# CHAPTER 2

# EXPERIMENTAL

Basic equipment used in this study is presented in this chapter. All instruments and apparatus used are firstly exhibited. After that the list of chemical reagents are subsequently shown. The preparation of standard solutions and other reagents are next described. A system used for preconcentration of trace elements by using knotted and serpentine reactors with detection by ICP-MS is then explained. The determination of Cr(VI) and total chromium by using knotted reactor for the FI-FAAS on-line preconcentration is further shown. The FI on-line system for preconcentration of low levels of Cr(VI) with ETAAS detection is finally presented.

## 2.1 Instruments and Apparatus

The apparatus and instruments used are listed below:

1. Peristaltic pump : two-channels (MP-3N); EYELA, Japan
2. HPLC pump : LC 20 separator, PYE UNICAM, UK
3. Flow injection system : Fisons Instrument PrepLab, UK
   : FIAS-200, Perkin-Elmer, Connecticut, U.S.A.
4. Rotary injection valve : V-451, six-ports valve, Upchurch Scientific, Inc., U.S.A.
5. Flame atomic absorption spectrometer : AA-670, Shimadzu, Japan

6. Electrothermal atomic absorption spectrometer : Model 2100, Perkin-Elmer, Connecticut, U.S.A.
7. Inductively Coupled Plasma Mass Spectrometer (ICP-MS) : VG Elemental Plasma-Quad $II^+$, VG Elemental, Winsford, Cheshire, UK.
8. Chromium hollow cathode lamp : Juniper, Harlow, Essex, UK.
   : Photron PTY. LTD., Australia.
9. pH-meter : pH 900, Precisa, Zurich, Switzerland
10. Water bath : Memmert, Germany
11. Analytical balance : Sartorius, Germany

## 2.2 Chemical Reagents

All of chemical reagents used in this work were of analytical reagent grade unless otherwise specified and purchased from various sources, as exhibited in Table 2.1.

## 2.3 Preparation of Standard Solutions and Other Reagents

All solutions were prepared with deionized water (Milli-Q water, 18.2 MΩ cm, Millipore, U.S.A.)

**Table 2.1** List of chemical reagents

| Chemical reagents | Companies |
|---|---|
| Ammonium pyrrolidine dithiocarbamate (APDC) | Fluka, Switzerland |
| Standard solution of Cr(VI), Cr(III), Pb(II), Zn(II), Mn(II), Fe(III), Cu (II), Cd(II), Ni(II), Co(II), 1000 mg/l | Standard AAS solution, Tritisol, Merck, Germany |
| Standard solutions of Li, Bi, Ce, In, U, La, Be, Ga, Rh, Ho, Mo(VI), W(VI), 1000 mg/l | SpectrosoL, BDH, UK |
| Sodium chloride, NaCl | Merck, Germany |
| Magnesium sufate ($MgSO_4 \bullet 7H_2O$) | Merck, Germany |
| Sodium hydrogen carbonate ($NaHCO_3$) | Fluka, Switzerland |
| Potassium peroxydisulphate ($K_2S_2O_8$) | BDH, UK |
| Ethylenediaminetetraacetic acid-disodium salt (EDTA) | Merck, Germany |
| Super purity nitric acid ($HNO_3$, 67-69% w/v) | Romil, Cambridge, UK |
| Nitric acid ($HNO_3$, 65% w/v) | Merck, Germany |
| Hydrochloric acid (HCl, 37% w/v) | Merck, Germany |
| Sulphuric acid ($H_2SO_4$, 98% w/v) | J.T. baker, U.S.A. |
| Absolute ethanol ($C_2H_5OH$) | Merck, Germany |
| Isobutyl methyl ketone (IBMK) | Merck, Germany |
| Potassium chromate ($K_2CrO_4$) | Merck, Germany |
| Thiourea ($CS(NH_2)_2$) | Merck, Germany |
| 8-Hydroxyquinoline ($C_9H_7NO$) | Merck, Germany |
| Potassium thiocyanate (KSCN) | BDH, UK |
| 1,10-Phenanthroline ($C_{12}H_8N_2 \bullet H_2O$) | Sigma, U.S.A. |
| Ascorbic acid ($C_6H_8O_6$) | Fluka, Switzerland |
| PTFE beads (100 μm particle size, density 2.10) | Aldrich, Germany |
| Standard Reference Material-NIST 2109 | National Institute of Standards & Technology, U.S.A. |
| Standard Reference Material-NIST 1640 | National Institute of Standards & Technology, U.S.A. |

### 2.3.1 Multielements Standard Solution for ICP-MS Measurement

The stock standard solutions (1000 ppb) of each Cr(VI), Ni(II), Co(II), Cu(II), Zn(II), Mo(VI), Cd(II), W(VI) and Pb(II) used in the preparation of external calibration and used for preparing synthetic samples were firstly prepared from the elemental stock standard solutions (1000 mg/l) by appropriate dilution with deionized water.

The working standard solutions were further prepared by appropriate dilution of the stock solutions 1000 μg/l with the 0.02% (v/v) nitric acid (super purity).

### 2.3.2 Internal Standard Solution for ICP-MS Measurement

The stock standard solutions (1000 μg/l) of each Ga, Rh, Ho and Bi were firstly prepared by three-stage dilution of a 1000 mg/l stock standard solution. The stock working internal standard (5 μg/l) solution in 2% (v/v) $HNO_3$ (super purity) was then prepared just before their used by stepwise dilution from 1000 μg/l stock standard solutions.

### 2.3.3 Tune Solution for ICP-MS Measurement

The tune solution used for calibrate the ICP-MS containing the elements Li, Bi, Ce, In, U, La, Be and Co at 10 μg/l in 2% (v/v) nitric acid (super purity) was prepared by stepwise dilution from 100 μg/l stock solution.

