CHAPTER 2

EXPERIMENTAL

2.1 Instrumentation

2.1.1. Instrumentation for Flow Injection Analysis

The flow injection system used in this thesis is shown in Figure 2.1 and the diagram of the complete system is shown in Figure 2.2. The essential components of the system may be described as follows.

2.1.1.1 Peristaltic Pump

A ISMATEC SA Peristaltic Pump (IPN/S 4-16) with eight-channels provided with a continuously variable speed controller to vary the total flow rate, was used for the flow injection system. The flow rate in each channel was controlled by varying size of the corresponding pump tubing. The pump tubings were Tygon tube with color code to indicate maximum flow rate.

2.1.1.2 Injection Port

A conventional septum-injection valve from a normal liquid chromatography (Figure 2.3) was used as injection port. It was made from stainless steel with internal diameter 1.0 mm..

Figure 2.1   The experimental Flow Injection System used in this
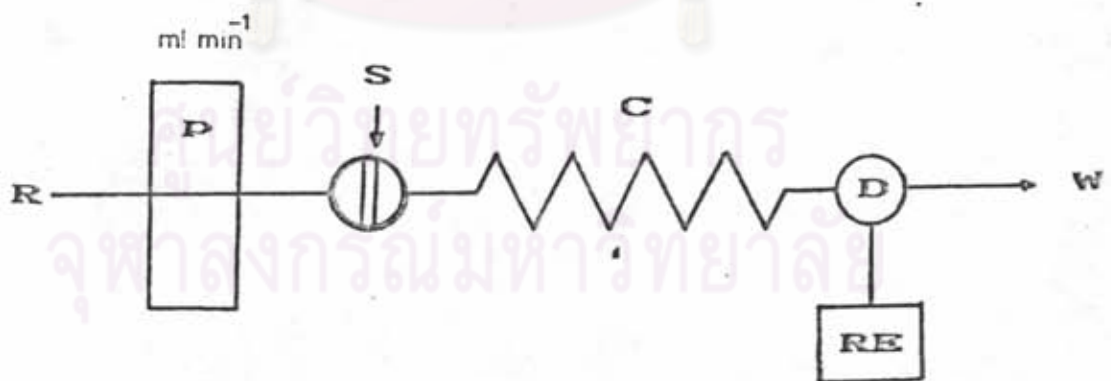thesis.

Figure 2.2   The diagram of the complete flow injection system,
R=carrier solution; P=pump; S=injection port; C=coil;
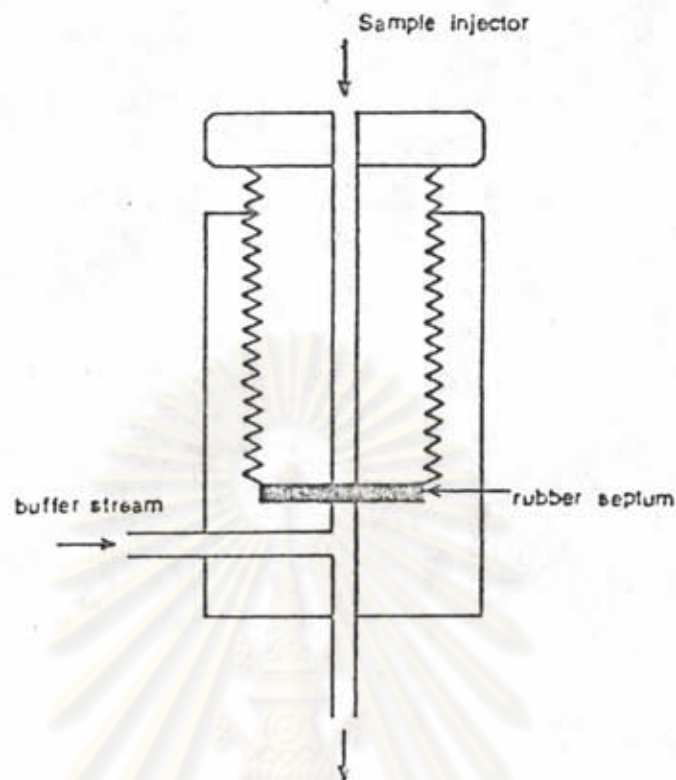D=detector; RE=recorder; W=waste.

