CHAPTER III

EXPERIMENTAL SECTIONS

3.1 Apparatus

- Flame atomic absorption spectrometer

Chromium concentrations were determined by a flame atomic absorption spectrometer (FAAS) model AAnalyst 100 (Perkin Elmer). The instrumental conditions are listed in Table 3.1.

Table 3.1 FAAS conditions for determination of chromium concentration in solutions

Operating conditions	Cr
Wavelength (nm)	357.9
Slit width (nm)	0.7
Lamp type	Hallow Cathode Lamp
Lamp current (mA)	25
Flame type	Reducing
C_2H_2 flow-rate (mL min^{-1})	3
Air flow-rate (mL min^{-1})	10

- pH meter

A pH meter model pH 211 (Hanna instruments) was used for pH measurements.

- UV-Vis spectrophotometer

UV-Vis spectrophotometer model HP 8453 (Hewllet Packard) was used for the characterization of chromium species.

- Peristaltic pump

A peristaltic pump REGLO Analog MS-4/8 model ISM 827 (ISMATEC®) was used for the control of flow rate of solutions passing through the column, with Tygon tubes R 3607 (i.d. 2.79 mm, wall 0.86 mm).

- Centrifuge

The centrifuge Centaur2 (Sanyo®) was used at 3500 rpm for 5 min to separate sorbents and extracted chromium solution in batch experiments.

3.2 Chemicals

All chemicals were standard analytical grade listed in Table 3.2. They were used without further purification unless otherwise noted.

Table 3.2 Chemicals lists

Chemicals	Supplier
Calcium choride	CARLO ERBA
Chromium standard solution (1000 mg L^{-1})	BDH
Ethylenediaminetetraacetic acid	Fluka
Hydrochloric acid 37%	MERCK
Hydrogen peroxide 100 volumes	Fisher Scientific
Nitric acid 65%	MERCK
Potassium chloride	AJAX CHEMICALS
Potassium chromate	Fisher Scientific
Potassium hydroxide	MERCK
Sodium chloride	CARLO ERBR
Sodium hydroxide	MERCK
Sodium nitrate	CARLO ERBR
Sodium sulphate	CARLO ERBR

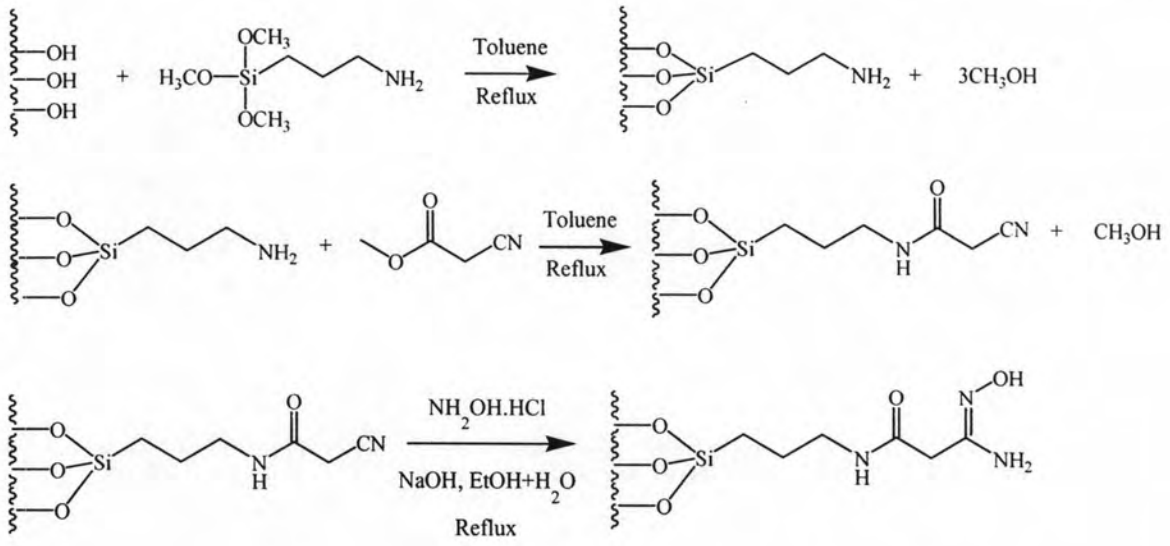
3.3 Preparation of solution

Working standard solutions of chromium were prepared by stepwise dilution of 1000 mg L^{-1} Cr(III) and 2000 mg L^{-1} Cr(VI) stock standard solutions to the required concentrations.

