Addendum A

Method Construction

Automisation and automatic instrumental development is of utmost importance in analytical chemistry. For this reason all experimental work done in this project was fully or partially run by a computer. The software package used was the FlowTEK programe which was specifically developed for flow injection analysis and sequential injection analysis by Marshall. [1] To explain the use of the FlowTEK program, as it was used in the experimental work of this flow injection project, experimental setup for the determination of copper in multivitamins (described in Chapter 5) was chosen. All technical data concerning the FlowTEK program can be obtained from the operation manual. [2]

As is evident from Figure 5.3, each run (or analytical sample measurement), consisted of an electrodialysing and a detecting step. The runs were separated from each other by a rinsing period of 60 seconds. The devices operated from the FlowTEK program was one peristaltic pump, two injection valves and a flame atomic absorption spectrophotometer (FAAS). (Even though two pumps were used in the experimental setup, the one pump (Pump 1, Figure 5.3) was never switched off and therefore there was no need to couple it to the computer) Following are the steps taken for the setup of the FlowTEK program before use in the experimental work.

A1 Setup of the FlowTEK program for device control and data collection

A1.1 Detector

The FAAS detector used gave maximum output at zero absorbance. For this reason the detector setup, in the FlowTEK program had to be changed from the default setting. (Default setting converts the peak directly as the signal is received from the detector, thus maximum output from the instrument will be at a peak maximum). The setting was done

as follows:

From the main menu select *Setup* (S). From the *Setup* menu select *Detectors* (D). The questions and demands which follow must be answered in the following way:

Enter number of detectors:	1	
Enter signal transformation for detector:	I	For inversion of the signal.
Enter analog input point for detector:	1	Indicate the position where the detector is coupled to the distribution box.

In the distribution box, the signal from the detector was set to be amplified 100x and the baseline was set by using the adjusting screw. Direct conversion of the signal could be monitored by using the hotkey F4.

A1.2 Pump and injection valves

The operation of the pump and the injection valves were managed by making use of a method. The detection electrodialysis and the detection step both were incorporated into the method constructed.. The method was constructed in the following way:

From the main menu select *Method* (M). First the devices used in the construction of the method must be identified. From the *Method* menu select *Type device* (T). Answer the following questions and commands:

Enter number of devices:	3	The pump and the two injection valves.
Enter type device 1:	GP	Gilson pump.
Enter digital output point for GP:	1	Indicates the position of connection of GP on the

		distribution box.
Enter type device 2:	IV	Injection valve.
Enter digital output point for IV:	3	
Enter type device 3:	IV	
Enter digital output point for IV	5	

After entering the above mentioned, the screen will divide itself into three horizontal columns, each representing one of the devices in the method of construction. At this moment there is a yellow straight line in each of the columns. At present this yellow line indicates that the Gilson pump is in the "off" position and the two injection valves are in the "load" position. At this point in time the experiment time has to be specified. To do this, in the *Method* menu, select *Expt time* (E) and answer the questions following:

Enter time to start data collection:	120
Enter experiment time:	190

Now only can the specific actions of the devices be entered. There are two ways by which it can be done. In the first way, by making use of the curser, the **Num Lock** key must be deactivated. At this stage a small green coloured square will be flashing in the bottom right corner of the screen. Hit any one of the arrow keys and the cursor will appear. Use the cursor to the column of the device in question and align it with the time for the change of a specific event. Example: Move the cursor to the top column (indicated GP on the right hand side of the screen). Align it with time 0 and enter. This time is now marked. From the *Method* select *Insert* (I) and answer the question to follow:

Enter event (FRO):	F	F indicates forward, R indicates reverse, O indicates off.

An event that was introduced previously can also be deleted in the same way. Instead of selecting *Insert* from the menu, one has to select *Delete*.

A better way of introducing and deleting events is to activate the **Num Lock** key. At this point a red square will flash in the bottom right hand corner of the screen. To insert an event select *Insert* (I) from the *Method* menu and answer the following questions: (The example to follow is for the insertion of an injection command for the first injection valve)

Enter device No:	2	
Enter time of event:	0	
Enter event (IL)	I	I indicates inject and L indicates load.

