



Chapter 1

Introduction

1.1 Introduction to Kaolins

Thailand has a long history of ceramics back to 7000 years ago when Banchiang earthenware appeared. More recent record is the production of Chinese-type glazed stoneware of Sukhothai reign at the end of the 13th Century. However, the active use of kaolin began in the last decade with regard to the rapid progress of ceramic industry. The first systematic investigation of kaolin deposits started in 1970 by Department of Mineral Resources. The data on the distribution, mineral composition and others are being accumulated.

Kaolin is a common raw material in Thailand. Pure and impure kaolin have been mainly used in ceramic industry, and to a lesser extent, in paper, paint, refractory, and insecticide industries. The name kaolin is derived from the Chinese term "Kauling" meaning high ridge, the name for a hill near Jauchau Fu, China, where the clay was mined centuries ago. China clay is ancient term originating from the use of clay, later found to be kaolinitic, in porcelain tableware and art objects in China. Apparently the first to use the name kaolinite for the mineral of kaolin were Johnson and Blake(1) (1867). The term kaolin is now variously used as a clay-mineral group, a rock term (consisting of more than one mineral), and industrial mineral commodity, and interchangeably with the term china clay. Kaolin may be defined as a clay derived by decomposition (weathering) of an

aluminous mineral such as feldspar, mica, etc. Ross and Kerr(2) (1931) defined that it is the rock mass which is composed essentially of a clay material that is low in iron and usually white or nearly white in color. The kaolin-forming clay are hydrous aluminium silicates of approximately the composition $2\text{H}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$, and it is believed that other bases if present represent impurities or absorbed materials. Kaolinite is the mineral that characterizes most kaolins, but it and other kaolin minerals may also occur to a greater or lesser extent in clays and other rocks that are too heterogeneous to be called kaolin.

Structurally, kaolinite consists of an alumina octahedral sheet and a silica tetrahedral sheet. These sheets form triclinic crystals. The theoretical composition of kaolinite is 46.54 % SiO_2 , 39.50 % Al_2O_3 , and 13.96 % H_2O . There is relatively little ionic substitution in the mineral lattice, although there is evidence suggestion minor substitution of iron for aluminium in some kaolinite.

The kaolin deposits of Thailand are genetically classified as (1) hydrothermal deposits, (2) sedimentary deposits, and (3) residual deposits(3). Kaolin deposits of hydrothermal origin occur as irregular zone, veintype and massive deposits and mostly embody granitic and rhyolitic rocks.

Hydrothermal deposits, this type of deposits was formed by hydrothermal alteration of rhyolite intrusive of post-Triassic ago. The rhyolite intruded into sedimentary rocks of Lampang group (Triassic) and Ratburi group (Permian). It underwent silicification following with kaolinization. Kaolinized rhyolite formed as irregular zone alternating with silicified rocks. The kaolinized rhyolite is

composed mainly of quartz kaolinite and illite, which together comprise from 70 to 90 percent of kaolinized rock. Fine mica, partial altered feldspar and rarely mafic minerals make up the remainder of the decomposed rock. One of the adjacent deposits of economic interest, Pangka, located 26 km north of Lampang province, northern Thailand is the biggest known kaolin deposit of this type. Hydrothermal deposit (Pneumatolysis), one of the most important kaolin deposits originated from pneumatolytic alteration of granitic rocks. Most of them are closely associated with cassiterite formation. The major kaolin deposit of this type occurs in 60 km long and 15 km wide granitic range in Ranong province, southern Thailand. At present, kaolins of Haad Sompan, Bangrin and Tungkha are only three active mines in this area.

Sedimentary deposits, several known kaolin deposits in Thailand are of this origin. They are predominantly flood plain deposits and subordinately lacustrine deposits. In general, the clays are fine to very fine grained with various colors: white, creamy, gray and black. They are semiplastic to plastic with considerable iron and titania content. "Maethan Clay" occurs in a small tertiary basin in the Metha district of Lampang province, northern Thailand.

Residual deposits, this type was formed by in situ weathering of various rock type. The important ones are granite, rhyolite and schist. Among these, weathered granite seems to be the most significant host in both quality and quantity. Residual kaolin derived from the weathering of Triassic granite occurs in Todeng village, Su-ngai Padi district of Narathiwat province, southernmost Thailand. The beneficiated kaolin of this type is high in quality and

suitable to use as paper filler and fine ceramic manufactures. The weathered rhyolite of post-Triassic is the host for illite formation. It occurs in Wangyang village, Muang district of Uttaradit province, northern Thailand. It is very fine grained and of white color. The wash illite is used as filler in paint, paper and insecticide manufactures. Residual clay derived from the weathering of schist (Devonian-Carboniferous) occurs in Khokmailai village of Prachinburi province, central Thailand. The white kaolin formation overlies the red kaolin formation under which the basement is schist. The washed kaolin of this area is used in the manufactures of pottery, refractory and as the filler in fertilizer industry.