Working standard solutions of Cr(III) and Cr(VI) were prepared by direct dilution from the stock standard solution of Cr(III) and Cr(VI). All working standard solutions were freshly prepared. The pH of solution was adjusted with 1-20% HNO_3, 1-20% HCl and 1-20% KOH solutions. All solutions were prepared by using Milli-Q water with 18 $M\Omega\,cm^{-2}$.

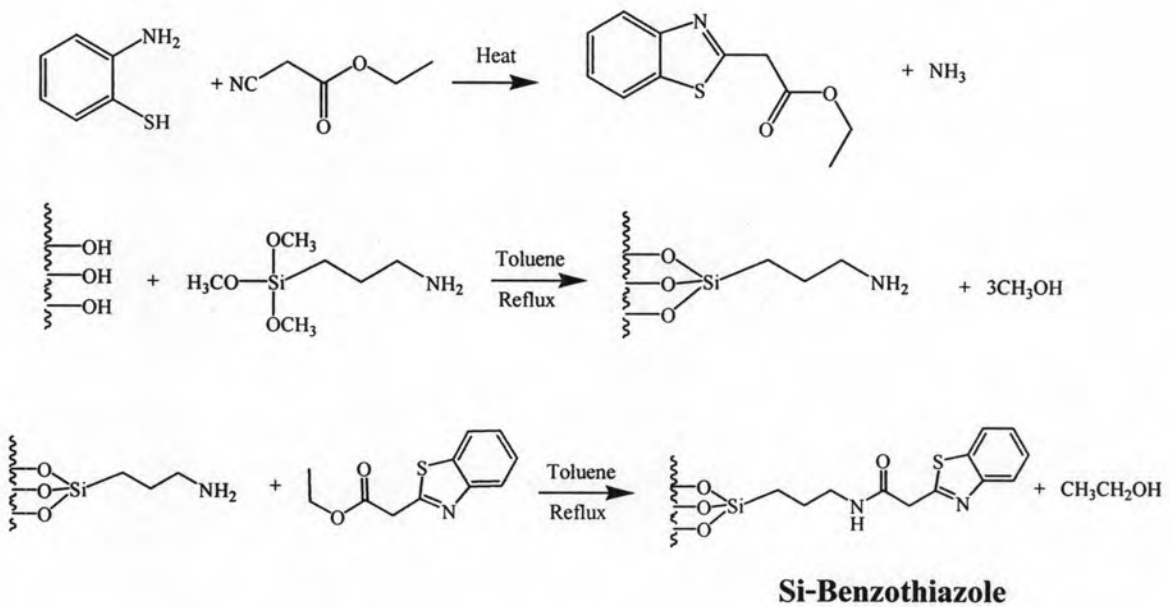
3.4 Extraction study

The study of extraction study was divided into two systems: batch and column systems. The two sorbents, chemically modified silica gel containing amidoxime (Si-Amidoxime) and benzothiazolyl (Si-Benzothiazole) employed in this research, were synthesized from Environmental Analysis Research Group, Department of Chemistry, Chulalongkorn University [59-60]. The synthetic pathways of these sorbents are shown in Scheme 3.1 and Scheme 3.2 for Si-Amidoxime and Si-Benzothiazole, respectively.



Si-Amidoxime

Scheme 3.1 Synthetic pathway of Si-Amidoxime



Si-Benzothiazole

Scheme 3.2 Synthetic pathway of Si-Benzothiazole

This work was devided into three parts: adsorption study, preconcentration study and speciation analysis.

3.4.1 Adsorption study: batch system

The effect of various parameters such as pH of solution, contact time, and sorption capacity on extraction efficiency was investigated on batch system, and all experiments were performed in triplicate.

3.4.1.1 pH of solution

A solution (5.0 mL) containing 5.0 mg L^{-1} Cr(III) or 8.0 mg L^{-1} Cr(VI) was taken in a test tube. The pH was adjusted to values ranging from 1.0 to 7.0 using various concentraton of KOH, HCl or HNO_3 solution. Then a 20 mg of Si-Amidoxime was added to the test tube and the mixture was stirred for 60 min at room temperature. The sorbent was separated by centrifugation at 3500 rpm for 5 min. The residual chromium concentration of the supernatant was determined by FAAS.

The adsorption of Cr(III) or Cr(VI) on Si-Benzothiazole was performed in the same procedure using an amount of 20 mg of Si-Benzothiazole.

3.4.1.2 Contact time

A solution of suspended 20 mg of Si-Amidoxime in 5.0 mL of 8.0 mg L^{-1} Cr(VI) solution (after adjusted its pH to 4.0) was stirred at different contact time in the range of 5-60 min at room temperature. The sorbent was separated by centrifugation at 3500 rpm for 5 min. Residual Cr(VI) concentration of the supernatant was determined by FAAS.