Various events were inserted to fulfill the requirements of the experiment in question. After the construction of a method, the method has to be saved. This is done by selecting the *File* (F) on the *Method* menu and answer the question:

Save, Retrieve or Erase (SRE):	S
Enter method file name:	c:\Temp1\data\Cuopt1.met (.met indicating a method file)

The method is now finished and the screen for the constructed method should look like Figure A.1

This method can now be used either directly or in a "procedure". (The creation and use of a procedure will be discussed)

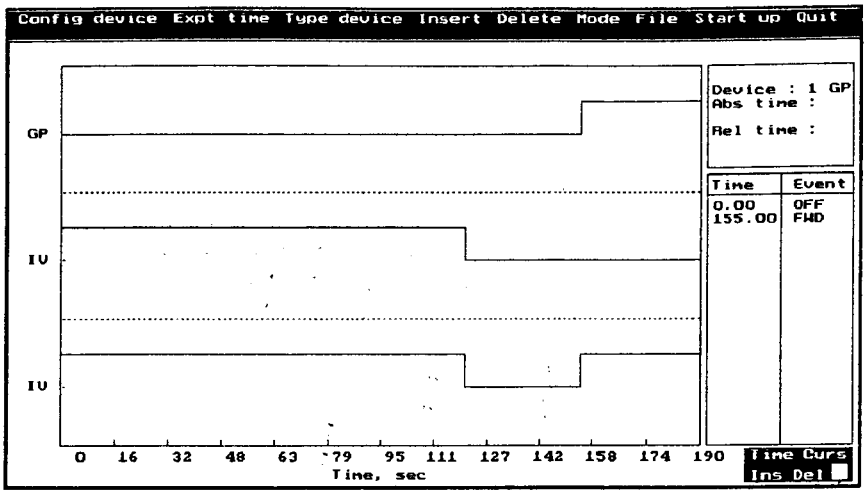


Figure A.1 *Method screen after the completion of a method.*

A2 The use of the FlowTEK program for device control and data collection

The method constructed in paragraph A1, can be applied directly or can be build into a procedure. For the direct application press *Once* (O) on the *Main* menu and the program shall run the method once. The method can be build into a procedure for repetitions of the same method or use it in conjunction with other methods. The procedure used was build as follows:

From the *Main* menu select *Repeated* (R). From the *Repeated* menu select *Build Proc* (B) and answer the following questions and commands:

Enter procedure file name:	c:\Temp1\data\Cuopt1.pdr (.pdr indicates a procedure file)
Enter procedure or method file name:	c:\Temp1\data\Cuopt1.met
Enter number of repetitions:	1
Enter procedure or method file name:	Wait
Enter time to wait (in sec)	60
Enter procedure or method file name:	c:\Temp1\data\Cuopt1.met

Enter number of repetitions: 1

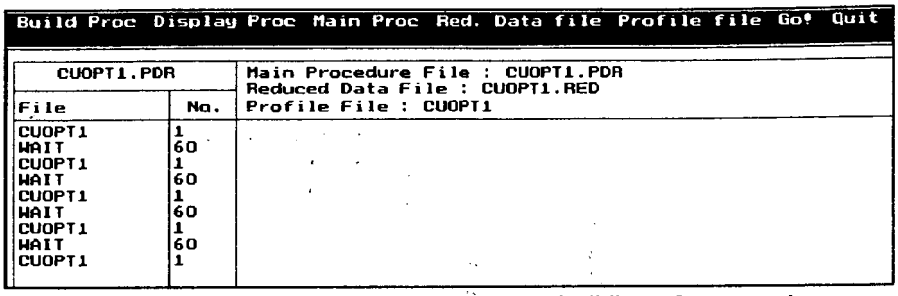


Figure A.2 *Repeated screen after of the building of a procedure was completed.*

This procedure can be build as to the number of repetitions of the above cycle required. The procedure indicated in Figure A.2 consisted of fife repetitions of the method, each separated by a 60 second rinsing period.

To terminate the definition of a procedure, use the **ESC** key. Hereafter the main procedure must be selected. This is the file that will be used to execute the experiment (that is the procedure just built). In the *Repeated* menu, select *Main Proc* (M) and answer the following command:

Enter main procedure file name: c:\Temp1\data\Cuopt1.pdr

The option *Red. Data file* on the *Repeated* menu selects a reduced data file for saving all the experimental information. Select *Red. Data file* (R) on the *Repeated* menu and answer the following command:

Enter reduced data file name: c:\Temp1\data\Cuopt1.red

The option *Profile file* on the *Repeated* menu selects the file root name for storing the profile data. The name extension gives the number of the experiment number.

To execute the main procedure select the option *Go!* (G) on the *Repeated* menu. To abort the main procedure press **ESC**.