For the economic evaluation of deposits, the probable reserves were estimated at 40 million tons for kaolin. According to this reserves, Thailand should be self-sufficient country for kaolin, especially for paper filler, paper coating, medicine and cosmetic has been traditionally met by imports.

There are two methods of quantitatively analyzing clay(4). One is known as the rational analysis and the other as ultimate or chemical analysis. In the rational analysis the composition of clay is expressed in terms of various mineral compounds present, such as kaolinite 62.40 %, quartz 28.00 %, total feldspar 8.30 %, etc. Calculations of the rational composition have been made from the chemical analysis but this method is open to criticism due to the false assumption that kaolinite, quartz, and feldspar are the dominant minerals. The chemical analysis of clay is a tedious and exacting procedure. In most cases its most effective usefulness is in providing a measure of the kinds and amount of impurities in the clay tested. The chemical composition of clay is usually expressed in

terms of the oxides the various elements, although they may be present in more complicated, and sometimes unknown forms. The chemical analysis of kaolin is usually used the method of ASTM D 718-86 (5).

1.2 Introduction to Lateritic soils

Bauxite is a generic term applied to a naturally occurring mixture of minerals rich in hydrated aluminium oxides(6). It is the raw material from which the most alumina used in the production of primary aluminium extracted. However, there are no commercial deposits of bauxite in Thailand but laterite and lateritic soil are of widespread occurrence. Laterite and lateritic soil are a superficial weathering product of various kinds of rocks and consist mainly of hydrated oxide of aluminium, and of oxides and hydrated oxides of iron, manganese, titanium and various other metals. Some laterites may contain more than 80 percent of iron oxide and little alumina while others may contain up to 60 percent of alumina and only a few per cent of iron oxides(7). In 1898, Bauer(8) shown that laterites are a possible source of aluminium. Some laterite containing high silica can be used as a source of aluminium by physical seperating of silica before used. Therefore, an analysis of chemical composition of laterites and lateritic soils in Thailand was made to search a possible source of aluminium.

Lateritic soil is often confused with laterite simply because the physical appearences and chemical properties are so similar. Laterite is a porous, indurated, concretionary material which is usually red to reddish brown in color. Lateritic soils vary in type form poorly grade sands to highly plastic clays and vary in color

from a red to a reddish brown. These soils characteristically exhibit some secondary iron cementation between grains; however, there are a wide variation in the degree of cementation. Although lateritic soils also harden upon drying, they soften readily upon wetting. The lateritic soils are finer grained materials than laterite and behave accordingly. An important physical difference between a laterite and lateritic soil, is that a laterite has a gravel component but a lateritic soil does not.

The name laterite is derived from Latin word Later which means "brick earth". This material was first observed and described by Buchanan(9) in 1807 during his travel through India. There are three types of laterite commonly encountered in tropical climate. Firstly, wormhole laterite (vermicular) is a massive concretionary formation with an iron-rich matrix and a slaggy or wormhole-like appearance. Pullet laterite (oolitic) consists of fine soil grains which are cemented by iron oxide into pullet-shaped particles. These pullet may be loosely consolidated or unconsolidated. The third type of laterite is a "soft-doughy" material of which hardness irreversibly upon exposure to alternate wetting and drying.

The utilization of lateritic soils have been evaluated by chemists and geologists as a source of iron and aluminium by using its chemical composition. The use of lateritic soils as a source of aluminium depends not only on its richness in alumina, but also on the presence of combined silica. The chemical analysis of lateritic soils is generally used a method of analysis of buaxite(10).

The determination of compositions of kaolins and lateritic soils by using the classical method is tedious analysis. The time of

analysis takes about 3 days for the determination of silicon and alumina. Large amount of reagents consumption were used in this method causes a high cost of analysis. Platinum crucible that must be used in this method was also very expensive. Therefore, an effort to evaluate the method of analysis on the basis of short time consumption of analysis, high accuracy and low cost of analysis was studied. Flow injection analysis is the method of analysis suitable for this object. It gives high accuracy and increasing speed of analysis. So, the use of flow injection analysis for the determination of alumina, silica and iron oxide in kaolins and lateritic soils is carried out in this thesis.

1.3 Flow Analysis

The ever-increasing demand for analyses in clinical, agricultural, pharmaceutical, industrial and other types of analytical control has led to the development of many different instruments for automated analysis. Developments in this field have been further stimulated by the additional advantages of automation, such as increased precision, decreased cost of individual assay, and the satisfactory reliability of automated equipment. The numerous instruments manufactured and suggested analysis of many individual sample solutions can be divided into two groups: batch analysers and continuous flow analysers.

Any wet chemical assay requires mixing of a precisely metered volume of a sample solution with a precisely metered volume of a reagent, followed by a time necessary to form a measurable product. Obviously, all operations must be precisely repeated each time; otherwise the conditions under which the standards and unknown have

been processed will not match, and the assays will yield erroneous results. It is the advantage of automation that a machine can perform these mundane tasks tirelessly and with superhuman precision.

