CHAPTER 3

RESULTS AND DISCUSSION

3.1 Preliminary conditions of the stopped-FI system for determination of phosphate

Stopped-flow injection system for determination of phosphate has been investigated. It involved the phosphate-molybdate-ascorbic acid reaction, in the molybdenum blue method as the following reactions [12].

$$PO_4^{3-} + \text{Acidic molybdate} \rightarrow \text{Heteropoly acid}$$

$$\text{Heteropoly acid} + \text{Ascorbic acid} \rightarrow \text{Molybdenum blue}$$

Ascorbic acid was selected as a reducing agent because it is more safe to the environment. Tin (II) chloride gives a heavy metal waste to the environment. Using sodium sulfite as reducing agent, the bubble of sulfur dioxide is evolved in the system.

In this work, the semi-automatic FI-analyzer was employed (see section 2.5.1). Via the controller, presetting can be made for travelling time (T), the period of flow between the point of injection to the point at which the flow is stopped so that the reaction development can be monitored at the flow cell; stopping time (S), the period during the flow stopped; washing time (W), the period when the stream is restarted to flow (after stopping) until this operation cycle ends and ready to start for the next cycle. The preliminary conditions employed are summarized in Table 3.1

During the stopped period, color intensity change of the injected zone which was in the flow cell to follow the kinetic of the reaction was continuously monitored. A stopped-FI signal profiles are illustrated in Figure 3.1.

Table 3.1 Preliminary conditions for determination of phosphate using the semi-automatic stopped-FI analyzer.

Condition	**Value**
Injection volume, µl	55
Flow rate, ml min^{-1}	4.0
Travelling time, s	3.0
Stopping time, s	10.0
Washing time, s	8.0
Wavelength, nm	630

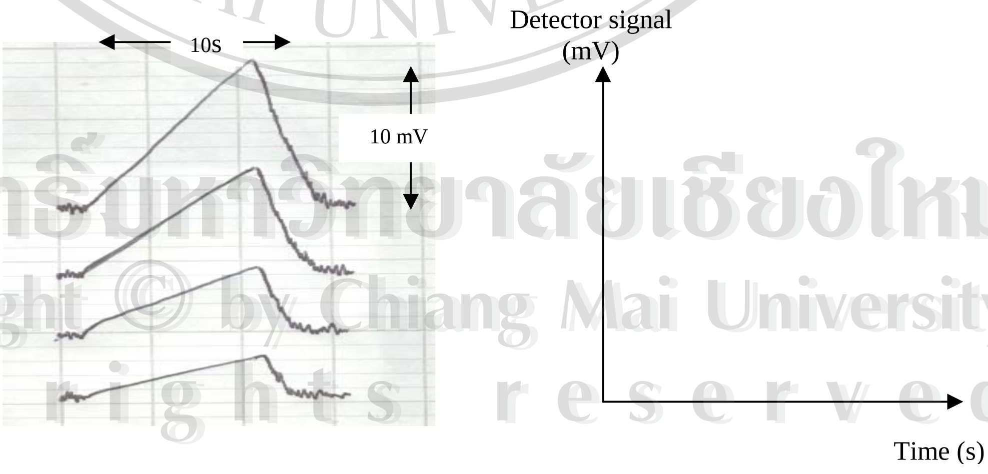

Figure 3.1 Examples of stopped-FI profiles obtained for phosphate

Slope of the FIA gram obtained was linearly proportional to the rate of the reaction, which depended on phosphate concentration. The method for measuring a slope of the FIAgram can see in Appendix A.

3.2 Determination of phosphate by stopped-FI method

3.2.1 Effect of sodium molybdate concentration

The sodium molybdate concentration was varied from 0.005 to 0.04 M, while ascorbic acid and nitric acid concentrations were fixed at 0.5% (w/v) and 0.08 M, respectively. A series of standard phosphate solutions was injected and calibration graphs (plot of slopes of the signals vs phosphate concentrations) were constructed. Slopes of the calibration graphs are shown in Table 3.2 and plotted versus the concentration of sodium molybdate, as illustrated in Figure 3.2.

