



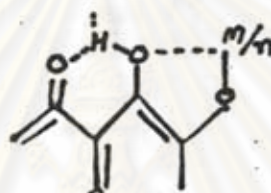
## CHAPTER IV

### CONCLUSIONS

The detailed studies presented in this thesis are a contribution to understanding of the Flow Injection Analysis (FIA). The system of flow injection analysis has been shown to be possible for the construction of a simple instrument for monitoring alumina, silica and iron oxide in kaolins and lateritic soils. Many laboratory instruments can be employed as detector in flow injection analysis provided that the instruments can be equipped with flow-through cell. In this work, the detection mode of study was spectrophotometry. Two types of cells, designed flow-through cell and commercial flow-through cell, were used in conjugation with the flow system. The construction of the designed flow-through cell was shown in this thesis. The relative performance of these two cells was evaluated on the basis of dispersion, sensitivity and peak tailing. The experimental factors for the colorimetric measurement by flow injection system such as carrier flow rate, injection volume, length and diameter of coil used have had to be optimized as a part of this thesis. The optimum conditions of these factors were used to determine alumina, silica and iron oxides in kaolins and lateritic soils.

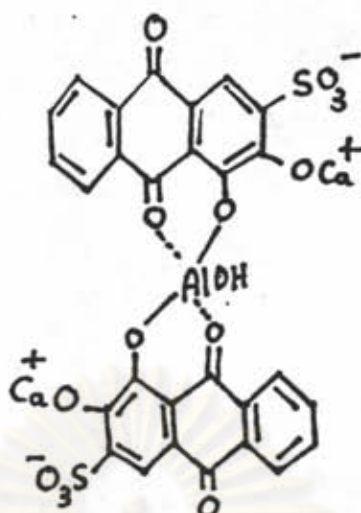
For the determination of alumina, alizarin red S was the better choice for colorimetric reagent in this determination. Complex formation between aluminium and alizarin red S was studied to determine the optimum condition. The absorption maximum of alizarin red S was at 435 nm while the absorption maximum of the complex was

at 490 nm. However, at the wavelength of 490 nm the absorption of reagent was also high and the absorption ratio of the complex to reagent at this wavelength was lower than that of 510 nm. Thus, the wavelength at 510 nm was used for the determination of aluminium to obtain the maximum sensitivity. Aluminium can react with alizarin red S in the ratio of 1:1, 1:2, or 1:3 depending on pH of solution. The structure of 1:1 chelates of alizarin or alizarin sulfonate can be presented as follow (50):



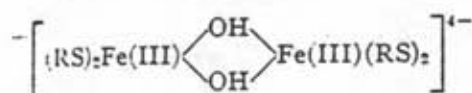
(M/n may be M-hydroxo species)

In the 1-position of alizarin red S, hydrogen on hydroxy group was replaced with M-hydroxo species to form quinoid with oxygen atom. The maximum color intensity is observed at pH 4.50 that agrees well with the experiment by Parker and Goddard (48). The color development takes about 5 min, and if the solution is heated to 60°C the development become more rapid. However, in the flow injection analysis, air bubbles will be generated and cause an error in the determination when the solution is heated to 60°C. In the study of interference ion, calcium and iron were found to give marked effect on the determination of aluminium. Calcium ion increased the absorption of Al-alizarin red S complex. The effect of the calcium ion is believed to form a complex with Al-alizarin red S and the following structure of this complex has been proposed (50).



However, if the calcium ion presence greater than 160 mg/L in the solution containing 1 mg/mL aluminium in 0.1 % alizarin red S, the absorption of the complex became constant. It can be concluded that at the concentration of calcium greater than 160 mg/L the calcium ion would be excess for the reaction with alizarin red S. Iron(III) and iron(II) can also formed complex with alizarin red S. This effect can be eliminated by masking with thioglycolic acid.

Ammonium thioglycolate that was commonly used as colorimetric reagent for the determination of iron, was unlike an alizarin red S that it was colorless reagent. The complex formation between iron and thioglycolate was very fast and the maximum absorption was at 535 nm. The complex formation was carried out in the medium at the pH range between 8.0-10.5. The structure of chelate of iron-thioglycolate can be presented as follows (42):



where RS refers to the divalent thioglycolate ion,  $-\text{SCH}_2\text{CO}_2^-$ .