Sample injector

buffer stream

rubber septum

Figure 2.3 Injection port for the flow injection system.

2.1.1.3 Mixing Coils

The mixing coils were made of Teflon tubing and coiled by winding an appropriate length around a glass tube (diameter 33.5 mm.o.d.).

2.1.1.4 Flow-Through Cell

The designed flow-through cell used in this thesis is shown in Figure 2.4. It was made of perspex glass with 10.0 mm. thickness, bored horizontally with a high speed drilling motor from one side to the other. It was then drilled vertically with the 0.10 mm. borer from the top to join the previous bore to get the inlet and outlet of sample solutions. The body was blacken cautiously

with color and covered the horizontal bore with transparent glass. So the flow-through cell volume computed from internal diameter and pathlength was 80 uL. The body of flow-through cell was glued to aluminium case in order to connect its inlet and outlet with tubing of sample by the use of screws.
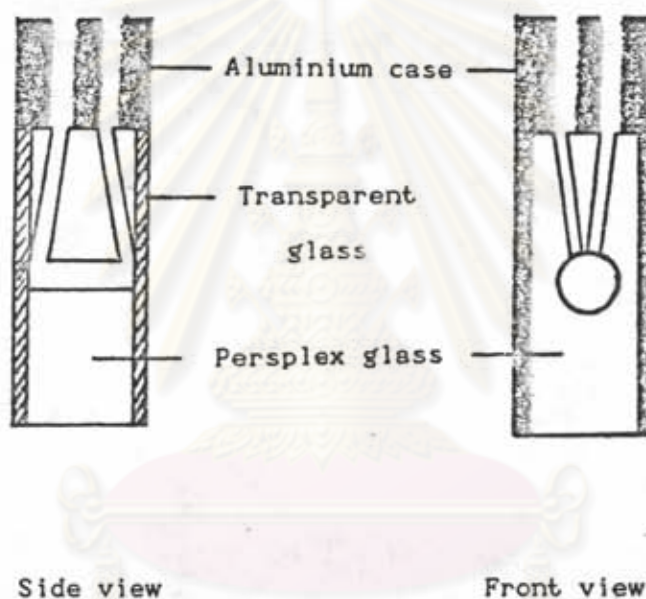

Side view   Front view

Figure 2.4 The designed flow-through cell for the flow injection system.

2.1.1.5 Detector and Recorder

The BAUSCH & LOMB (Spectronic 21) spectrophotometer, fitted with a 75 uL commercial flow-through cuvette cell 10.0 mm. pathlength was used and connected to a PERKIN-ELMER 56 stripchart recorder.

2.1.2 Other Instrumentation

2.1.2.1 The ENDECOTTS 100 mesh sieve (ASTM E 11-70) was used for screening samples by hand and the samples were fused in HERAEUS 1200 °C furnance.

2.1.2.2 Hamilton micro-syringes (10,100 and 250 uL) were used for the injection of the sample solution into the carrier stream for the flow system.

2.1.2.3 A Sartorius balance, no. 1602 MP8-1 was used for weighing samples quantitatively.

2.1.2.4 The Baird & Tatlock water bath was used for controlling temperature of the mixing coils and depolymerising silicic acid.