After the optimisation of the experimental parameters, use can be made of the calibration function of the FlowTEK program. (This option was not used in the experiment and therefore imaginary values are used) This can be done as follows:

On the *Main* menu select *Calib* (C). On the *Calib* menu select *Setup* (S) and answer the questions following:

Enter no of calibration standards:	5
Enter no of replicates for each standard:	1
Enter concentration units:	mg/l
Now enter the different concentrations	
Enter reduced data file name (ESC for manual input):	ESC

On the *Calib* menu select *Pk param* (P) and answer the commands or questions to follow:

Enter peak parameter (H A W T):	A
Std to edit (1-5; 0 for all; ESC):	0

Enter the responses. In this case the responses were manually entered but it is also possible to do it via the reduced data file. It was found to be easier to do it manually since the program cannot discriminate against any shooters out.

Enter the calibration model (L Q T E H A):	L

The calibration file was saved by selecting *File* (F) on the *Calib* menu.

Save, Retrieve or Erase (S R E):	S

Enter calibration file name: c:\Temp1\data\Cuopt1.cal

Figure A.3 is an indication on how the screen will look like after the setup of the calibration file.

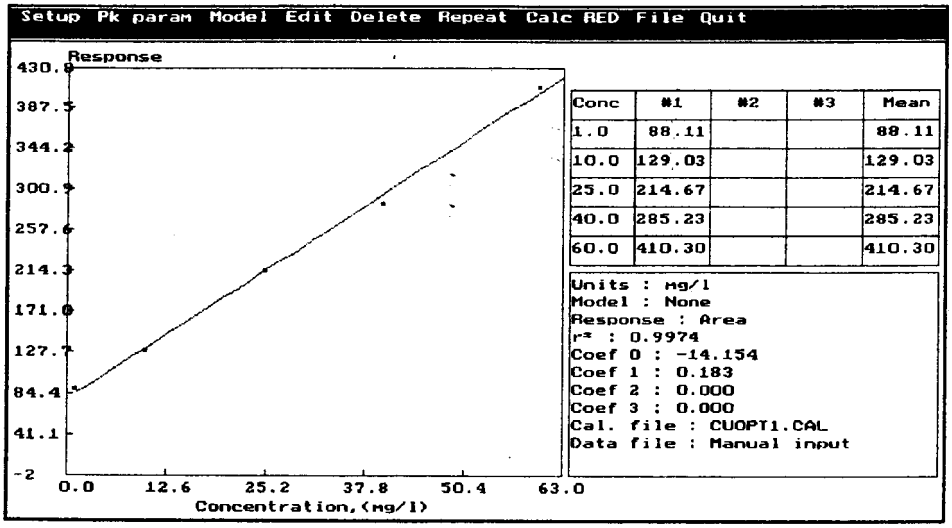
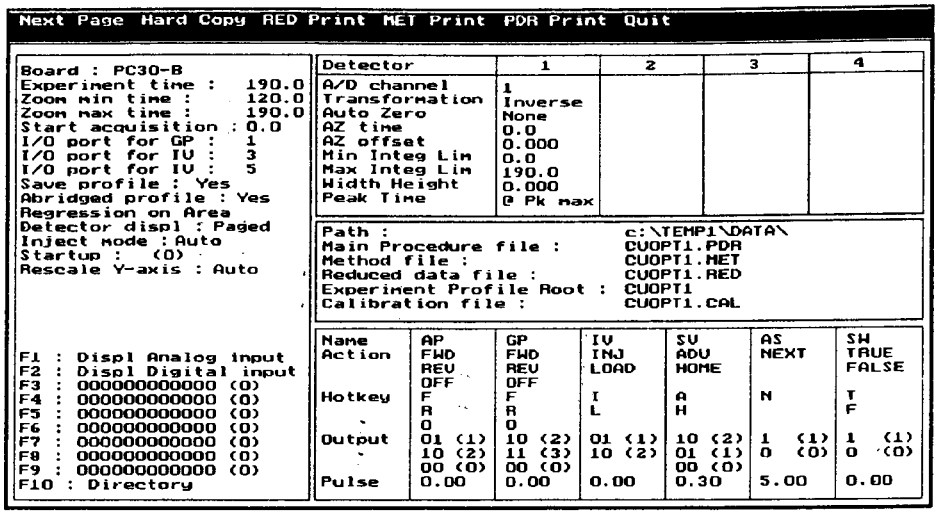


Figure A.3 Calib screen after setup of calibration.

All device descriptions can be viewed under the *Notepad* menu. This menu can be obtained from the *Main* menu by selecting *Notepad* (N). The notepad consist of two pages. For the purposes of the experimental work done, the second page was not needed. If needed however, type **N** on the *Notepad* menu. Figure A.4 is the *notepad* screen for the experiment done.



