CHAPTER 2

Experimental

2.1 Instruments and Apparatus

The apparatus and instruments used are listed below:

1. Peristaltic pump: two-channels (MP-3N); EYELA, Japan
   : three-channels (SMP-23S); EYELA, Japan
2. Rotary injection value: six-ports; home-made injection valve
   : six-ports; GC injection valve
3. Spectrophotometer: Hitachi U-2000, Japan
4. Spectrophotometer: Spectronic 21 Milton Roy Company, USA
5. Atomic absorption spectrometer: AA-680, Shimudzu, Japan
   : AA-275 Series, Varian techtron, Australia
6. Chart recorder: Servograph Pen Drive REA-310, Denmark
7. Flow through cell: 178.711-QS, Hellma, Geramany
8. pH-meter: 5986-2S, Cole-Parmer, Taiwan
9. Shaker bath: GFL (Gesellschaft Für Laboratechnik mb M D3006 Burgwedel), Germany
10. Microwave digester: Multiwave, Microwave Sample Preparation System, Paar Physica, Austria
11. Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES): Perkin Elmer DV 3300, USA

2.2 Chemicals

All chemicals were analytical grade, listed as follows:

1. Nitroso-R salt (Disodium 1-nitroso-2-napthol-3,6-disulfonate), $C_{10}H_5NNa_2O_8S_2$, Merck, Germany
2. Sodium Hydroxide, $NaOH$, Merck, Germany
3. Sodium Chloride, $NaCl$, Fluka, Switzerland
4. Sodium Nitrate, $NaNO_3$, BDH, England
5. Sodium Acetate, $CH_3COONa.3H_2O$, Carlo Erba, Italy
6. Sodium Fluoride, NaF, Merck, Germany
7. Calcium Carbonate, $CaCO_3$, Merck, Germany
8. Potassium Chloride, KCl, Merck, Germany
9. Lead(II) Nitrate, $Pb(NO_3)_2$, Standard AAS 1000 mg/l, Merck, Germany
10. Zinc(II) Nitrate, $Zn(NO_3)_2$, Standard AAS 1000 mg/l, Merck, Germany
11. Magnesium Nitrate, $Mg(NO_3)_2$, Standard AAS 1000 mg/l, Merck, Germany
12. Manganese Nitrate, $Mn(NO_3)_2$, Standard AAS 1000 mg/l, Merck, Germany
13. Copper(II) Nitrate, $Cu(NO_3)_2$, Standard AAS 1000 mg/l, Merck, Germany
14. Iron(III) Nitrate, $Fe(NO_3)_3$, Standard AAS 1000 mg/l, Merck, Germany
15. Chromium(III) Nitrate, $Cr(NO_3)_3$, Standard AAS 1000 mg/l, Merck, Germany
16. Sodium Dihydrogen Phosphate Dihydrate, $NaH_2PO_4.2H_2O$, Merck, Germany
17. Sodium Sulphate, Na_2SO_4, Carlo Erba, Italy
18. Sodium Nitrite, $NaNO_2$, Carlo Erba, Italy

19. Nickel(II) Nitrate Hexahydrate, $Ni(NO_3)_2.6H_2O$,Carlo Erba, Italy
20. Cobalt(II) Chloride Hexahydrate, $CoCl_2.6H_2O$, BDH, England
21. Nitric Acid 65% (w/v), HNO_3, Merck, Germany
22. Glacial Acetic Acid 99.8% (w/v), CH_3COOH, Merck, Germany
23. Hydrochloric Acid 35.4% (w/v), HCl, Merck, Germany

2.3 Preparation of Standard Solutions and Reagents

All solutions were prepared with deionized water.

(1) The stock standard solutions of 10 and 100 mg/l copper(II). These standard solutions were prepared from a copper(II) solution for atomic absorption spectrometry (1000 mg/l; Merck, Germany).

(2) Working standard solutions. The more dilute working standard copper(II) solutions were prepared by appropriate dilution of the stock solutions [10 and 100 mg/l Cu(II)] with 1% (v/v) nitric acid or deionized water.

(3) Nitroso-R salt solution (0.4% w/v). This reagent solution was prepared by dissolving 0.40 g nitroso-R salt in water and adjusting to a volume of 100 ml. Further dilutions were made for appropriate concentrations.

(4) Acetate buffer pH 7 (0.5 M)

The buffer solution was prepared by dissolving 67.6641 g of sodium acetate in 800 ml of deionized water and 2.8 ml of 1 M acetic acid. Then the solution was adjusted the pH to 7 with 1 M NaOH or 1 M acetic acid and diluted to 1 l with deionized water.

(5) Eluent solution (2% (w/v) $NaNO_3$)

It was prepared by dissolving 2 g of sodium nitrate in deionized water then the solution was adjusted to 100 ml.