Table 3.2 Calibration graph data using different sodium molybdate concentrations.

Concentration of sodium molybdate (M)	**Calibration graph data**		
	Slope (mV/s.ppm)	**Y-intercept (mV/s)**	**R^2**
0.005	1.09	4.22	0.6539
0.010	5.53	2.91	0.9814
0.020	6.46	0.76	0.9922
0.030	6.30	2.67	0.9738
0.040	1.63	1.88	0.9525

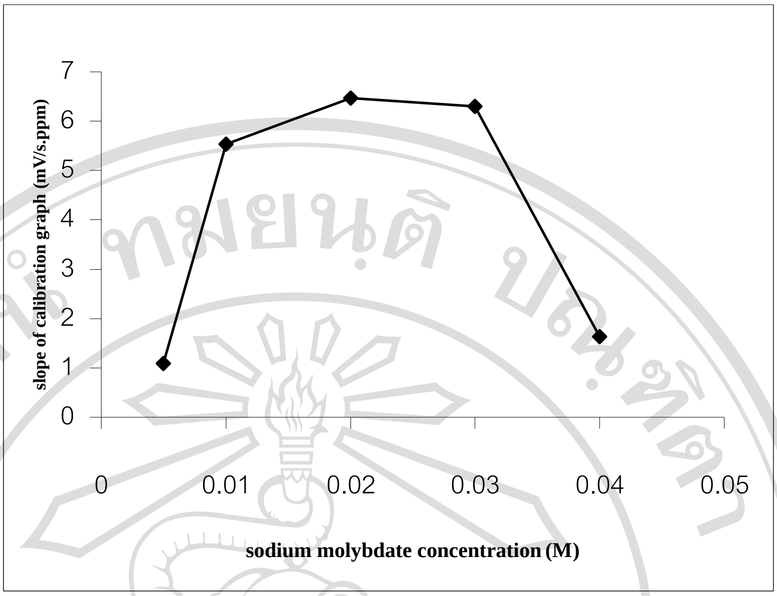

Figure 3.2 Effect of sodium molybdate concentration

The concentration of sodium molybdate at 0.02 and 0.03 M gave closely sensitivity and higher than the other concentrations. But 0.02 M sodium molybdate was chosen because it provided a little higher sensitivity than 0.03 M, with better Y-intercept and R^2 and also used lower amounts of reagent. At the concentration higher than 0.3M, slope of the calibration graph decrease continuously because of closely values of the slopes of stopped-FIgram.

3.2.2 Effect of ascorbic acid concentration

The ascorbic acid concentrations was varied from 0.05 to 2%w/v, while sodium molybdate and nitric acid concentrations were fixed at 0.02 and 0.08 M, respectively. Calibration graph data obtained from the study were summarized in

Table 3.3 and the slope was chosen for plot, tiny it versus the concentration of ascorbic acid (Figure 3.3).

Table 3.3 Calibration graph data for each asorbic acid concentration.

Concentration of ascorbic acid (%w/v)	Calibration graph data		
	Slope (mV/s.ppm)	Y-intercept (mV/s)	R^2
0.05	5.74	1.58	0.9810
0.25	7.17	0.62	0.9964
0.50	6.46	0.76	0.9922
1.00	10.21	3.01	0.9974
2.00	18.47	5.59	0.9781