Yellow silicomolybdate method was used in the determination of silica in kaolins and lateritic soils. Complex formation between silicon and molybdic acid was carried out in acid medium. The maximum absorption of silicomolybdate was at 355 nm, however, at this wavelength the blank absorption can not be adjusted to zero by using a single beam Spectronic 21. Therefore, the wavelength at 410 nm was used in this thesis in order to adjust the blank solution to zero. The structure of silicomolybdate still have not been suggested.

In the studies of flow-through cell used in this thesis, the commercial flow-through cell and the designed flow-through cell were conjugated with the flow system. By evaluating these flow-through cell on the basis of dispersion, sensitivity, and peak tailing, it was clear from the results obtained that the designed flow-through cell could be used as well as the commercial flow-through cell.

From the studies of the rate of reaction between aluminium and alizarin red S, it was clear that the rate of complex formation was rather slow. Therefore, the increase of tube length and diameter of coils in flow injection system increased the height of recorded peak. However, the increase of flow rate would decrease the height of recorded peak. At the flow rate greater than  $5.0 \text{ mL min}^{-1}$ , the dispersion of physical diffusion was more significant than the rate of complex formation in this analysis. Therefore, the carrier flow rate of  $5.0 \text{ mL min}^{-1}$  was used in the determination of alumina by 75  $\mu\text{L}$  sample injection with 150 cm of 1.0 mm diameter of coil in order to get the maximum sensitivity of analysis. The accuracy of the method, comparing with the classical method, showed that the flow injection method for determinating of

alumina in kaolins and lateritic soils gave good precision and accuracy. The sample can be analysed at the rate upto 120 determinations per hour with a relative standard deviation of 1.31 %. Calibration graph was linear, with the correlation factor of 0.999, in the range 3.0-25.0 ppm of aluminium in the solution injected. Detection limit was at 2.0 ppm. There was no interference from the presence of potassium, lithium, magnesium, calcium, manganese, and nitrate at the concentration upto 200 ppm do not interfere. However, only a few percent of these ions were found in soil sample, therefore, they would not interfere the determination of aluminium. The iron interference can be masked with thioglycolic acid. Cobalt at the concentration greater than 50 ppm in the sample solution will increase the peak height of the detector response. These effect need not be concerned in this work as the cobalt to aluminium ratio is very low in kaolins and lateritic soils. Effect of calcium ion can be overcome by adding calcium chloride at the concentration of 200 mg/L in to reagent solution.

The comparison of this work to the other colorimetric procedures for determining amount of aluminium are summerized in Table 4.1. Sampling rate of this work was higher than the other methods. The advantage of this method over the other flow injection system is that the working range is higher than the other method. It is therefore suitable for the determination of samples containing high quantity of aluminium with no need for sample dilution.

**Table 4.1** Determination of aluminium by flow injection analysis with various colorimetric reagents.

Reagent	Working range, ppm	Sample rate s h <sup>-1</sup>	Ref.
Chromeazurol S	0.05-0.5	---	32
Eriochrome cyanide R	0-20.0	120	57
Bromopyrogallol red	0-0.1	20	33
Xylenol orange	---	50	34
Aluminon	0-4.0	120	35
Pyrocatecholviolet	0.05-0.50	90	51
Alizarin red S	3.0-25.0	120	This thesis

The rate of reaction for iron-thioglycolate complex was very fast comparing to that of Al-alizarin red S complex. Therefore, an increasing carrier flow rate, length and diameter of coil would bring to a decrease in height of recorded peak. The maximum sensitivity of this method was at the flow rate of 5.0 mL min<sup>-1</sup>. The optimum condition was 75  $\mu$ L injection sample volume with 50 cm of 1.0 mm i.d. coil length. In the determination of iron in real sample, the precipitation of metal hydroxide such as hydroxide of aluminium was appeared and gave the tailing in recorded peak. These effect can be protected by adding ammonium citrate. The method could be carried out at rate upto 180 determinations per hour with very low carry-over

(0.40 %) and a relative standard deviation of 2.40 %. Calibration graph was linear, with the correlation factor of 0.999, in the range 1.0-40.0 ppm of iron. Detection limit was 0.25 ppm. Cobalt was found to be an interference in the iron analysis if the sample contained cobalt more than 50 % of iron. However, the percentage of cobalt in the soil sample especially kaolins has never exceeded 50 % of iron(45) The comparison of this work to the other colorimetric procedures for the determination of iron are summarized in Table 4.2. The sample rate of this method is lower than the other method excepted that of 2,4,6-tripyridyl-1,3,5-triazine method. The sample rate of this method may be increased by using the other injecting method such as injection valve or autoinjector. However, this method has the working range wider than the other method, except that of hydrochloric acid method, that it is suitable for determination of iron in high content sample especially for lateritic soil.