In the batch analyser, the mechanization of these operations advanced along predictable lines. The small test tubes, to which sample (or standard) solutions were mechanically pipetted, were moved by a miniconveyor belt through sequentially arranged stations where reagent(s) were added and contents mixed (by shaking or stirring) and finally transferred into a detector for measurement. Therefore, cross-contamination is minimal, and this allows a high sampling rate. However, the disadvantage of such mechanics is complexity of their moving parts, which eventually become worn during use and are expensive to manufacture. The fast parallel analysers based on the transfer of samples and reagents by centrifugal force can be gave a higher sampling rates. This most interesting system, originally developed at the Oak Ridge National Laboratory(11), employs a rotor containing cavities to hold samples and reagents. By spinning at speeds of about $1200 \text{ rev min}^{-1}$, the solutions are mixed and transferred into set of fifteen cuvettes arranged radially; the cuvettes spin past the stationary beam of light of a photometer and the absorbances are displayed as a series of peaks on an oscilloscope. Thus, fifteen analyses are executed simultaneously, within 1-2 min, depending on the reaction rate, but the washing of the rotor and pipetting of the samples and reagents into their cavities also take some time. Yet, batch analysers find wide application, especially for one-component determinations in chemical laboratories.

Continuous flow analysers differ visibly from the above-mentioned batch analysers in that all samples move sequentially

through the same tubing (Figure 1.1). Samples from individual cups, placed in a carousel, are aspirated by a peristaltic pump. The moving stream is segmented by air, and the reagent streams join the segmented sample stream at strategic points along the main channel. Sample and reagent solutions are homogeneously mixed by multiple successful inversion of the solution segments as they pass through the mixing coils. Air segmentation was used to prevent carry-over of material from one sample to the next, and there has been a great deal of effort to make the air segmentation as effective as possible. Owing to the versatility of the continuous flow analysers, designed by Skeggs(12) more than 30 years ago, became the most successful tool of automation of serial assays. Today, Autoanalyser, which are based on Skeggs' idea and produced by Technicon, form an indispensable part of any clinical laboratory and find an increasing number applications in all other types of routine laboratory.

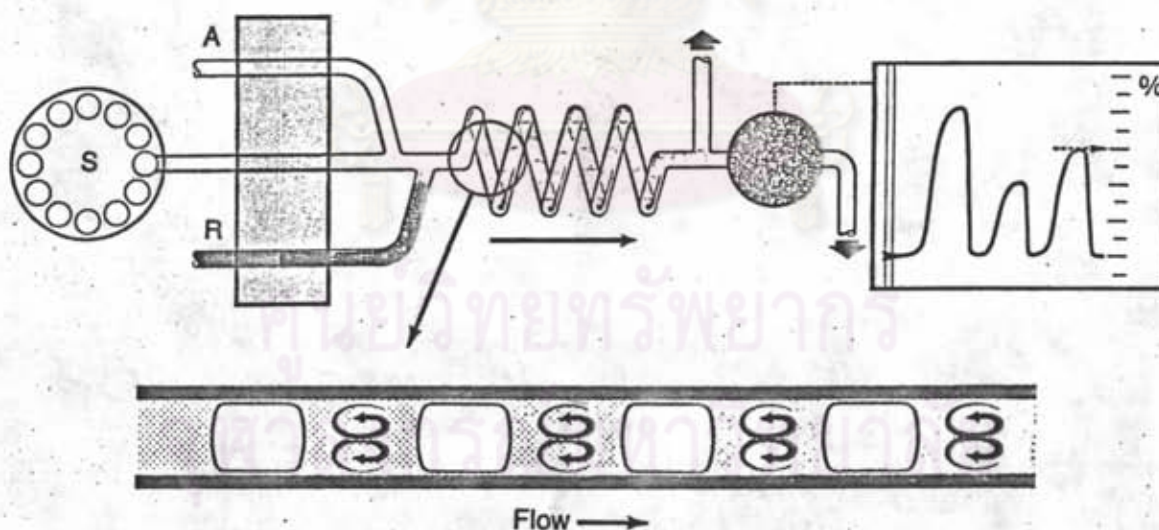


Figure 1.1 Schematic diagram of continuous flow analysis

A= air, S= sample and R= reagent.

From the Skeggs' concept of continuous, air-segmented flow which being truly ingenious, had resulted in the widespread use of

continuous flow systems for performing discrete chemical analysers. Thus, it became generally assumed that air segmentation and the attainment of the "steady-state" signal were essential prerequisites for performing continuous flow analysis. Yet, although the presence of air decreases the carry-over, this air also prevents miniaturization of the system and limits its usefulness: because of the inherent compressibility of air which causes the stream to pulsate; because the air has to be added to the stream and then removed prior to measurement; and because the air segmentation unselectively hinders dispersion of the sample zone with the sole aim of decreasing the carry-over.