2.4 Procedure

2.5.1 FIA Spectrophotometric Determination of Copper Using Nitroso-R Salt as a Complexing Agent

Figure 2.1 shows a flow diagram of the FIA spectrophotometric determination of copper(II) system, which is a two channels FIA manifold consisting of a merging-zone system with two streams, acetate buffer solution (B) and nitroso-R reagent solution (C), having the same flow rate of 3.2 ml/min. A 103 μl sample solution (S) is injected into the system via an injection valve and mixed with the reagent in a mixing coil (1.5 diameter, 30 cm long) (M) where the complexation reaction takes place. The resulting colored complex is then passed through the flow cell in the spectrophotometer where the absorbance is measured at 492 nm.

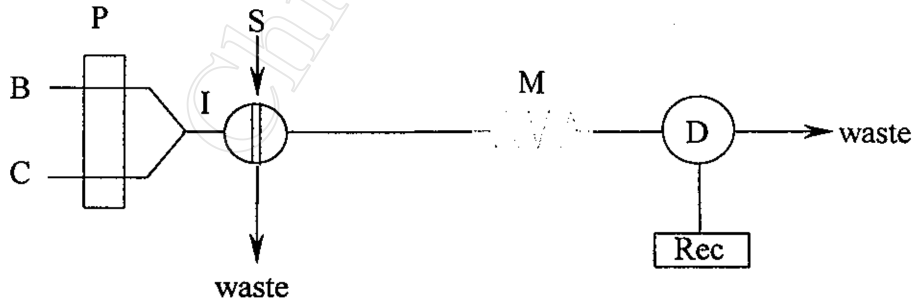


Figure 2.1 Flow injection system for the determination of copper(II). S, sample; B, acetate buffer pH 7 (0.5 M); C, nitroso-R reagent (0.04% w/v); P, peristaltic pump; I, home made injection valve; M, mixing coil; D, spectrophotometer; and Rec, recorder.

(1) Procedure for decomposing copper ore samples

A suitable amount of the ore sample (0.5 g) was accurately weighed and transferred into a 250 ml glass beaker. Then 25 ml concentrated nitric acid was added, the beaker was covered with a watch glass and heated gently on a hot plate to approximately 80°C. After each sample solution was evaporated to near dryness. The solution was cooled to room temperature, a further 50 ml of 1% (v/v) nitric acid was added and warmed for 10 min. The solution was then filtered through a Whatman No. 40 filter-paper into a 200 ml volumetric flask and diluted to the mark with deionized water.

(2) Procedure for collecting and treatment of wastewater samples

Industrial wastewater samples were filtered through a 0.45 μm membrane filter at the site where the water samples were collected and stored in polyethylene plastic containers that has been previously washed with 10% (v/v) nitric acid and rinsed with deionized water. After filtration, a 5 ml volume of concentrated nitric acid was added to each liter of water sample. A 50 ml portion of the treated water was pipetted and transferred into a 100 ml beaker, followed by 5 ml concentrated nitric acid; the mixture was carefully heated on a hotplate to the lowest possible volume (about 10 ml). After the solution was cooled, a 20 ml volume of water was added. The sample was transferred into a 100 ml volumetric flask (filtered if necessary) and diluted to the mark with deionized water. Appropriate dilutions of the digested samples were made prior to injection into the FIA system.

2.5.2 Study of Copper Adsorption on Perlites and Synthetic Zeolites from Perlites as Packing Material for FIA on-line Preconcentration Column

(1) Preparation of perlite materials

The natural and expanded perlite samples were obtained from Thai Tridymite Co., Ltd. (Thailand). The starting material was ground to approximately 100 mesh, then sieved by a 100-mesh sieve. The perlite fines (less than 100 mesh) were then washed with hydrochloric acid solution and deionized water until the pH of the effluent was about pH 7. The solid thus obtained was filtered and dried at temperature of 100-110°C for 2 hours.

(2) Zeolitization [122]

The zeolite was prepared from perlite by treatment of 30 g perlite with 150 ml of NaOH solutions (100 mg/l) and heated under reflux at a temperature of 90°C for 3 hours in closed system. The residues obtained from the reaction were filtered and washed with deionized water. The product of synthetic formed was then dried in oven at 110 °C for 2 hours and kept at room temperature in the desiccator.

(3) Procedure for sorption characteristic

Appropriate volume (50 ml) of each copper standard solution in the concentration range of 2.0-10.0 mg/l was added to 0.2 g of the sorbent in a plastic bottle and shaken in a mechanical temperature controlled shaker bath with a speed of 160 rpm at various pH (1-7) and at temperatures 22-40°C for different retention times (10-80 min). At the end of the predetermined time interval the sorbents were removed by filtration. The copper(II) ion concentration in the supernatant was measured by FAAS. Blanks were also prepared to find out the adsorption onto the internal surface of the bottles, if any. The effect of pH on the sorption phenomenon, was studied by adding either 1 M. HCl or NaOH in to the copper(II) solutions to obtained the required pH range. The influence of a specific process parameter was determined by calculating copper(II) ions uptake by perlites and synthetic zeolites, and changing that parameter and keeping other parameters constant. The mean of percentage retention of copper on the sorbent was calculated from duplicate experiments by using the equation:

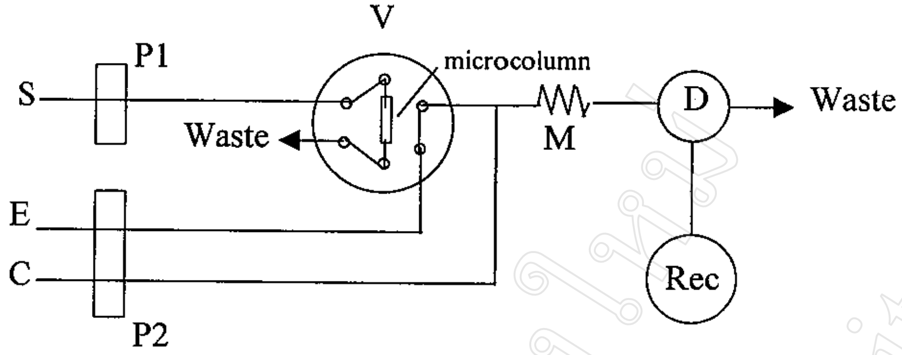
$$\text{Uptake, \%} = [(C_o - C_{eq}) / C_o]\ 100$$

Where C_o and C_{eq} are initial and the equilibrium concentrations respectively **[123]**.

2.5.3 FIA On-line Column Preconcentration for Trace Copper Determination

The FIA manifold for on-line column preconcentration of copper(II) is illustrated in Figure 2.2. The sorbent column is nested within the six-ports valve. Pump 1 (P1) loads the sample or standard solution (2 min of load time) to sorbed copper(II) ions on to the column with flow rate 3.1 ml/min during the load cycle, while pump 2 (P2) provides a constant flow at 2.4 ml/min of eluent solution (2% (w/v) $NaNO_3$) (E) and nitroso-R reagent (0.02% w/v) in acetate buffer pH 7 (0.5 M) (C) at 2.6 ml/min to the detector to establish a baseline. During the injection cycle, pump P1 is stopped, while P2 propels the eluent through the micro-column with 0.5 min elution time, allowing the concentrated copper(II) ions to be eluted from the column into the coloring reagent stream (C) and mixed with the reagent in the mixing coil (1.5 diameter, 20 cm long) (M) where the complexation reaction is taken place. The resulting complex is passed through the detector (D) where the absorbance is measured at 492 nm.

Load



Inject

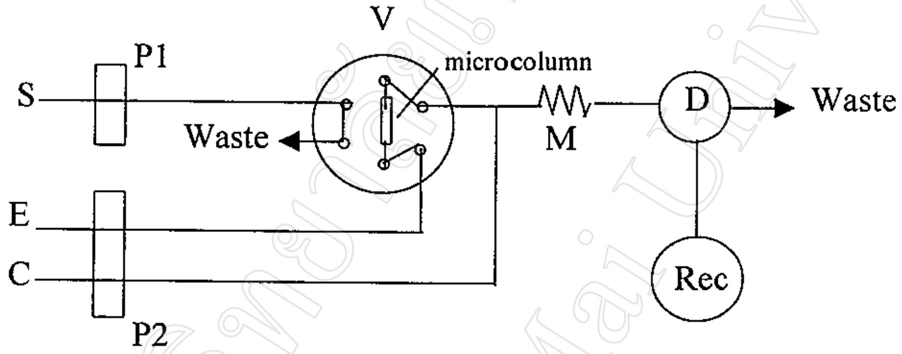


Figure 2.2 Flow manifold used in the on-line column preconcentration for the determination of copper(II) with both load and inject configurations shown. S, sample; C, nitroso-R reagent (0.02% w/v) in acetate buffer pH 6-7 (0.5 M); E, eluent; P1 and P2, peristaltic pumps; V, six-ports injection valve; M, mixing coil; D, spectrophotometer; and Rec, recorder.

(1) Pretreatments of Drinking Water Samples

The drinking water samples used were first filtered through a Whatman No. 40 filter-paper into a 250 ml volumetric flask to remove any particles which might be present in the water samples. The samples were spiked with 1 ml of a 10 mg/l copper(II) standard solution then the pH was adjusted to about 2.5-3.0 using 1% (v/v) HNO_3 and diluted to the mark with deionized water.

(2) Microwave Digestion of Mining Discharge Water Samples.

A 45 ml of mining discharge water was pipetted in each quartz vessel and 5 ml concentrated HNO_3 was added. The vessels were closed and put microwave oven and a PAAR programme's PAAR001M (Table 2.1) was set. After cooling at room temperature the vessels were opened and the product was transferred to a 50 ml volumetric flask and dilute to volume with deionized water.

Table 2.1 Microwave digestion parameters for mining discharge water samples by PAAR method's No. PAAR001M.

Step	**Time (min)**	**Power (w)**
1	5	500
2	20	1000
3	15	0

Note. Total time for eight samples was 40 min.
Eight samples per cycle.