For the determination of silicon, the decrease in carrier flow rate in the flow injection system would increase the height of recorded peak. The height of the recorded peak was increased according to the increase in injection volume, but was decreased according to the increase in length and diameter of coils. The analysis of 75  $\mu$ L sample solution with 50 cm of 1.0 mm coil is the suitable condition for this determination. Determination of silicon in the real sample gave a good result in precision and accuracy and the sampling rate of 120 determinations per hour with no carry-over was obtained with a relative standard deviation of 1.95 %. The detection limit was 1.0 ppm with linear calibration in the range 5.0-200 ppm. Phosphate at the concentration up to 30 ppm in the sample

**Table 4.2** Determination of iron by flow injection analysis with various colorimetric reagents.

Reagent	Working range, ppm	Sample rate $s\ h^{-1}$	Ref.
Potassium thiocyanate (KSCN)	-	250	52
Hydrochloric acid	0.9-60.0	280	53
2,2'-dipyridyl	0.0-7.0	200	38
2,4,6-tripyridyl-1,3,5-triazine	0.05-1.0	90	54
Thioglycolate	1.0-40.0	180	This thesis

solution containing 100 ppm of silicon did not interfere this determination. The comparison of this method with the other flow injection method is shown in Table 4.3. The sample rate of this method is higher than the method by molybdenum blue and other yellow molybdic acid. The linear concentration range of this flow injection method is also higher therefore, it is suitable for determination of silica in high content sample especially for kaolin and lateritic soil samples.



**Table 4.3** Determination of silicon by flow injection analysis with colorimetric methods.

Reagent	Working range, ppm	Detection limit, ppm	Sample rate s h <sup>-1</sup>	Ref.
Molybdenum blue	0.01-1.00	0.03	35	55
Yellow silicomolybdic acid	-	-	70	39
Yellow silicomolybdic acid	5.0-300	5.0	150	This thesis

In conclusion, the determination of aluminium in the synthetic kaolin and the synthetic lateritic soil by the flow injection method allows the determination with 100.02 % and 99.41 % recovery, respectively. For the analysis of various kaolins and lateritic soils, the precision of the method is about 1 % for kaolins and in the range 1-2 % for lateritic soils. In the determination of iron oxide, per cent recovery for the synthetic kaolin and the synthetic lateritic soil is 96.67 % and 99.45 %, respectively. The precision of the method is about 3 % and about 1 % for the analysis of various kaolins and lateritic soils, respectively. However, in the determination of silica in the synthetic kaolin and the synthetic lateritic soil, percent recovery are 99.64 % and 99.83 %, respectively. In the determination of silica in various kaolins and

lateritic soils the precision of method is about 1 % for both types of sample. The flow injection method was found to give similar results of sample content as the classical method for the analysis of the synthetic and the real soil samples, however, accuracy and precision of the flow injection method were found to be better. Furthermore, an advantage of the flow injection method for the determination of alumina, silica and iron oxide over the classic method is that it is faster and uses smaller sample and reagent consumptions which results in lower cost per analysis.

Apart from the classical method, the only method found in literature on the determination of alumina, silica and iron oxide in kaolin was reported by Yoshinobu and Itsuma (56). They determined these components by X-ray fluorescence spectrometric method with accuracy and precision lesser than 0.1 % and 2 %, respectively. However, this method needed a time for fusing the sample for 1 hour and allowed the fused cake to cool slowly to room temperature to form a glass pellet. Therefore, this method still needs longer analysis time than the flow injection method.

Flow injection analysis was developed in this work as a means of improving sample rate for determination of alumina, silica and iron oxide in kaolins and lateritic soils. However, this method can be used not only for kaolins and lateritic soils, but it can also be applied for the determination of alumina, iron oxide and silica in high content sample such as feldspar, ball clay, bauxite, etc.