Thiers et al.(13) were the first to make general observations on mutual sample interactions; their work, which was confirmed and extended by Walker et al.(14) remains the basis of quantitative considerations in determining the highest practicable sampling rate. To increase the sampling rate, which is usually around 60 samples per hour, two approaches have been used: (a) modification of the original continuous flow analysis design e.g. flow injection analysis; and (b) introduction of an appropriate correction factor(15) or even computer regeneration(16) of the recorded curve. The most significant changes in the design have been electronic rather than mechanical timing of the sampler, a rapidly moving sampling probe(17) a bubble-gating flow cell(18) or a computer-watched flow cell through which the air bubbles are allowed to pass. These innovations together with computerized curve regeneration(16), or even more recently rising curve slope computing techniques, lead to complex and inevitably more expensive instrumentation. However, the modification of the original continuous flow analysis by using unsegmented flow system, results in an increased in sample rate without complexity and

expensiveness of instrumentation. Therefore, this modification becomes popular for the high sampling rate of analysis.

1.3.1 Flow injection system

Since Skeggs' classic work, it has been assumed that air segmentation of the flowing stream and attainment of the steady-state signal are essential parts of continuous flow analysis. Ruzicka and Hansen(19) and Stewart et al.(20) have independently performed similar experiments of injecting the sample directly into a rapidly flowing carrier stream which has not been segmented by air. They have proved that analysis without air segmentation is not only possible but also advantageous and have termed it Flow Injection Analysis (FIA).

In 1970, a similar concept was also introduced by Nagy et al.(21) A sample solution was injected into a non-segmented stream of an electrolyte with a silicon-rubber based graphite electrode as a detector.

The theoretical basis, techniques, applications, and trends occurring in flow injection analysis have been extensively described by Ruzicka and Hansen(22). Since the publication of Betteridge's review(23) on flow injection analysis, the system has received steadily increasing recognition. A monograph(24), several reviews(25), and more than 800 papers(26) have been published on flow injection analysis.

Flow injection analysis has been considered as a hybrid of segmented flow analysis and high pressure liquid chromatography (HPLC)(27). The success of the method stems from the

use of controlled sample dispersion for mixing of sample and reagent. It allows high sampling rates with almost instant availability of the analytical readout due to short dwell times. In addition Ruzicka and Hansen(22) pointed out that the most important feature of the technique may well be the concept of controlled dispersion. The technique is founded on a combination of the following three principles: sample injection, controllable sample dispersion, and reproducible timing.

1.3.1.1 Sample Injection

The purpose of sample injection is to insert a discrete slug of sample into a continuous moving carrier stream in such a way that the movement of the stream is not disturbed. The amount of sample need not be known accurately but it must be introduced into the carrier stream precisely, so that the volume and length of the slug can be reproduced exactly from sample to sample. The injection techniques are more precise than timed aspiration, used in segmented-flow analysis. In early work, samples were injected with a syringe through a septum(19) or a flap valve(23). Later developments included rotary valves with bores as sample containers and various forms of loop valves of the type use in liquid-chromatography system(28).

In the absence of air segmentation, some of the sample zone will disperse into the reagent-containing carrier stream as it is swept through the narrow-bore tubing towards the detector. A clear understanding of this dispersive process is crucial to the design of efficient FIA systems. The concept of controlled dispersion, which is probably the most important aspect of this new

analytical technique, is described below.

1.3.1.2 Controlled Dispersion

Sir Isaac Newton observed that when water flowed slowly and steadily through a pipe the frictional forces between the layers of moving liquid established a longitudinal velocity profile. Under such conditions of laminar flow the layer of liquid in contact with the tube surface is practically stationary and the velocity of centrally placed molecules is twice the mean velocity of the liquid(29). This gives rise to a parabolic velocity profile. Diffusion of molecular between the carrier and sample bolus serves to limit the convective dispersion and effectively mixes sample and reagent.

Changes in mean flow velocity, tube diameter, monitoring distance, diffusion coefficient of analyte, or any combination of these will obviously alter the dispersion of the sample in the carrier stream as seen by the detector. Originally, the low carry-over of flow injection analysis was attributed to turbulent flow(19), but it is now recognized that flow injection analysis operates effectively only under conditions of laminar flow(23). Taylor(29) in 1953 studied the dispersion of a zone of potassium permanganate in a slowly moving stream of water and derived a mathematical description of dispersion as related both to convective flow and the molecular diffusion. His equations have been expanded(30) and recently Vanderslice et al.(31) have adapted this approach to flow injection analysis conditions to produce expressions for the dispersion and residence times of samples in terms of experimentally defined parameters. For example, the travel

time, t (in seconds), of sample is given by the expression:

$$t = \frac{109 a^2 d^{0.025}}{f} \cdot \frac{(l)^{1.025}}{q}$$

and for the baseline-to-baseline dispersion in time, At :

$$At = \frac{35.4 a^2 f}{d^{0.36}} \cdot \frac{(l)^{0.54}}{q}$$

where:

q = the flow rate (mL min^{-1}),

d = the molecular diffusion coefficient ($\text{cm}^2 \text{s}^{-1}$),

l = the tube length (cm),

a = the tube radius (cm),

f = a factor to account for the effect of concentration and detector sensitivity on t and At .