### 2.3.4 Standard Solution of Cr(VI) for ETAAS Measurement

Standard solutions of Cr(VI) for calibration were prepared by three-stage dilution of a 1000 mg/l stock solution. The acidity of the standards were adjusted to 0.015 M with hydrochloric acid.

### 2.3.5 Standard Solution of Cr(VI) for FAAS Measurement

The stock standard Cr(VI) solution (50 mg/l) was prepared by dissolving 0.0184 g $K_2CrO_4$ in water and adjusting to a volume of 100 ml. Further dilutions were made for appropriate concentrations with 0.15 M HCl.

### 2.3.6 Standard Solution of Cr(III) for FAAS Measurement

The stock standard solution of 50 mg/l Cr(III) was prepared by three-stage dilution of a 1000 mg/l stock standard solution with deionized water. Appropriate concentrations used were then diluted with 0.15 M HCl.

### 2.3.7 Stock Solution of APDC

The stock APDC solution (1.0% w/v) was prepared daily by dissolving approximately 1.0 g APDC in water and adjusting to 100 ml with water. Further dilutions were prepared by stepwise aqueous dilution just before used.

### 2.3.8 Stock Solution of 0.01 M Potassium Peroxydisulphate

This solution was freshly prepared by dissolving 0.1350 g $K_2S_2O_8$ in deionized water and adjusting to 50 ml with water. Appropriate concentrations were then prepared by further dilution.

### 2.3.9 Stock Solution of 5% (w/v) EDTA

This solution was made up by dissolving approximately 5.00 g of EDTA in 100 ml of deionized water. The more dilute working solutions were prepared by appropriate aqueous dilution.

### 2.3.10 Diluted Nitric Acid for ICP-MS Measurement

The 0.02% (v/v) and 2.0% (v/v) $HNO_3$ solutions used for ICP-MS measurements were prepared by stepwise dilution from super purity nitric acid (67-69%). These solutions were freshly prepared in date of ICP-MS measurement.

### 2.3.11 Diluted Hydrochloric Acid for ETAAS and FAAS Measurement

The 0.015 M and 0.15 M HCl solutions used for ETAAS and FAAS measurement, respectively, were prepared by appropriate dilution of concentrated HCl with deionized water.

### 2.3.12 Diluted Sulphuric Acid for Oxidation of Cr(III)

The 0.1 M stock solution of sulphuric acid for using in Cr(III) oxidation process was prepared by stepwise dilution from the concentrated sulphuric acid (98%).

### 2.3.13 Synthetic Seawater Samples

The synthetic seawater was prepared by dissolving 33.8 g NaCl, 10.92 g $MgSO_4 \bullet 7H_2O$ and 0.22 g $NaHCO_3$, respectively, making the solution up to 2000 ml

with Milli-Q water; this matrix corresponds to the composition of coastal seawater [40, 45] used for internal calibration.

## 2.4 Procedures

### 2.4.1 A Comparison of Enrichment Factor of Knotted and Serpentine Reactors Using Flow Injection Sorption and Preconcentration for the Off-line Determination of Some Trace Elements by ICP-MS

The ICP-MS instrument was used as a detector. The instrument was calibrated before use, using tune solution containing the elements Li, Bi, Ce, In, U, La, Be and Co at 10 μg/l in 2% (v/v) nitric acid. The instrument operating parameters are given in Table 2.2.

The preconcentration process was manually operated using a Fisons Instrument PrepLab system. The scheme of the FI manifold used in this section is presented in Fig. 2.1. A reactor of 150 cm length of each knotted and serpentine reactor made of PTFE tubing (0.35 mm i.d.) was used as the sorption medium for complexes formed with the analytes under investigation. The configuration of knotted and serpentine reactors used is shown in Fig. 2.2 (a) and (b), respectively. The tygon tubings as flow lines and the peristaltic pump were employed to propel the sample, reagent, eluent and wash solution.

The operation sequence of the FI on-line preconcentration on the PrepLab system is presented in Table 2.3. In the prefill stage (step 1) as shown in Fig, 2.1a, pump 1 activated and the injector valve was in 'inject position', so that the

tubing was filled with sample and reagent solution. In step 2 (Fig. 2.1b), pump 1 was still running while the injector valve was switched to 'load position'. The metal-PDC

**Table 2.2** Operating parameters for the ICP-MS

| Parameters | Condition |
|---|---|
| Radio frequency power | 1350 W |
| Coolant gas flow rate | 13.0 l $min^{-1}$ |
| Auxiliary gas flow rate | 0.80 l $min^{-1}$ |
| Nebuliser gas flow rate | 0.88 l $min^{-1}$ |
| Data acquisition mode | Peak jumping |
| Channels per amu | 7 |
| Dwell time | 10000 μs |
| Detector mode | Pulse counting |
| Isotopes measured | $^{52}Cr$(VI), $^{58}Ni$(II), $^{59}Co$(II), $^{63}Cu$(II), $^{64}Zn$(II), $^{98}Mo$(VI), $^{114}Cd$(II), $^{184}W$(VI) and $^{208}Pb$(II) |