2.1.2.5 The ultrasonic cleaner (Kaijo Denki) was used for cleaning microsyringes.

2.1.2.6 Mortar grinder (Retsch type RMO) was used for pulverising and homogenizing synthetic kaolin and lateritic soil.

2.1.2.7 Platinum and zirconium crucibles were used for fusing kaolins and lateritic soils, respectively.

2.2 Reagents and Stock Solutions

All reagents used were analytical reagent grade and all water used was triple distilled water. Alizarin red S, thioglycolic acid

(mercaptoacetic acid) and ammonium heptamolybdate used were FLUKA reagents. The other chemicals used were BDH reagents.

2.2.1 Reagents for alumina analysis

2.2.1.1 Ammonia solution (3 N) was prepared by adding 14.5 mL of ammonia solution (sp.gr. 0.91) into 250 mL distilled water.

2.2.1.2 Acetic acid (5 M) was prepared by adding 9.5 mL of glacial acetic acid (sp.gr. 1.05) into 100 mL distilled water.

2.2.1.3 Calcium chloride (14 g/L) was prepared by dissolving 12.50 g. of calcium carbonate in 50 mL 1:1 hydrochloric acid and diluting to one litre with distilled water.

2.2.1.4 Alizarin red S (0.10 g.) was dissolved in water, filtered off the small amount of sediment and made up to a 100-mL with distilled water. Twenty-five mL of this 0.10 % stock solution was adjusted to pH 4.50 with 50.0 mL of 5 M acetic acid and 25.0 mL of 3 M ammonia solution and made up to a volume of 500 mL with distilled water.

2.2.2 Reagent for Silica Analysis

Ammonium heptamolybdate (0.375 %) was prepared by dissolving 3.75 g in 0.20 M sulfuric acid and made up to a volume of 1-litre with the same acid. This solution can be used after standing overnight in a plastic bottle.

2.2.3 Reagent for Iron Oxide Analysis

Ten mL of thioglycolic acid was added into water, neutralized with diluted ammonia solution and made up to a volume of 100-mL with distilled water. Ten mL of this 10.0% stock solution was added into 50.0 mL of 3 M ammonia solution and made up to a volume of 500-mL with distilled water.

2.2.4 Stock standard solutions

Aluminium stock solution (1000 ug/mL) was prepared by weighing accurately 1.0000 g of pure aluminium wire in 20.0 mL of 6 N hydrochloric acid, heating until clear solution was obtained, cooling and diluting to 1 litre with distilled water.

Iron stock solution (500 ug/mL) was prepared by weighing accurately 0.5000 g of pure iron wire in 500-mL beaker, adding 30.0 mL of 6N hydrochloric acid and 1.0 mL bromine water, boiling to expel excess bromine, cooling and diluting to 1 litre with distilled water.

Silicon stock solution (500 ug/mL) was prepared by fusing 5.0 g of sodium hydroxide in zirconium crucible, cooling and weighing accurately 0.5348 g (99.8 percent content silica) of quartz powder in the previous crucible and then fusing again for 3-5 min. The crucible was cooled, extracted the melt with water and diluted to the volume in a 500-mL volumetric flask with distilled water.

2.3 Procedures

2.3.1 Synthetic composition of kaolin

In general, kaolin consists substantially of natural kaolinite [hydrous aluminium silicate $(H_8Al_4Si_4O_{18})$] that has an ideally chemical composition of Al_2O_3, 39.5 % and SiO_2, 46.5 %. However, in nature, kaolin is found to contain kaolinite, quartz, mica and iron oxide, and the typical chemical composition of kaolins (45) are Al_2O_3 38.8 % (range 37.0 % to 42.0 %), SiO_2 45.4 % (range 48.0 to 43.0 %), Fe_2O_3 0.30 % (max 0.50 %), TiO_2 1.50 % (max 2.00 %), and other oxides. In this thesis, the synthetic composition of kaolin has the chemical composition as follows:

$$SiO_2, \% = 50.0$$
$$Al_2O_3, \% = 45.0$$
$$Fe_2O_3, \% = 1.50$$
$$TiO_2, \% = 1.00$$
$$MnO_2, \% = 0.50$$
$$CaCO_3, \% = 0.50$$
$$MgSO_4, \% = 0.50$$
$$K_2CO_3, \% = 0.50$$
$$NH_4HPO_4, \% = 0.50$$

The synthetic kaolin was prepared by weighing accurately dry standard chemicals of quartz, alumina, iron oxide, etc. into a mortar grinder and then grinded until they became homogenous.