The volume dispersion, v , can also be calculated from $v=q At$.

Ruzicka and Hansen(22) borrowed the chemical engineering model of "tanks-in-series" to describe dispersion and concentration profiles in flow injection system, and to identify the main variables that can be manipulated to achieve the desired degree of mixing. The equation is the tanks-in-series model which is used to evaluate the role of all empirical parameters, except in the case of a flow injection system using the narrow tube for which Taylor's equation is most appropriate.

1.3.1.3 Timing

Reproducible timing is of the utmost importance in flow injection analysis. The time from introduction of the sample into the carrier stream until it is detected solely dependent on the pumping speed. Because there are no compressible air bubbles in the system, good reproducibility in timing is easily obtained with conventional peristaltic pumps. By adjusting the experimental variables, the residence time can be adjusted to give the required sample dispersion as well as sufficient time for the reaction to take place. Not only long but also extremely short residence times can be reproducibly maintained. Precise timing allows the concept of the steady-state to abandon, and the reaction is usually monitored before equilibrium is reached. Because the response curves do not reach the steady-state plateau and the samples pass through the detector quickly, the curves have the form of sharp peaks, which are characteristic of flow injection analysis. Any fluctuations in flow rate that effect the residence time of the sample in the system will result in imprecise peak heights.

1.3.1.4 Detection methods in flow injection analysis

Generally, many laboratory instruments can be employed as detectors in flow injection analysis provided that the instruments can be equipped with flow-through cell. A wide range of detection methods have been successfully used in flow injection analysis including spectrometric methods, electrochemical methods, kinetic methods, separation methods, etc(26). The broad acceptance of flow injection analysis is undoubtedly due to its

versatility, which allows the method to be used in conjunction with a wide variety of detectors and analytical techniques, and for the assay of a multitude of organic and inorganic substances. A closer look at the variety of detection principles used in conjunction with flow injection analysis in Figure 1.2 shows that optical methods (and particularly visible spectrometry) predominate(26). This is not surprising considering that spectrophotometry generally accounts for approximately 50 % of all detection principles used in analytical chemistry. In this thesis spectrophotometer was also used as a detector in conjunction with flow injection analysis .

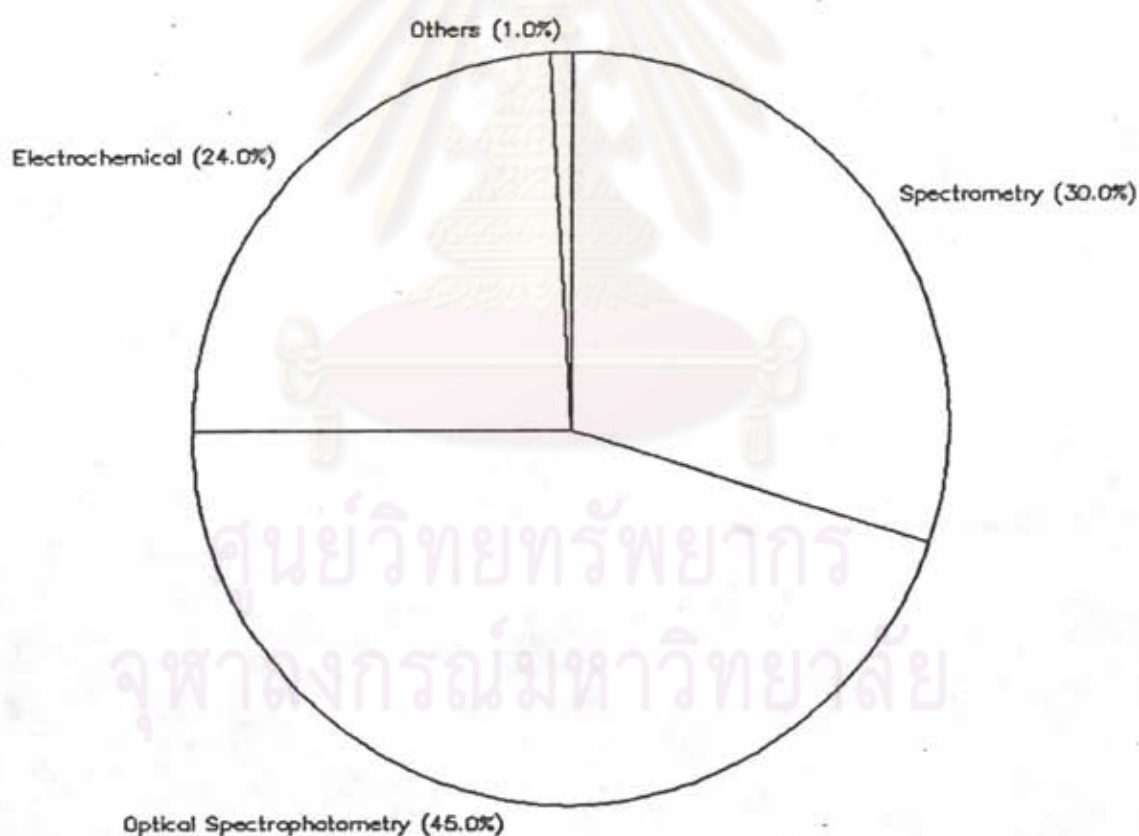


Figure 1.2 Distribution of the detection principles used in conjunction with flow injection analysis.