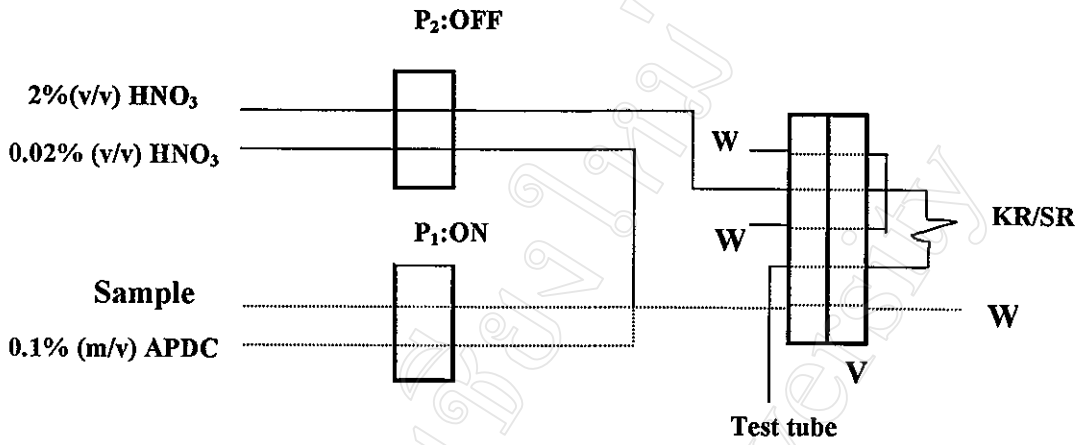
complex was formed and sorbed onto the inner walls of the reactor, the effluent from the reactor flowing to waste. In step 3 (Fig 2.1c), the injector valve was still in load position but pump 1 was stopped while pump 2 was actuated, so that a flow of 0.02% (v/v) $HNO_3$ was gone to waste. Finally, in step 4 (Fig. 2.1d), the injector valve was turned to injected position while pump 2 was still running. A flow of 2% $HNO_3$ was introduced into the reactors to elute the adsorbed analyte and to deliver the analyte into the test tube. The final 5 ml volume was collected for sufficient duplicated

determinations per test tube. The concentration of the analyte in the solution in the test tube was then determined by ICP-MS. The total time required for single preconcentration step in PrepLab system was 240 s. The four replicate determinations (four test tubes) were carried out for all experimental data points.

**Table 2.3** Operating sequences of FI on-line preconcentration in PrepLab system

| Step | Function | Valve position | Duration (s) | Pump active | Medium pumped | Flow rate (ml $min^{-1}$) |
|---|---|---|---|---|---|---|
| 1 | Prefill the sampling tubing | Inject | 20 | $P_1$ | Sample | 1.20 |
| | | | | | 0.1%(m/v)APDC | 0.50 |
| 2 | Load sample | Load | 120 | $P_1$ | Sample | 1.20 |
| | | | | | 0.1%(m/v)APDC | 0.50 |
| 3 | Rinse reactor | Inject | 10 | $P_2$ | 0.02% (v/v) $HNO_3$ | 2.85 |
| | | | | | 2% (v/v) $HNO_3$ | 3.30 |
| 4 | Elute the adsorbed analyte | Load | 90 | $P_2$ | 0.02% (v/v) $HNO_3$ | 2.85 |
| | | | | | 2% (v/v) $HNO_3$ | 3.30 |

(a) Prefilling




(b) Sample loading

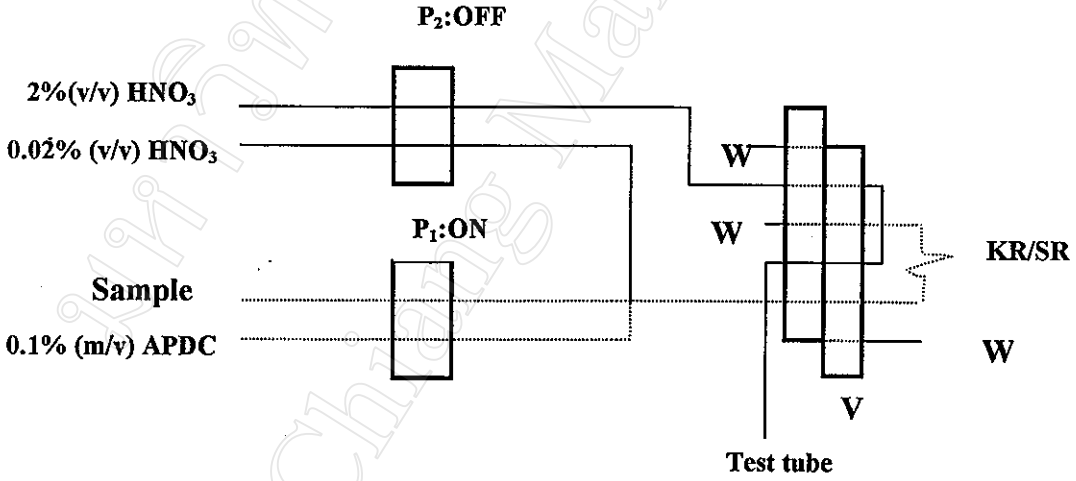
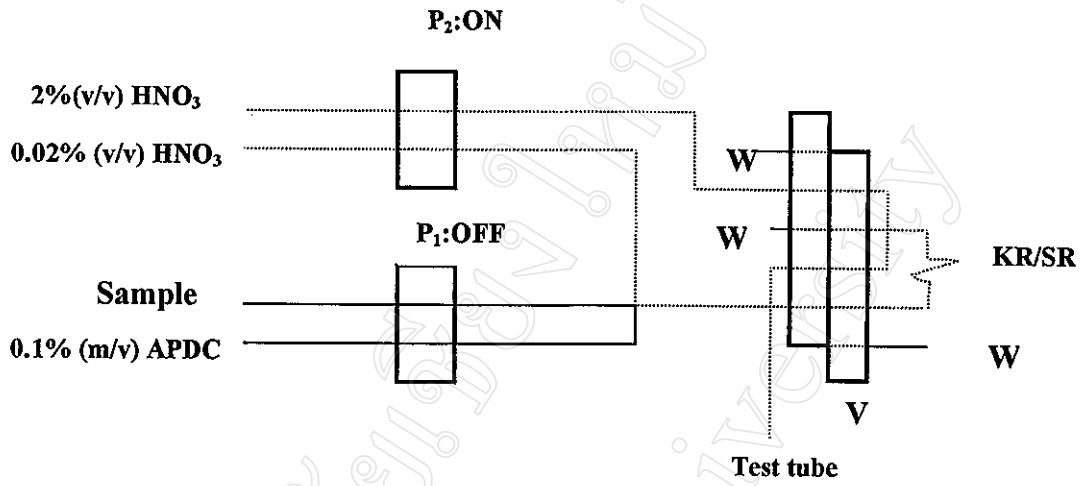