Next Page Hard Copy RED Print MET Print PDR Print Quit

Board : PC30-B
Experiment time : 190.0
Zoom min time : 120.0
Zoom max time : 190.0
Start acquisition : 0.0
I/O port for GP : 1
I/O port for IV : 3
I/O port for IV : 5
Save profile : Yes
Abridged profile : Yes
Regression on Area
Detector displ : Paged
Inject mode : Auto
Startup : (0)
Rescale Y-axis : Auto

F1 : Displ Analog input
F2 : Displ Digital input
F3 : 000000000000 (0)
F4 : 000000000000 (0)
F5 : 000000000000 (0)
F6 : 000000000000 (0)
F7 : 000000000000 (0)
F8 : 000000000000 (0)
F9 : 000000000000 (0)
F10 : Directory

Detector	1	2	3	4
A/D channel	1			
Transformation	Inverse			
Auto Zero	None			
AZ time	0.0			
AZ offset	0.000			
Min Integ Lim	0.0			
Max Integ Lim	190.0			
Width Height	0.000			
Peak Time	@ Pk max			

Path : c:\TEMP1\DATA\
Main Procedure file : CUOPT1.PDR
Method file : CUOPT1.MET
Reduced data file : CUOPT1.RED
Experiment Profile Root : CUOPT1
Calibration file : CUOPT1.CAL

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

Figure A.4 Notepad screen.

A3 References

1. Marshall G.D., Van Staden J.F. (**1992**) Anal. Instrum. 20: 79.
2. FlowTEK Reference Manual,(**1993**) Device Control and Data Acquisition software. Version 1.1. Mintek.

Addendum B

Correspondence resulting from this project

Publications:

1. Incorporation of electrodialysers into the conduits of FIA systems. Enhancement of the mass transport of chloride anions through passive neutral membranes. **Talanta** 45 (1998) 485-492.
2. Incorporation of electrodialysers into the conduits of FI/AAS systems . Determination of copper(II) ions in multivitamin tablets after enhancement of mass transfer through a passive neutral membrane. **Journal of Analytical Atomic Spectrometry** 13 (1998) 23-28.
3. The determination of zinc in pharmaceutical products using an electrodialyser incorporated into a flow injection system. **Fresenius' Journal of Analytical Chemistry**. (In press)
4. The direct determination of phosphate in fertilisers. (Submitted)
5. The indirect determination of phosphate (Submitted)

Conference proceedings:

1. SACI, Cape Town, South Africa (January 1996) One poster.
2. Euroanalysis (IX), Bologna, Italy (September 1996) One poster.
3. ICFIA'97, Orlando, Florida, USA (January 1997) One poster.
4. Flow Analysis (VII), Piracicaba, Brazil (August 1997) One poster.
5. Euroanalysis (X), in Basel, Switzerland (September 1998) Oral presentation.
6. SCAR (Romanian Society of Analytical Chemistry) (XIV), Pietra Niamţ, Romania (September 1998) One poster.
7. Analytica' 98, Midrand, South Africa (October 1998) One oral presentation and one poster.

Addendum C

Legend of Symbols

R	resistance / membrane mass transfer resistance / gas constant
A	area
ρ	resistivity
κ	conductivity
S	reciprocal ohm
Λ_m	molar conductivity
c	molar concentration
Λ_m^0	limiting molar conductivity
ν	number of ions per formula unit
λ	molar conductivity of either cat- or anions
α	degree of ionisation
J	Flux
D	diffusion coefficient
N	number density
$\Delta\phi$	potential difference
E	uniform electric field
ℓ	length or distance
Γ	frictional force / force
f	friction coefficient
s	speed
η	viscosity
a	radius / activity
u	mobility of an ion / convective flow
z	sign of the charge

e	elementary charge
t	time interval or transport number
N	Avogadro's number
F	Faraday's constant
I	current
V	volume
ε	electric permittivity / surface porosity / fraction of pores/pore area ratio
T	temperature
w	work required
D	diffusion coefficient
v	velocity or diffusional flow
P	probability / permeability
d	distance
ΔX	gradient potential across a membrane
n_p	number of pores
τ	pore tortuosity
A_m	membrane area
x_i	mole fraction
Δx or ℓ	membrane thickness
S	solubility
k_d	Henry's law constant
b	hole affinity constant
c'_h	saturation constant
m	reciprocal friction
D_T	thermodynamic diffusion coefficient
N_0	number of particles at time t = 0
v	velocity/diffusional flow
K_i	solubility constant

P	pressure
$\Delta\mu$	chemical potential difference
ΔF	electrical potential difference
γ	activity coefficient
k_d	Henry's law constant
m	mobility coefficient
D_T	diffusion coefficient