The most commonly used detector in flow

analysis is a colorimetric or a uv-vis. spectrophotometer. The concentration of a substance may be determined directly if it is color or indirectly if it is colorless by reaction with a chromogenic reagent. The flow injection system reported in this thesis was designed for determination of alumina, silica and iron oxide in kaolins and lateritic soils. The determination of aluminium by continuous flow and flow injection analysis in soils and water samples was reported by Zoeltzer and Schwedt(32). The interferences of iron(III) were eliminated by reduction with ascorbic acid and then aluminium was formed complex with chromazurol S. However, this method was not suitable for the determination of aluminium in a high content samples such as kaolins and lateritic soils as it will give a complexity in dilution of samples.

A sensitive spectrophotometric method for the determination of aluminium with bromopyrogallol red in the presence of n-tetradecyltrimethyl ammonium bromide has been proposed and applied to determine micro amounts of aluminium in natural waters. The adaptation of this spectrometric reaction of flow injection analysis for the determination of aluminium in river waters was made by Wyganowski and coworkers(33). This method was also not suitable for the determination of aluminium in kaolins and lateritic soils.

Edwards and Cresser (34) determined aluminium in natural waters, soil extracts and plant digests by continuous flow analysis. The automated colorimetric procedure is based on the complex formation between aluminium and xylenol orange. The procedure described obviates the need for separating of iron(III) by reverting to the use of EDTA masking, but employs an ethanolic

solution of the reagent and moderate heating at 55 °C to accelerate color formation and bleaching of iron complex. However, this method was not suitable for flow injection analysis as it would generate air bubbles and then caused erroneous when the system was heated to 55 °C.

The aluminon colorimetric method for determination of aluminium in soils and plant extracts was employed widely. Bertsch and coworkers(35) reported on analysis of aluminium by using automated method with aluminon procedure. This method employed ascorbic acid for removal of iron(III) interference. However, it was suitable for the analysis of aluminium not more than 1.2 ppm. Above 1.2 ppm of aluminium in solution, the standard curve deviates from linearity. Therefore, this method was not suitable for the determination of sample containing aluminium in high level.

A flow injection analysis procedure for the determination of total iron in natural water and plant digests by using 1,10-phenanthroline was described by Mortatti and coworkers(36). Burguera and Burguera(37) used this method followed by atomic absorption spectrometry for the determination of iron(II) and total iron. For the determination of total iron, iron(III) must be reduced to iron(II) with reducing agent such as ascorbic acid and therefore leads to the complexity in sample preparation.

Hongbo and coworkers (38) determined the total iron in soil extracts by flow injection analysis. The iron in soil HCl extracts formed complex with 2,2'-dipyridyl. Results were linear over the range 0 to 7.0 ppm and the detection limit was 0.02 ppm. However, this method was not suitable for the determination of total iron in sample containing high iron such as lateritic soils.

The method of yellow silicomolybdic acid was employed in conjugation with flow injection analysis for the determination of silicon in silicate rocks(39). Sample solution was prepared by fusing the silicate rock and then dissolving in 1 M HCl. The fusion solution was filtered through cation-exchange to isolate silicic acid and then depolymerized in alkaline solution. In the flow injection analysis, color development system was designed to accelerate the reaction by raising the temperature of mixing coil with water-bath to 50 °C. Although this method can be operated at the sample rate upto 70 samples per hour, it needs a long period of time for sample preparation.

Although there are several reagents used for the determination of aluminium, iron and silicon, the study of these reagents to select the best reagent in this thesis should be done. Table 1.1(40) shows the investigation of colorimetric reagents for aluminium analysis such as Eriochrome cyanide R, stilbazo, 8-hydroxyquinoline, alizarin red S, etc. With Eriochrome cyanide R, close control over time of standing is essential because the optical densities of both the aluminium complex and reference solutions decrease on standing and the results are of slight deviations from Beer's law. Stilbazo has similar deficiency however the deviations from Beer's law are slightly more severe. The complex compound of aluminium with 8-hydroxyquinoline is soluble in organic solvents, giving an intense yellow coloration. As the determination of aluminium is based on the photometric determination of the extract and the organic solvent employed in the extraction is usually chloroform, the complexes obtained in the chloroform will be darken in sunlight that lead to a consequent increase in the optical density