**Figure 2.1**. FI manifold and operational sequences for preconcentration: $P_1$, $P_2$, peristaltic pump; W, waste; KR, knotted reactor; SR, serpentine reactor; V, injection valve; dotted lines, active lines; solid lines, inactive lines; (a) Prefilling; (b) Sample loading; (c) Reactor rinsing; (d) Elution.

(c) Reactor rinsing.




(d) Elution

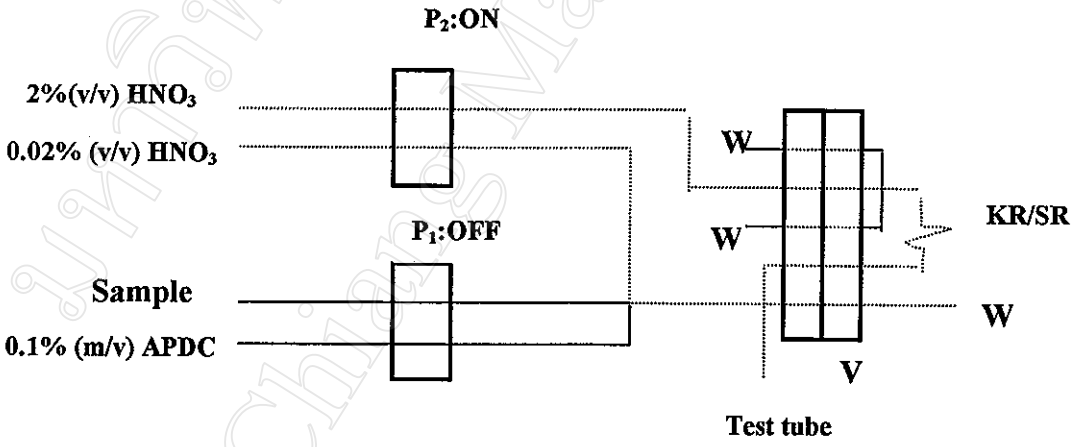
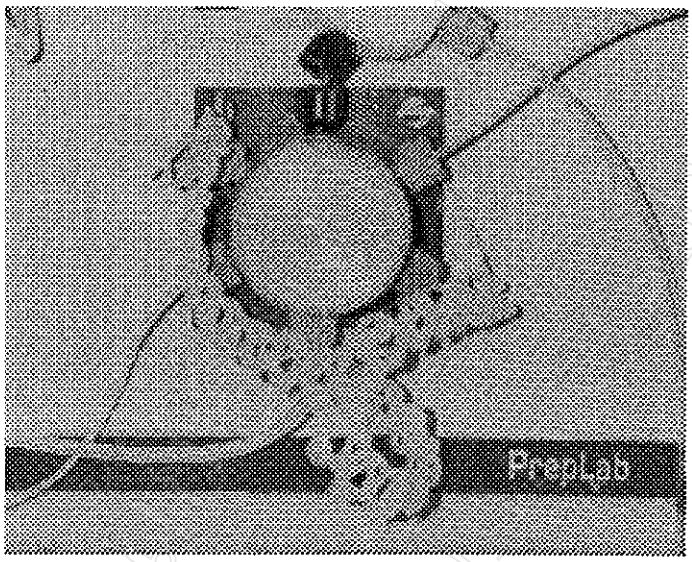



**Figure 2.1**. (continue) FI manifold and operational sequences for preconcentration: $P_1$, $P_2$, peristaltic pump; W, waste; KR, knotted reactor; SR, serpentine reactor; V, injection valve; dotted lines, active lines; solid lines, inactive lines; (a) Prefilling; (b) Sample loading; (c) Reactor rinsing; (d) Elution.

**(a)**



**(b)**

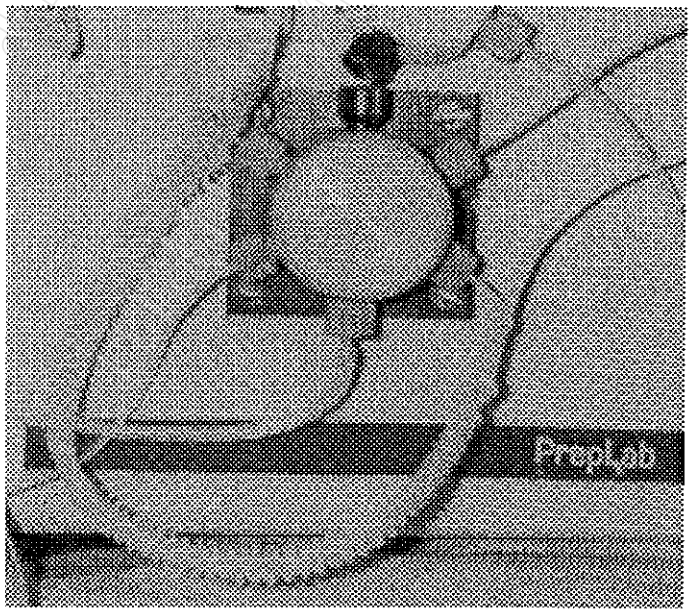


**Figure 2.2** Configuration of reactor (a) Knotted reactor, (b) Serpentine reactor.

### 2.4.2 FI On-line Sorption and Preconcentration of Chromium (VI) and Total Chromium Using a Knotted Reactor with Detection by FAAS

#### 2.4.2.1 Determination of Cr(VI) by FI-FAAS

A atomic absorption spectrometer (AA-670, Shimadzu, Japan) equipped with a deuterium-arc background corrector was used for the analysis. A chromium hollow cathode lamp (Photron PTY. LTD., Australia) was used at a wavelength of 357.9 nm with a spectral bandpass of 0.7 nm, and was operated at 8 mA. The observation height was set at 8 mm. The flame composition was less reductive than usual, as in this case the aerosol contains organic solvent (IBMK) to dissolve the complexes in the sorption reactor. The nebulizer uptake rate was adjusted to give an optimum response for conventional sample aspiration. The signal as peak height of the transient chromium atomic absorption signal was obtained and printed out by Graphic Printer PR-4 (Shimadzu, Japan).

