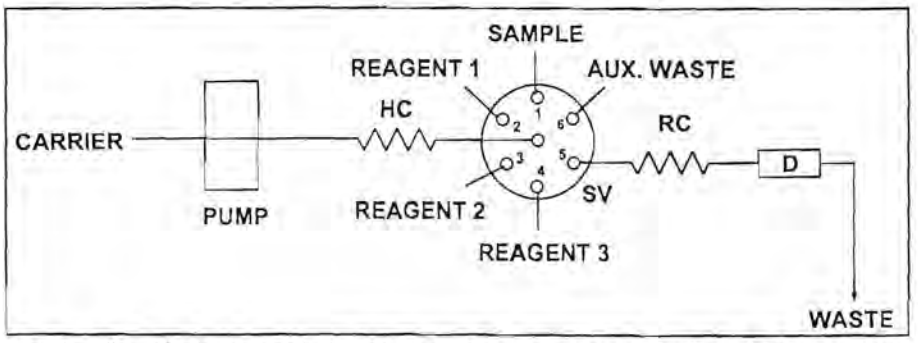


**Fig. 4** A typical sequential injection system used to determine single analytes (components). HC - holding coil, SV - selection valve, RC - reaction coil and D - detector.

Since the device definitions for both the pump and the valve are supplied with the software, it does not need any programming. The pump (GP) and valve (SV) can just be selected from the *notepad* (see Fig. 1). From the *main menu* the letter **M** must be typed to obtain the *method menu*. The two devices needed can be selected using the option **Type** (of) **device**. The questions or commands which followed can be answered as follow:

| | | |
|---|---|---|
| *Enter number of devices:* | **2** | |
| *Enter type device 1:* | **GP** | |
| *Enter digital point for GP:* | **1** | (This represent the first position the device occupy on the interface board) |
| *Enter type device 2:* | **SV** | |
| *Enter digital point for SV:* | **3** | |

The screen is now divided into two panels, each containing a straight line in the middle of the panel. The position of these lines represent the 'OFF' position of each device. Programming of each device are now allowed. Device events are entered by choosing the option **Insert** in the *method* menu. It is important to switch on **NUM LOCK** when using the **Insert** or **Delete** options. The programming for the different operations needed can be done as follows:

**Insert**

| | | |
|---|---|---|
| *Device number:* | **2** | (selection valve) |
| *Enter time of event:* | **0** | |
| *Hotkey (A H):* | **H** | (Select HOME position - connected to the sample inlet) |

**Insert**

| | | |
|---|---|---|
| *Device number:* | **1** | (Gilson pump) |
| *Enter time of event:* | **4** | |
| *Hotkey (F R O):* | **R** | (Switch pump on in the reverse direction) |

**Insert**

| | | |
|---|---|---|
| *Device number:* | **1** | (Gilson pump) |
| *Enter time of event:* | **6** | |
| *Hotkey (F R O):* | **O** | (Switch pump off) |

**Insert**

| | | |
|---|---|---|
| *Device number:* | **2** | (selection valve) |
| *Enter time of event:* | **7** | |
| *Hotkey (A H):* | **A** | (Select second port - reagent 1) |

**Insert**

| | | |
|---|---|---|
| *Device number:* | **1** | (Gilson pump) |
| *Enter time of event:* | **8** | |
| *Hotkey (F R O):* | **R** | (Switch pump on in the reverse direction) |

**Insert**

| | | |
|---|---|---|
| *Device number:* | **1** | (Gilson pump) |
| *Enter time of event:* | **10** | |
| *Hotkey (F R O):* | **O** | (Switch pump off) |

**Insert**

| | | |
|---|---|---|
| *Device number:* | **2** | (Selection valve) |
| *Enter time of event:* | **11** | |
| *Hotkey (A H):* | **A** | (Select third port - reagent 2) |

**Insert**

| | | |
|---|---|---|
| *Device number:* | **1** | (Gilson pump) |
| *Enter time of event:* | **12** | |
| *Hotkey (F R O):* | **R** | (Switch pump on in the reverse direction) |

**Insert**

| | | |
|---|---|---|
| *Device number:* | **1** | (Gilson pump) |
| *Enter time of event:* | **14** | |
| *Hotkey (F R O):* | **O** | (Switch pump off) |