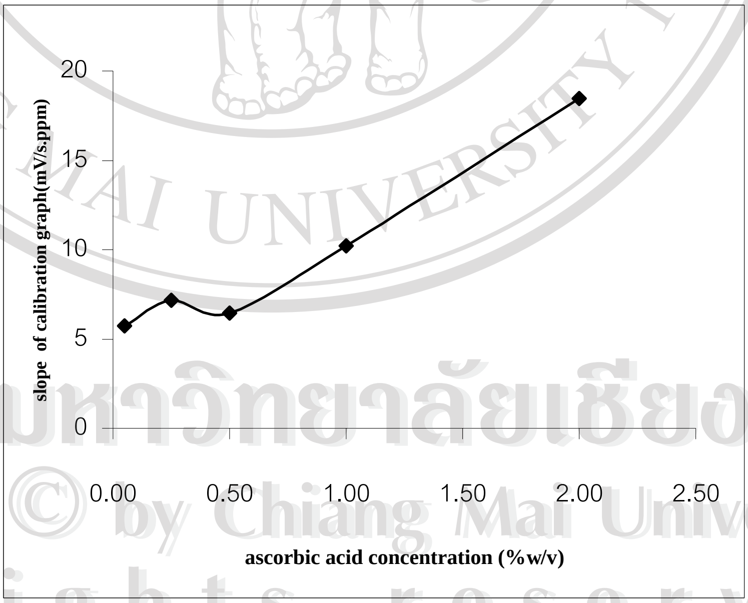

Figure 3.3 Effect of ascorbic acid concentration

From the graph, although the concentration of ascorbic acid at 1 and 2%w/v provided much higher sensitivity than 0.05, 0.25 and 0.5%w/v, both of these concentrations gave a high noise signal from high concentration of ascorbic acid that caused difficulty in measuring the slope of stopped-FIAgrams as shown in Figure 3.4. Ascorbic acid of 0.25%w/v was chosen because it provided a higher sensitivity than 0.05 and 0.5%w/v.

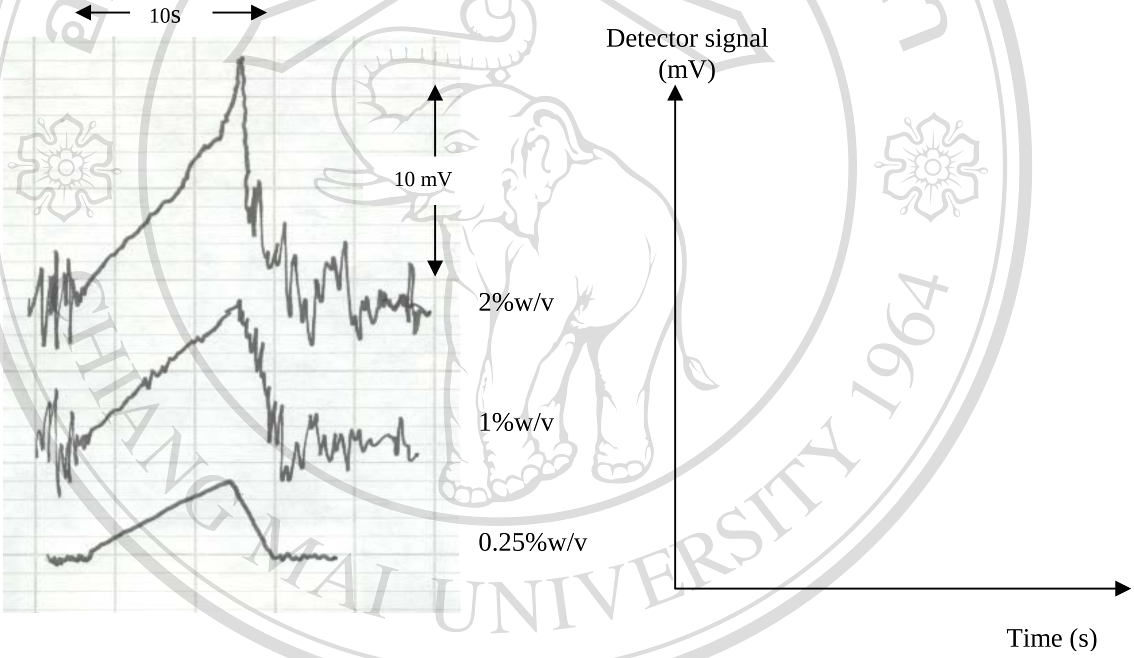

Figure 3.4 Stopped-Figrams using the concentration of ascorbic acid at 0.25, 1 and 2 %w/v