All the connections and conduits in the FI-manifold consisted of PTFE-tubings with the diameters of 0.50 mm i.d. and 1.66 mm o.d.. Tygon tubes were employed as flow lines in conjunction with a peristaltic pump to propel the sample and reagent. A silicone pump tube was used to introduce the eluent, IBMK, into the KR. The knotted reactors (125 cm) for preconcentration were made from PTFE-tubing (i.d./o.d.= 0.50 mm/1.66 mm) by tying interlaced knots of ≈5 mm diameter loops. The performance of the knotted reactor was stable during all experiments with practically unlimited lifetime.

The schematic diagram of the FI system designed and operational sequences for the sorption preconcentration of Cr(VI) with optimized parameters are shown in Fig 2.3 and Table 2.4, respectively.

**Table 2.4** Flow injection operation for on-line preconcentration and elution of Cr(VI)

| Step | Function | Valve position | Time (s) | Pump active | Medium pumped | Flow rate (ml $min^{-1}$) |
|---|---|---|---|---|---|---|
| 1 | Prefill the sample tubing | Inject | 5 | $P_1$ | Sample | 5.0 |
| | | | | | APDC | 4.0 |
| | | | | $P_2$ | IBMK | 1.0 |
| 2 | Preconcentration | Load | 180 | $P_1$ | Sample | 5.0 |
| | | | | | APDC | 4.0 |
| | | | | $P_2$ | IBMK | 1.0 |
| 3 | Elute the adsorbed analyte | Inject | 40 | $P_2$ | IBMK | 1.0 |

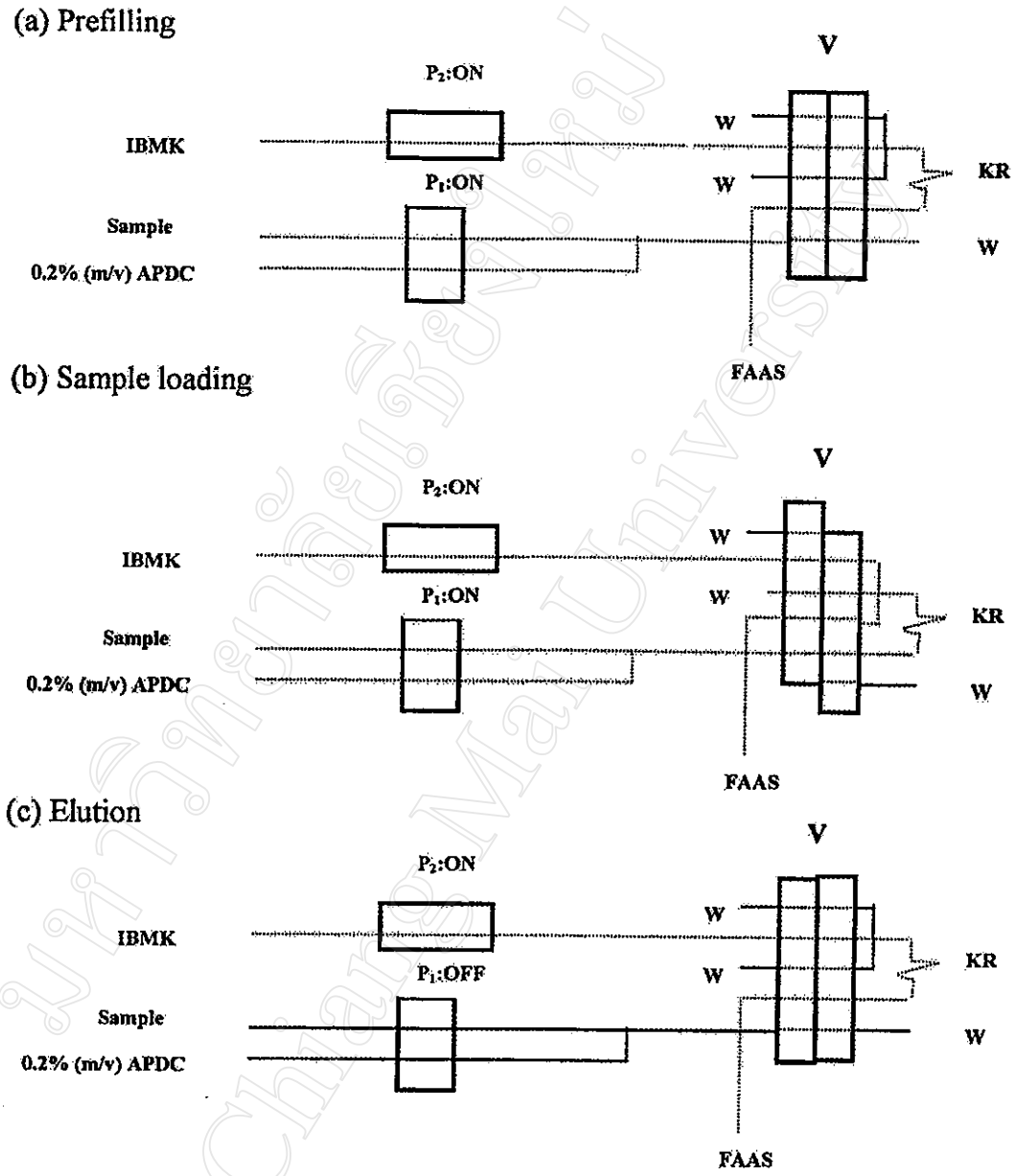



**Figure 2.3** FI manifold and operational sequences for the preconcentration, separation and determination of chromium: $P_1$, peristaltic pump; $P_2$, HPLC pump; W, waste; KR, knotted reactor; V, injection valve; dotted lines, active lines; solid lines, inactive lines; (a) Prefilling; (b) Sample loading; (c) Elution.