**Insert**

| | | |
|---|---|---|
| *Device number:* | **2** | (Selection valve) |
| *Enter time of event:* | **15** | |

| | | |
|---|---|---|
| *Hotkey (A H):* | **A** | (Select fourth port - reagent 3) |
| **Insert** | | |
| *Device number:* | **1** | (Gilson pump) |
| *Enter time of event:* | **16** | |
| *Hotkey (F R O):* | **R** | (Switch pump on in the reverse direction) |
| **Insert** | | |
| *Device number:* | **1** | (Gilson pump) |
| *Enter time of event:* | **18** | |
| *Hotkey (F R O):* | **O** | (Switch pump off) |
| **Insert** | | |
| *Device number:* | **2** | (Selection valve) |
| *Enter time of event:* | **19** | |
| *Hotkey (A H):* | **A** | (Select fifth port - detector) |
| **Insert** | | |
| *Device number:* | **1** | (Gilson pump) |
| *Enter time of event:* | **20** | |
| *Hotkey (F R O):* | **F** | (Switch pump on in the forward direction - to pump stack of zones through detector) |
| **Insert** | | |
| *Device number:* | **1** | (Gilson pump) |
| *Enter time of event:* | **60** | |
| *Hotkey (F R O):* | **O** | (Switch pump off - end of analytical cycle) |

the auxiliary waste port can be use to rinse the manifold. The rest of the procedure are the same as described on pages 308 and 309.

## References

1. G. D. Marshall, **Analytical Instrumentation**, **20**(1) (1992) 79.
2. **FlowTEK Reference Manual, Device Control and Data Acquisition software, ver 1.1**, Mintek, 1993.
3. G. D. Marshall, **Sequential-Injection Analysis**, PhD-Thesis, University of Pretoria, 1994.

# ADDENDUM B

# ADDENDUM B

# Publications and Presentations

## Publications

1. R. E. Taljaard and J. F. van Staden, *Simultaneous Determination of Cobalt(II) and Ni(II) in Water and Soil Samples with Sequential Injection Analysis*, **Anal. Chim. Acta**, **366**, (1998) 177.
2. R. E. Taljaard and J. F. van Staden, *Application of Sequential Injection Analysis as Process Analysers*, **Lab. Rob. Autom.**, **10** (1998) 325.
3. R. E. Taljaard and J. F. van Staden, *Simultaneous Determination of Cadmium(II) and Mercury(II) in Aqueous, Urine and Soil Samples using Sequential Injection Extraction (SIE)*, **S. Afr. J. Chem.**, **52** (1999) 36.
4. R. E. Taljaard and J. F. van Staden, *Tandem Sequential Injection Analysis: Determination of Iron and Sulphate*, **Anal. Chim. Acta**, In Press.
5. R. E. Taljaard and J. F. van Staden, *Simultaneous Determination of Mercury(II) and Cadmium(II) in Aqueous, Soil and Biological Solutions using a Simple Sequential Injection Extraction Method*, In Preparation.
6. R. E. Taljaard and J. F. van Staden, *Determination of Lead(II), Copper(II), Zinc(II), Cobalt(II), Cadmium(II), Iron(III) and Mercury(II) using Sequential Injection Extraction*, In Preparation.

## Presentations

1. Simultaneous Determination of Cobalt(II) and Ni(II) in Water and Soil Samples with Sequential Injection Analysis

   **R. E. Taljaard**

   **Flow Analysis (FIA 7), Piracicaba, Brazil. 26 August 1997.**

2. Simultaneous Determination of Cadmium(II) and Mercury(II) in Aqueous, Urine and Soil Samples using Sequential Injection Extraction (SIE)
**R. E. Taljaard** and J. F. van Staden
**7th International Chemistry Conference in Africa and 34th Convention of the South African Chemical Institute. Durban. South Africa. 6 - 10 July 1998.**

3. Simultaneous Determination of Cadmium(II) and Mercury(II) in Aqueous, Urine and Soil Samples using Sequential Injection Extraction (SIE)
**R. E. Taljaard** and J. F. van Staden
**ICFIA 98. Ninth International Conference on Flow Injection Analysis. Seattle. Washington. USA. 23 - 27 August 1998.**

4. Simultaneous Determination of Cadmium(II) and Mercury(II) in Aqueous, Urine and Soil Samples using Sequential Injection Extraction (SIE)
**R. E. Taljaard** and J. F. van Staden
**Euroanalysis X. Working Party on Analytical Chemistry of the Federation of European Chemical Societies and the New Swiss Chemical society. Basel. Switzerland. 6 - 11 September 1998.**

5. Simultaneous Determination of Cadmium(II) and Mercury(II) in Aqueous, Urine and Soil Samples using Sequential Injection Extraction (SIE)
**R. E. Taljaard** and J. F. van Staden
**SCAR'98 XIVth National Conference on Analytic Chemistry. Division of Analytical Chemistry of the Federation of European Chemical Societies and the Roman Society of Analytical Chemistry. Piatra Neamt. Romania. 24 - 26 September 1998.**

6. Simultaneous Determination of Cadmium(II) and Mercury(II) in Aqueous, Urine and Soil Samples using Sequential Injection Extraction (SIE)
**R. E. Taljaard** and J. F. van Staden

ANALYTICA'98. Third National Symposium on Analytical Science. S A Chemical Institute. Midrand. South Africa. 12 - 14 October 1998.