2.3.2 Synthetic composition of lateritic soil

Lateritic soil consisting of sesquioxides of iron and aluminium as compared to other constituents is the main characteristic of the lateritic soil. These constituents sometimes have Al_2O_3 higher than 60.0 % and a little amount of Fe_2O_3, and sometimes have Fe_2O_3 higher than 80.0 % and only little amount of Al_2O_3. The analysis of some Thailand laterites by Pendleton and Sharasuvana (46) in various types were found an average percentage of silica, alumina and iron oxide were 32.8%, 16.2% and 38.7% respectively. In this work, the chemical composition of the synthetic lateritic soil is described as follows:

$$SiO_2 \quad \% \quad = \quad 35.0$$

$$Al_2O_3 \quad \% \quad = \quad 17.0$$

$$Fe_2O_3 \quad \% \quad = \quad 40.0$$

$$TiO_2 \quad \% \quad = \quad 2.00$$

$$MnO_2 \quad \% \quad = \quad 1.50$$

$$CaCO_3 \quad \% \quad = \quad 1.50$$

$$K_2CO_3 \quad \% \quad = \quad 1.00$$

$$MgSO_4 \quad \% \quad = \quad 1.00$$

$$NH_4HPO_4 \quad \% \quad = \quad 1.00$$

This synthetic lateritic soil was prepared similar as the synthetic kaolin in section 2.3.1.

2.3.3 Sample preparation for Classical Analysis

The sample had to be quartered until approximately 100 g of sample was obtained and then the size of the sample was then

reduced with a mortar by hand until all of it can pass through a 100-mesh sieve. After thoroughly mixing, the sample must be dried to a constant weight at 105 °C and stored in an airtight glass container. This sample must be weighed rapidly from the container to avoid change in moisture content.

2.3.3.1 Sample preparation for the determination of alumina, silica and iron oxide in kaolin

Sample preparations for alumina and iron oxide analyses in kaolin were based on the standard method of ASTM D 718-86 (5) and of ASTM D 717-73 (45), respectively as described below:

A dried sample is weighed accurately 1.00 g in a platinum crucible and carefully mixed with 5.0 g of sodium carbonate. The crucible is heated until the entired contents are completely fused in a molten state and then the temperature of 1100°C is maintained for 20 min. When the fusion is complete, the crucible is cooled and its contents are rinsed quantitatively with hot water into 600-mL pyrex beaker and boiled until the melt is disintegrated. The solution is carefully acidified with concentrated hydrochloric acid by keeping a watch glass over the beaker to avoid loss by spattering, and then excess of 1:20 HCl:water (by volume) is added. Evaporation to dryness on a steambath is carried on until the material appears completely dry (no odor of HCl detected). The evaporation is repeated and baked for 1 hour in an oven at 105°C. The residue is drenched with 25.0 mL of concentrated HCl and followed by 175.0 mL of water and then boiled until all soluble salts are dissolved. Silica is filtered with a Whatman paper. The residue is washed with diluted HCl and hot water. The filtrate is collected in a

250-mL volumetric flask for determination of other oxides. The paper and washed silica are transfered to a clean platinum crucible, ignited gently first until the filter paper was consumed, and then at 1200°C for 20 min, cooled and weighed. Silica is then determined by evaporating to dryness with 5 drops of concentrated H_2SO_4 and 15.0 mL of HF. The loss in weight of residue represented the SiO_2 can be calculated by the following relationship.

$$SiO_2, \text{percent} = \frac{\text{grams of } SiO_2 \text{ loss x 100}}{\text{grams of sample used}}$$

If an appreciable residue remains after the treatment with HF, it must be fused with a small amount of $K_2S_2O_7$ until it is dissolved. The pyrosulfate melt is leached out of the crucible with water and combined with the filtrate reserved before. The volume of the combined solution is diluted to 250 mL in a volumetric flask with distilled water.