The procedure for the determination of Cr(VI) consisted of three steps. In stage 1, the prefill step, pump 1 and pump 2 were activated while the injector valve was in 'inject position', the sample or standard and reagent solutions were pumped by pump 1 for five seconds to wash out the previous sample solution remaining in the conduit. In stage 2, the preconcentration step, which lasted for 180 seconds, the valve was switched to 'load position' as shown in Fig 2.3 (b). Sample or standard solutions were sucked and merged with the reagent solution. The Cr(VI)-PDC complex formed was then sorbed on the inner wall of the knotted reactor. In stage 3, pump 1 was stopped and the valve turned to 'inject position' as shown in Fig 2.3 (c). The adsorbed analyte was eluted by IBMK and delivered to the nebulizer burner system of the FAAS instrument. Absorbance as peak height of the transient chromium signal was used for quantification.

**2.4.2.2 Determination of total chromium by FI-FAAS**

Total chromium contents in the samples can only be preconcentrated and determined after oxidation of Cr(III) to Cr(VI). For the determination of total chromium, 45 ml of standards or samples were added with 5 ml of 0.01 M $K_2S_2O_8$ and 2.5 ml of 0.1 M $H_2SO_4$. Then, the solution was transferred into a 125 ml erlenmeyer flask, and heated in a water bath at 80 $^0$C for 30 minutes for complete oxidation of chromium (III) to chromium (VI). After cooling to room temperature, the solution was added with 8 ml of 5% (w/v) EDTA and 3 ml of 5 M HCl and then made the volume up to 100 ml with water. Finally, the solution was introduced into the flow system in a similar manner as described earlier for the determination of Cr(VI) (section 2.4.2.1). The Cr (III) concentration was then

calculated by the difference between the total chromium concentration and the chromium (VI) concentration found in the sample solution.

### 2.4.3 FI On-line Preconcentration of Low Levels of Cr(VI) with ETAAS detection

The FI manifold for the preconcentration, separation and determination of Cr(VI) together with the operational sequences are presented in Fig 2.4 and Table 2.5, respectively.

**Table 2.5** Sequences of operations for the FI on-line sorption preconcentration and elution procedures for very low levels of Cr(VI)

| Sequence | Figure for details | Valve position | Time (s) | Function |
|---|---|---|---|---|
| 1 | Fig. 2.3 (a) | Fill | 5 | Cleansing preparation |
| 2 | Fig. 2.3 (b) | Inject | 25 | Cleansing of FI system |
| 3 | Fig. 2.3 (c) | Fill | 60 | Preconcentration |
| 4 | Fig. 2.3 (d) | Inject | 10 | Washing the KR/packed column reactor |
| 5 | Fig. 2.3 (e) | Inject | 30 | Removal of the sample solution from KR/column by air |
| 6 | Fig. 2.3 (f) | Fill | 5 | Eluent loading |
| 7 | Fig. 2.3 (g) | Inject | 85 | Elution and introduction of the concentrate to ETAAS |