The study of Cr(III) on Si-Benzothiazole was performed in the same procedure using 20 mg of Si-Benzothiazole.

3.4.1.3 Sorption capacity

A suspension of 10 mg of Si-Amidoxime in 5.0 mL of Cr(VI) solution of which the concentration was varied between 10.0-70.0 mg L^{-1} under optimum pH 4.0 in a test tube was stirred for 5 min, and the temperature was controlled at 298±1 K. The solid sorbent was separated by centrifugation at 3500 rpm for 5 min. The residual Cr(VI) concentration of the supernatant was determined by FAAS.

The adsorption of Cr(III) onto Si-Benzothiazole was performed in the same manner using 5 mg of Si-Benzothiazole, contact time was 60 min and the concentration was varied between 2.0-8.0 mg L^{-1}.

3.4.2 Preconcentration study: column system

The column system was investigated to obtain the optimum conditions for retention and elution of chromium. The effects of flow rate, type of eluent, sample volume and interfering ions were evaluated in triplicate.

A laboratory-made mini-column (2.79 mm i.d.) was packed with 50 mg of Si-Benzothiazole or 20 mg of Si-Amidoxime.

3.4.2.1 Sample flow rate

5.0 mL of 8.0 mg L^{-1} Cr(VI) solution at pH 4.0 was passed through a mini-column packed with Si-Amidoxime at different flow rates from 0.5-4.0 mL min^{-1} controlled with a peristaltic pump. The residual Cr(VI) concentration of the effluent was determined by FAAS.

The study of Cr(III) was performed in the same manner using a mini-column packed with Si-Benzothiazole and the initial concentration of Cr(III) was 5.0 mg L^{-1}.

3.4.2.2 Eluent

A working standard solution containing 8.0 mg L^{-1} Cr(VI) (pH 4.0, 5.0 mL) was passed through a mini-column packed with Si-Amidoxime at a flow rate of 2.0 mL min^{-1} controlled with a peristaltic pump. The elution of sorbed Cr(VI) from Si-Amidoxime was investigated using 5.0 mL of eluting agent passed through the mini-column at a flow rate of 0.5 mL min^{-1}. The eluents used were 0.1-1.0 M NaOH and 10 % (v/v) H_2O_2 in 0.1 M NaOH. The amount of Cr(VI) in the stripped solution was determined by FAAS.

The desorption of Cr(III) was performed in the same manner but the initial concentration of Cr(III) was 5.0 mg L^{-1} at pH 4 was passed through a mini-column packed with Si-Benzothiazole. The eluents used were 1-10 % (v/v) HNO_3, 0.0005 M EDTA in acidic and basic medium and 10 % (v/v) H_2O_2 in 0.1 M NaOH.

3.4.2.3 Sample volume

Sample solutions of different volume (25-500 mL) spiked with 500 µL of 50 mg L^{-1} Cr(VI) solution were adjusted pH to 4.0 and then passed through a mini-column packed with Si-Amidoxime at a flow rate of 2.0 mL min^{-1} controlled with a peristaltic pump. The sorbed Cr(VI) was eluted by 5.0 mL of 10 % (v/v) H_2O_2 in 0.1 M NaOH at a flow rate of 0.5 mL min^{-1}. The amount of Cr(VI) in the effuent was determined by FAAS.

Sample solutions of different volume (5-100 mL) spiked with 500 µL of 30 mg L^{-1} Cr(III) solution were adjusted pH to 4.0 and then passed through a mini-column packed with Si-Benzothiazole at a flow rate of 0.5 mL min^{-1} controlled with a peristaltic pump. The sorbed Cr(III) was eluted by 5.0 mL of 10 % (v/v) H_2O_2 in 0.1 M NaOH at a flow rate of 0.5 mL min^{-1}. The amount of Cr(III) in the effluent was determined by FAAS.

3.4.2.4 Interfering ions

The solution containing cations such as Na^+, K^+ and Ca^{2+} and the anions such as Cl^-, NO_3^- and SO_4^{2-} at 10, 100 and 1000 mg L^{-1} were prepared by dissolving the appropriate amount of NaCl, KCl, $NaNO_3$ and $NaSO_4$ in Milli-Q water.

100 mL of sample solution containing interfering ions (Cl^-, NO_3^- and SO_4^{2-}) spiked with 500 µL of 50 mg L^{-1} Cr(VI) solution were adjusted pH to 4.0 and then passed through a mini-column packed with Si-Amidoxime at a flow rate of 2.0 mL min^{-1} controlled with a peristaltic pump. The sorbed Cr(VI) was eluted by 5.0 mL of 10 % (v/v) H_2O_2 in 0.1 M NaOH at a flow rate of 0.5 mL min^{-1}. The amount of Cr(VI) in the effluent was determined by FAAS.