One hundred mL of filtrate solution is transfered into a 500-mL beaker, added with 10.0 to 15.0 mL of concentrated HCl and a few drops of methyl red indicator solution (0.20% in EtOH), and heated to boiling. A concentrated NH_4OH solution is added dropwise until the last drop can change the color of solution to a distinct yellow. The solution containing precipitated hydroxides is heated to boiling for 1 or 2 min., filtered, and washed the precipitate on the filter with hot NH_4NO_3. The paper and precipitate are transfered to a weighed platinum crucible, heated slowly until the paper is charred and finally ignited to a constant weight at 1050°C to 1100°C. The mixed oxide (R_2O_3) is weighed as $Al_2O_3+TiO_2+Fe_2O_3$ and the percent of mixed oxide

was calculated from the following relationship.

$$\text{mixed oxide, percent} = \frac{\text{grams of } R_2O_3 \times 100}{\text{grams of sample used}}$$

The mixed oxides are generally consisted of the oxides of aluminium, iron, titanium, zirconium, phosphorus and so forth. For specially accurate work, the oxides of iron, titanium and other oxides must be determined and deducted to obtain the percentage of aluminium oxide .

The oxide of iron (Fe_2O_3) is determined by transfering 100.0 mL of the filtrate solution into a 250-mL Erlenmyer flask, adding small amount of concentrated HCl and evaporating to 50.0 mL volume. Ferric ion must be reduced to ferrous ion by adding $SnCL_2$ solution (5.0 g/100 mL) dropwise until the solution is decolorized and then adding 2 or 3 drops in excess. The solution of 10.0 mL saturated $HgCl_2$ is added to protected the excess of $SnCl_2$ from titration with dichromate ion. The total iron is determined by titrating the solution with 0.05 N $K_2Cr_2O_7$ solution by the use of sodium diphenylamine sulfonate as indicator to give an intense deep blue-violet end point. The percentage of Fe_2O_3 can be calculated as follows:

$$\text{Percentage of } Fe_2O_3 = \frac{[(N \times V \times 0.0798)] \times 100}{2.50 \times S}$$

where:

S = grams of sample used,

V = milliliters of $K_2Cr_2O_7$, and

N = normality of the $K_2Cr_2O_7$

The percentage of titanium oxide (TiO_2) was determined by transfering an aliquot containing 0.20 to 0.30 mg of TiO_2 into a 50-mL volumetric flask. For samples containing 0.50 to 3.0 per cent TiO_2, a 10 mL aliquot was suitable. The aliquot solution was added with small amount of concentrated phosphoric acid and 5.0 mL of 3% H_2O_2 and diluted to the volume with 1:9 $H_2SO_4:H_2O$. The colorimetric reading is obtained at 410 nm by using a prism or grating spectrometer and then compared with an appropiate set of TiO_2 standards similarly treated and plotted on a graph establishing a suitable curve for the instrument used.

The oxide of aluminium can be calculated from the percentage of mixed oxide as follows:

$$\% \ Al_2O_3 = \% \ R_2O_3 - (\% \ TiO_2 + \% \ Fe_2O_3)$$

where: $\% \ R_2O_3$ = percentage of mixed oxides

2.3.3.2 Sample preparation for the determination of alumina, silica and iron oxides in lateritic soils

Preparation of samples for alumina, silica and iron oxides in lateritic soils are based on an AWWA STANDARD for BAUXITE (AWWA B401-53) (10) described as follows.