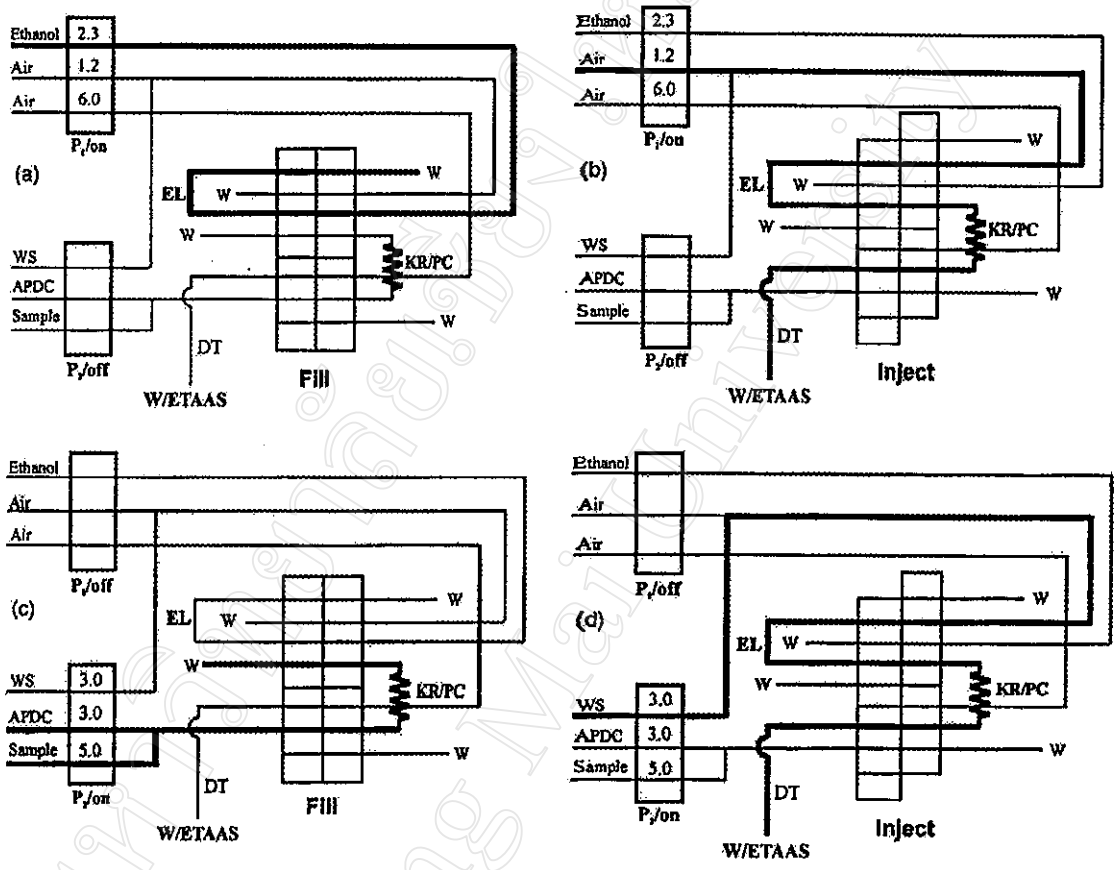



**Figure 2.4** Schematic diagram of the FI-manifold for sample preconcentration and elution, (a)-(g) showing operational sequences. The stated pumping rates depicted at the peristaltic pumps, $P_1$ and $P_2$, are the optimized ones. APDC, ammonium pyrrolidine dithiocarbamate; WS, washing solution; W, waste; KR, PTFE KR (length = 125 cm); PC, packed column reactor with PTFE beads; EL, eluent loop; and DT, delivery tube.

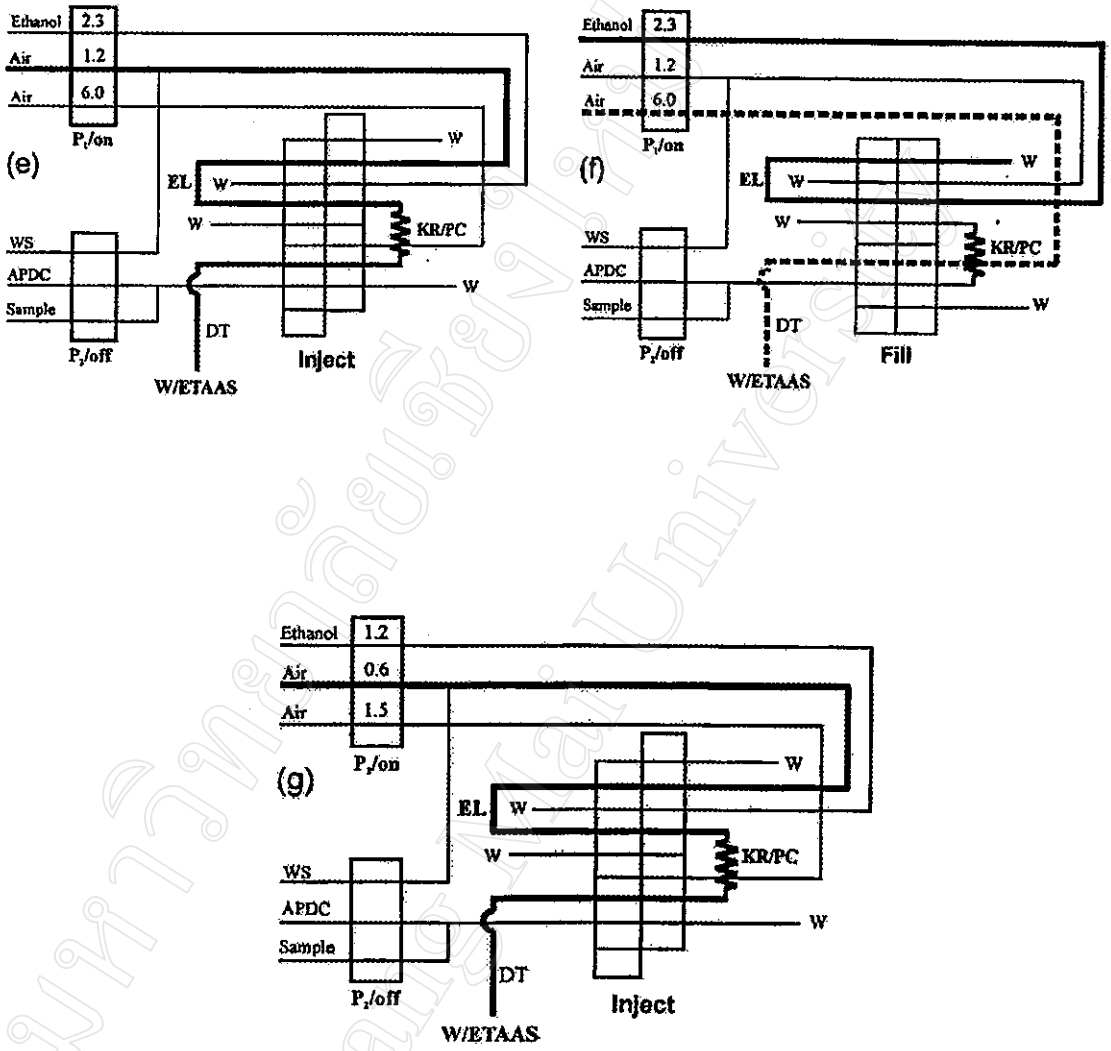



**Figure 2.4 (continued)** Schematic diagram of the FI-manifold for sample preconcentration and elution, (a)-(g) showing operational sequences. The stated pumping rates depicted at the peristaltic pumps, $P_1$ and $P_2$, are the optimized ones. APDC, ammonium pyrrolidine dithiocarbamate; WS, washing solution; W, waste; KR, PTFE KR (length = 125 cm); PC, packed column reactor with PTFE beads; EL, eluent loop; and DT, delivery tube.