Table 1.1

RESULTS OF INVESTIGATIONS ON COLORIMETRIC REAGENTS

	Alizarin red S - calcium reagent 490 m μ	Arsenazo 580 m μ	Eriochrome cyanine R (Solochrome cyanine RS) 532 m μ	8-Hydroxyquinoline 392 m μ	Stilbaro 520 m μ
Optimum wavelength for colour measurement					
pH for colour development	4.4 to 4.65	6.1 to 6.8	Approximately 6.1	Extraction at pH 4.9 to 5.0	Approximately 6.8
Conformity to Beer's law. (Range tested shown in brackets.)	Conforms (0 to 80 μ g of aluminium per 100 ml)	Conforms (0 to 100 μ g of aluminium per 100 ml)	Slight but consistent deviations detected (0 to 60 μ g of aluminium per 100 ml)	Conforms (0 to 300 μ g of aluminium per 100 ml)	Deviations suggesting the existence of more than one compound (0 to 100 μ g of aluminium per 100 ml)
ϵ at optimum wavelength	1.8×10^4	1.2×10^4	6.75×10^4	6.7×10^2	3.8×10^4
Concentration range and cell size	0 to 80 μ g of aluminium per 100 ml in 2-cm cells	0 to 100 μ g of aluminium per 100 ml in 2-cm cells	0 to 60 μ g of aluminium per 100 ml in 0.5-cm cells	0 to 100 μ g of aluminium per 100 ml in 4-cm cells	0 to 70 μ g of aluminium per 100 ml in 1-cm cells
Interferences: Effect on optical density at optimum wavelength—					
(a) Beryllium	{ Slight increase 40 μ g Be = 1 μ g Al	{ Drastic increase 0.7 μ g Be = 1 μ g Al	{ Drastic increase 2 μ g Be = 1 μ g Al	None	{ Slight increase 40 μ g Be = 1 μ g Al
(b) Other elements listed on page 492 at levels specified	None	None. Higher levels of chromium cause increase	None. Higher levels of chromium cause decrease	None	None
Notes on reagent	The reaction of sodium alizarin sulphonate with aluminium in the presence of calcium ions has been used in analysis of rocks, slags and coal ash. ^{10,11,12}	The orange coloured aqueous solution forms a cherry-red complex with aluminium. ¹³ (The reagent used was from Tokyo Kasei Kogyo Co. Ltd., Japan.)	Acidified (nitrated) solutions of Merck's Eriochrome cyanine R and Gurr's Solochrome cyanine RS were found to give identical re- actions. This reagent has been widely used for aluminium deter- minations in steels. ^{3,4,7}	Aluminium hydroxy- quinolate is extracted from the aqueous phase with chloroform yielding a pale yellow solution. This reaction has been used in steel ¹⁴ and cast-iron ¹⁵ analyses.	The reaction with alu- minium to form a reddish brown complex has been used in steel analyses. ^{16,17}

and erroneous results (40). Aqueous reagent solutions of arsenazo and alizarin red S are stable, and the optical density of the aluminium complex remains constant in the interval from 1 to 4 hours after the development. This thesis is of the opinion that alizarin red S-calcium reagent is the most suitable colorimetric reagents and there was no report about it on determination of aluminium in the flow injection system.

Table 1.2 (41) shows the investigation of colorimetric reagents for iron analysis. Reagents which require adjustment of pH within a narrow range are obviously not very desirable. Thiocyanate is an extensively reagent for the determination of iron, but suffers from the disadvantage of giving a product of which the color fades rather rapidly. For the most accurate determination of minute amounts of iron, the use of 1,10-phenanthroline and 2,2'-bipyridyl are recommended. However, they are not suitable for the determination of total iron as they are colorimetric reagent for ferrous ion and therefore ferric ion in the sample solution must be reduced to the form of ferrous. This leads to complexity in analysis. Mercaptoacetic acid (thioglycolic acid) was a common colorimetric reagent for ferric and ferrous ion (42). The optical densities of this iron complex was stable for several hours. Absorption of the excess reagent and the deviation from Beer's law are not severe. Therefore, mercaptoacetic acid should be suitable reagent for determining iron with colorimetric detection and also there was no report about it on the determination of iron in the flow injection system.