The study of Cr(III) was performed in the same manner using 100 mL of sample solution containing interfering ions (Na^+, K^+ and Ca^{2+}) spiked with 500 µL of 30 mg L^{-1} Cr(III) solution at pH 4.0 was passed through a mini-column packed with Si-Benzothiazole at a flow rate of 0.5 mL min^{-1}.

3.4.3 Speciation analysis: dual column system

The chromium speciation was investigated using dual mini-column system. The first column was packed with 20 mg of Si-Amidoxime and the second column was packed with 50 mg of Si-Benzothiazole. The mixture of Cr(III) and Cr(VI) solution at pH 4.0 was passed through dual mini-column. Cr(VI) was collected on Si-Amidoxime whereas Cr(III) was collected on Si-Benzothiazole. The chromium speciation pathway is illustrated in Figure 3.1.

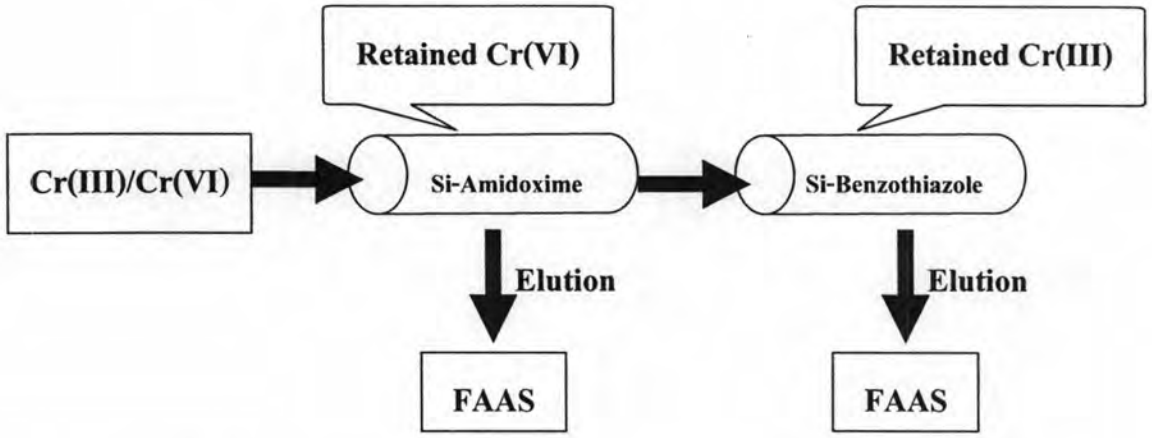


Figure 3.1 Speciation of chromium pathway using dual mini-column system

In this part, the chromium speciation study was investigated with synthetic sample by the following manner:

A solution (100 mL) containing 150 μg L^{-1} Cr(III) and 250 μg L^{-1} Cr(VI) at pH 4.0 was passed through a dual mini-column with a flow rate of 0.5 mL min^{-1} controlled with a peristaltic pump. The retained chromium species in each column was eluted by 5.0 mL of 10 % (v/v) H_2O_2 in 0.1 M NaOH at a flow rate of 0.5 mL min^{-1}. The amount of chromium in the eluted solution was determined by FAAS. This experiment was performed in triplicate.

Individual chromium solutions were performed in the same manner.

3.4.3.1 Method development

Optimization of the most influential parameters should be undertaken. Obviously, optimization should initially be performed using spiked synthetic solutions, but it must be followed by the use of certified reference materials or spiked real sample as matrix components (such as ligands or other ions) may change the trace element retention on the sorbent, thereby decreasing recoveries of the considered species may result.

The validation data required are accuracy, precision and limit of detection. The accuracy is calculated as percent recovery, describing the capability of the method to recover a known amount of analyte added to a sample. The precision can be described by relative standard deviation. The limit of detection is calculated by standard deviation of at least 7 measurements of a reagent blank. The procedure using spiked synthetic solutions is performed by repeating the same experiment, as described in section 3.4.3, in 6 replicates. The procedure using spiked real sample is followed:

Drinking water (100 mL) spiked with 500 µL of 30 mg L^{-1} Cr(III) solution and 500 µL of 50 mg L^{-1} Cr(VI) solution was adjusted pH to 4.0 and then passed through a dual mini-column with a flow rate of 0.5 mL min^{-1} controlled with a peristaltic pump. The retained chromium species in each column was eluted by 5.0 mL of 10 % (v/v) H_2O_2 in 0.1 M NaOH at a flow rate of 0.5 mL min^{-1}. The amount of chromium in the eluted solution was determined by FAAS. This experiment was performed in 6 replicates.