A Perkin-Elmer Model 2100 atomic absorption spectrometer was used in combination with Perkin-Elmer Model FIAS-200 flow-injection system equipped with two individually controlled peristaltic pumps and an 8-port FI-valve. A chromium hollow cathode lamp (Juniper, Harlow, Essex, UK) was used at a wavelength of 357.9 nm with a spectral bandpass of 0.7 nm, and was operated at 9 mA. The output signals were processed with a time constant of 0.5 s in the peak area mode (integrated absorbance) and recordings from the graphics screen were printed out by an Epson Model FX-850 printer. The sample manipulations of the FI-procedure were controlled automatically by the 8-port valve (V) and the activation of the two peristaltic pumps ($P_1$ and $P_2$ - see Fig.2.4). The actuation times of the injection valve and the two pumps were programmed and controlled by a separate computer using the Perkin-Elmer FIAS VI.5 software.

All the connections and conduits in the FI-manifold (see Fig. 2.4) consisted of (i.d./o.d.) = (0.50 mm/1.66 mm) PTFE-tubing. Ismaprene pump tubes were employed to propel the sample, reagent, washing solution, and air. A silicone pump tube was used to introduce the eluent, ethanol. A 60 cm PTFE delivery tube (DT) of (i.d./o.d.= 0.50 mm/1.20 mm) was used to mount and connect the FI system with the ETAAS unit by means of a specially made rocker-arm that could be readily adjusted three-dimensionally to the optimal position. It permitted accurate and reproducible transfer of the eluate onto the platform of the graphite tube as well as the commercial auto-sampler arm of the instrument.

The knotted reactors for preconcentration were made from PTFE-tubing (i.d./o.d.= 0.50 mm/1.66 mm) by tying interlaced knots of $\approx$5 mm diameter loops. The preconcentration column was made from PTFE tubing of (i.d./o.d. = 2.25

mm/ 2.95 mm). 1.5 cm column was filled with 72 mg of PTFE beads (100 μm particle size, density 2.10; Aldrich) which offered a total surface area corresponding to the same inner surface area as that of a 125 cm KR made from 0.50 mm i.d. PTFE tubing. The ends of each side of the column were plugged with glass wool for keeping the packing material in place and connected to the 0.50 mm i.d. PTFE manifold tube via PTFE tubing of appropriate diameter. The performance of the packed column was stable throughout all experiments with practically unlimited lifetime.

The FI-procedure runs through a cycle of seven sequences. A complete cycle of the FI-operation lasts ca. 220s. For clarity, the operational sequence is in the following explained by first cleansing of the system, subsequently the preconcentration step, and finally the ensuing elution process.

In *sequence 1* (Fig. 2.4(a)) with pump 1 active and the valve in the fill position, the eluent loop (EL), which was adjusted to contain exactly 35 μl of eluent, was filled with ethanol. This step is a cleansing preparation.

In *sequence 2* (Fig. 2.4(b)) with the valve switched to the inject position and pump 1 still running, an air flow propelled the eluent from the loop EL through the KR (alternatively, the packed column) and the delivery tube (DT) to clean the pertinent conduits to avoid carry-over between individual samples and subsequently prepare the preconcentration of the next sample.

In *sequence 3* (Fig. 2.4(c)) with the valve switched back to the fill position and pump 2 being activated, reaction and on-line preconcentration of Cr(VI) with APDC (0.17% (w/v)) solution was achieved. The Cr(VI)-PDC complex formed was subsequently sorbed on the inner wall of the KR (or on the PTFE beads), while

the sample effluent was discharged to waste. After preconcentration for 60s, and with pump 2 still running, the valve was switched to the inject position.

*Sequence 4* (Fig. 2.4(d)) was initiated: The KR/packed column was washed with the washing solution (0.015% (w/v) APDC). Interfering matrix components were thus removed from the surface of the retained analyte in this step.

In *sequence 5* (Fig. 2.4(e)) with the valve still in the inject position, pump 2 was stopped and pump 1 was reactivated, and an air flow expelled the residual solution from the EL, the KR/packed column and the DT before following elution step.

In *sequence 6* (Fig. 2.4(f)) with pump 1 still active, the valve was switched to the fill position, a well-defined volume of 35 µl of ethanol was loaded into EL while the DT was repeatedly flushed by air. Then, the tip of DT, which conduit was mounted on the rocker-arm and connected with the FI-manifold, was manually inserted into the hole of the graphite tube.

In *sequence 7* (Fig. 2.4(g)) with pump 1 still running, the valve was switched to the inject position. Air was pumped into line DT. The eluent segment entrapped in EL was hence transported reproducibly to elute the concentrated analyte and to place the eluate onto the platform of the graphite tube. The graphite furnace temperature program was then initiated.

The FI-system and the ETAAS instrument were coupled and operated completely synchronously. The furnace temperature program for Cr(VI) determination is shown in Table 2.6.

**Table 2.6** Graphite furnace temperature program for the determination of Cr(VI) in the ethanolic eluate using pyrolytically coated graphite tubes with platform

| Step | Temperature ($^0$C) | Ramp (s) | Hold (s) | Ar flow rate (ml min$^{-1}$) |
|---|---|---|---|---|
| 1 | 60 | 5 | 20 | 300 |
| 2 | 90 | 5 | 20 | 300 |
| 3 | 120 | 5 | 25 | 300 |
| 4 | 1100 | 5 | 25 | 300 |
| 5 | 2400 | 0 | 5 | 0 |
| 6 | 2700 | 1 | 3 | 300 |