For the determination of silicon, there are

Table 1.2 Properties of Some Reagents for the Colorimetric Determination of Iron^a

Reagent	Sensitivity, ^b γ Fe/cm. ²	Stability of color	pH range	Effect of excess reagent	Beer's law
2,2'-Bipyridine (α,α'-bipyridyl)	0.007 (522 mμ)	1 year	3-9	None	Obeeyed
2,2',2''-Terpyridine	0.005 (552 mμ)	1 year	3-10	None	Obeeyed
2,6-Bis(4-phenyl-2-pyridyl)-4-phenylpyridine	0.002 (583 mμ) in CHCl ₃ -C ₂ H ₅ OH	Stable		None	Obeeyed
4,7-Biphenyl-1,10-phenanthroline	0.0025 (533 mμ) in C ₂ H ₅ OH-H ₂ O	Stable		None	Obeeyed
Disodium-1,2-dihydroxybenzene-3,5-disulfonate	0.009 (480 mμ)	Months or years ^c	8.5->9.5 ^d	None	Obeeyed
Ferron	0.015 (610 mμ)	1-2 weeks	2.7-3.1	Change in hue	Not obeyed
Hydrochloric acid	0.018 (343 mμ); 0.008 (230 mμ)	Stable	6 N	Slight	Obeeyed
4-Hydroxybiphenyl-3-carboxylic acid	0.03 (575 mμ)	1 day	ca. 3	Increases intensity	Obeeyed
Mercaptosuccinic acid	0.014 (540 mμ)	Several hours	7-12	None	Obeeyed
Nitroso-R salt	0.0023 (720 mμ) 0.007 (620 mμ)	6 hours	3.9-5.1		Obeeyed
1,10-Phenanthroline	0.005 (508 mμ)	6 months or more	2-9	None	Obeeyed
Salicylaldoxime	0.011 (480 mμ)	1 day	6.2-6.6	None	Obeeyed
Salicylic acid	0.03 (520 mμ)	2-3 days	2.5-2.7	Increases intensity	Obeeyed
Sulfosalicylic acid	0.01 (430 mμ filter)	1 day or more	7		Obeeyed
Sulfuric acid	0.032 (320 mμ)	Stable	Strongly acid		Obeeyed
Thiocyanate	0.008 (480 mμ)	Fades rapidly unless stabilized	0.05->1 N	Increases intensity	Slight deviation
Thiocyanate and acetone	0.004 (480 mμ)	Fades	0.05->1 N	Increases intensity	Slight deviation
Thiocyanate and tributylammonium in amyl acetate	0.0025 (480 mμ)	1 day	3-4		Obeeyed
Versene-hydrogen peroxide ^e	0.13 (450 mμ)				

^a From various sources. ^b Number of micrograms of iron in a column of solution of 1 cm.² cross section giving an extinction of 0.001.

^c Color increases slightly first 18 hours, then constant. ^d Blue color in weakly acidic medium, which is less sensitive than red color in basic solution. ^e A. Ringbom, S. Siitonen, and B. Saxén, *Anal. Chim. Acta*, 16, 541 (1957). The complex, formed in basic solution, is believed to have the composition Fe(O₂)Y³⁻ or Fe(O₂)(OH)Y²⁻.

two photometric methods for this subject, yellow and blue silicomolybdic acid. In the yellow method, the photometric method was based on the ability of silicic acid to form yellow heteropoly acids with molybdate ions in acid solution. However, in the blue method, when reducing agents act on yellow heteropoly acids, intensely blue products of the reduction molybdenum are formed. Photometric determinations based on this reduction are about five times more sensitive than determinations of the yellow heteropoly acids(43). The reducing agent and the experimental conditions must be chosen so that the complexed molybdate alone is reduced and the excess of free molybdate remains unchanged. Strong reducing agents are not suitable for this purpose as they react not only with bound molybdate, but also with free molybdate and the obtained results for silicon will be too high. Weak reducing agents do not act on the excess molybdate, but they reduce silicomolybdic acid very slowly, and the reduction itself is often not quantitative(44). However, silicon contents in kaolins and lateritic soils are very high, therefore, the use of the blue method will not be necessary. The choice of method for determination of silicon in this thesis was the yellow method.

1.4 Aim of the thesis

It is the aim of this thesis to develop flow injection analysis for the determination of alumina, silica and iron oxide in kaolins and lateritic soils. The determination of alumina, silica, and iron oxide by classical method would need a long period of time for each sample, such as 3 days. By this classical method, chemicals consumption for each samples was high and expensive. Flow injection system is a simple, accurate and rapid analytical technique that makes it possible to carry out a large number of determination with

a minimum consumption of sample and reagents. Characteristics of the designed flow injection system for these analyses are reported using a spectrophotometer as a detector.

Firstly, in static solution, characteristic of the complex formation between colorimetric reagents and the studied ions were investigated to optimize condition for the flow injection analysis. The absorption ratios between complex and reagents were investigated. The effects of pH and temperature of medium solution on the rate of reaction and the limit of complex formation, and interference ions were also studied.

Secondly, the flow-through cell was homemade for the use in this thesis. The sensitivity of this flow-through cell was compared with the commercial flow-through cell. The suitable conditions studied in static solution were used in this flow injection analysis. Experimental parameters such as sample injection volume, carrier flow rate, coil length and coil diameter were investigated to optimize condition. Characteristics of recorded peaks were performed on sensitivity, linear range, reproducibility and detection limit.

Finally, application study was performed on the use of the flow system for the determination of alumina, silica, and iron oxides in some kaolins and lateritic soils in Thailand.