A dried sample is weighed accurately 1.00 g in a medium-size casserole or pyrex beaker, added carefully with 60 mL of the acid mixture (485 mL of distilled water, 115 mL of concentrated sulfuric acid, 200 mL of concentrated hydrochloric acid,

200 mL of concentrated nitric acid). The reaction mixture is covered with watch glass and heated slowly until the liquid is driven off and sulfur trioxide fumes have been evolved for minutes. Approximately 100 mL of cold distilled water is added by pouring gently down the side of the casserole, using the watch glass to protect from spattering, and heated to boiling. The mixture is filtered through quantitative paper into a 250-mL flask and the residue is washed carefully with hot water. The residue and filtrate are kept for subsequent analyses as described in section 2.3.3.1 .

2.3.4 Sample preparation for Flow Injection Analysis

Five grams of NaOH is fused in zirconium crucible and cooled in dessicator. Accurately weighed 0.200 g. of kaolin or lateritic soil is put into the previous crucible, fused again for 3-5 min. and cooled to room temperature. The melt is extracted with water (filter if necessary), and then diluted to the volume of 250 mL with distilled water.

For silica analysis, a suitable aliquot containing about 5 mg Si is pipetted to 250-mL plastic beaker, The solution is converted to basic with sodium hydroxide pellet, warmed on a water bath for 5 min. The hydroxide precipitate is filtered off through the Whatman paper into a 50-mL volumetric flask, washed carefully with hot water, made to acid again with 1:1 sulfuric acid solution and diluted to the mark with distilled water.

For alumina analysis, a suitable aliquot containing about 0.75 mg Al is pipetted to 50-mL volumetric flask. The solution is converted to basic with ammonia solution (the

precipitate appears), then turned back to the acid again with acetic acid (the precipitate disappears) and finally diluted to the volume with distilled water.

For iron analysis, sample dilution is not necessary for kaolin. For lateritic soils, a suitable aliquot containing about 1 mg Fe is transfered into 50 mL volumetric flask and diluted to the volume with distilled water.

2.3.5 Response Studies

In order to achieve maximum sensitivity and sample processing rate, various parameters which have the effect on the sensitivity of the flow injection system including the flow rate of carrier stream, the length and diameter of mixing coils, the volume of injection sample, the time of analysis, etc. are studied.

2.3.6 Measurement of Flow Rate

Flow rates were determined by measuring the volume of reagent required in mL (by filled in graduated cylinder) from the system in a minute.

2.3.7 Measurement of Peak Height

Peak recording of samples were used to determine peak heights by measurement the distance between the peak summit and the base line. The height was converted into transmittance unit by the factor of peak height in full scale of 100 % transmittance and then converted to absorbance unit by the aid of computer.

2.3.8 Measurement of Carry-over

The degree of sample intersection between consecutive samples for a chosen sampling rate was expressed in terms of carry-over percentage, % CO, which is given by the following relationship:

$$\% \text{ CO} = \frac{\text{peak height (1') } - \text{ peak height (1)}}{\text{peak height (h)}} \times 100 \%$$

For carry-over measurements, test solution at low concentration (1), followed by a high concentration (h), and then a repeat of the low solution (1) [to give peak height (1')] were sampled consecutively at the chosen sampling rate.

2.3.9 Measurement of Reproducibility

The degree of reproducibility of 10 replicate measurements was expressed in terms of the relative standard deviation (RSD), given in the following relationship:

$$\text{RSD} = \frac{\text{standard deviation}}{\text{mean of 10 replicate measurements}} \times 100 \%$$

2.3.10 Measurement of Detection Limit

The detection limits were determined by measurement of the lowest sample concentration that can give the detectable peak .

2.3.11 Measurement the percentage of Recovery

The composition of synthetic samples were determined and then calculated, % recovery, by the following relationship:

% Recovery = $\dfrac{\text{mean composition of synthetic sample analysed x 100 \%}}{\text{real composition of synthetic sample}}$