3.2.3 Effect of nitric acid concentration

Nitric acid concentration was varied from 0.05 to 0.4 M. Sodium molybdate and ascorbic acid concentration were fixed at 0.02 M and 0.25% w/v, respectively. Calibration graphs data that obtained from the study are summarized in Table 3.4. A plot of the slopes versus the concentrations of nitric acid was made as shown in Figure 3.5.

Table 3.4 Calibration graph data for each nitric acid concentration

Concentration of nitric acid (M)	Calibration graph data		
	Slope (mV/s.ppm)	Y-intercept (mV/s)	R^2
0.05	3.23	1.52	0.9974
0.08	5.98	0.55	0.9611
0.10	6.94	1.58	0.9938
0.15	9.07	-1.48	0.9997
0.20	6.13	4.47	0.9796
0.40	4.05	2.23	0.9745

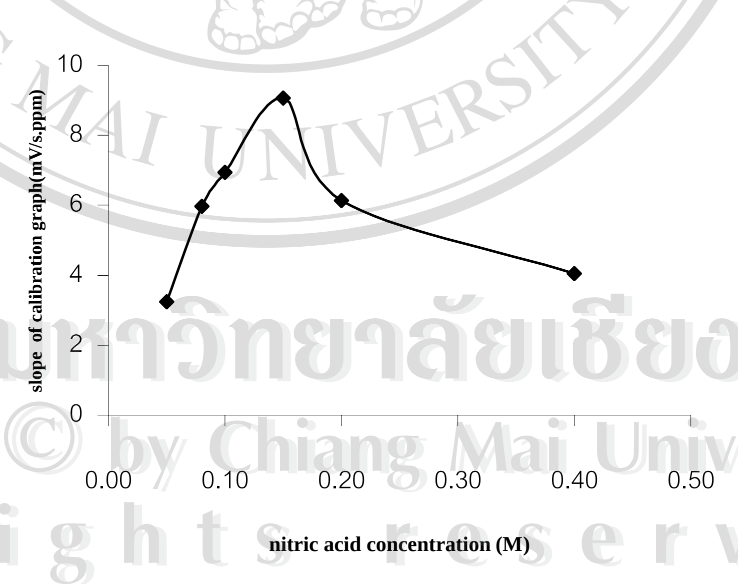

Figure 3.5 Effect of nitric acid concentration

From this graph, 0.15 M nitric acid gave a highest sensitivity and was then chosen. But at a lower concentration of nitric acid, the reaction may occur incompletely and gave low slope. So, a slope of calibration graph was also lower. At higher concentration of nitric acid, high acidity had the effect for this reaction and reduced the sensitivity of calibration graph. In addition, using sulphuric acid of different concentrations, a similar trend was observed.

3.2.4 Summary of the selected conditions

The selected concentrations of reagents; sodium molybdate, ascorbic acid and nitric acid, for determination of phosphate in the range of 0.3-6 mg P l^{-1} are 0.02 M, 0.25%w/v and 0.15 M respectively. The other conditions are the same as shown in Table 3.1.

3.2.5 Determination of phosphate in soil samples

3.2.5.1 Calibration graph

A calibration data and graph obtained in the range of 0.3-6 mg P l^{-1} with a detection limit of 0.02 mg P l^{-1} are shown in Table 3.5 and Figure 3.6, respectively.

Table 3.5 Calibration data of 0.3-6 mg P l^{-1}

Concentration of P (mg l^{-1})	**Slope of stopped-FI gram[a] (mV/s)**
0.3	8.32
0.5	10.39
1.0	15.31
2.0	26.01
4.0	47.39
6.0	65.08

[a] = mean of triplicates

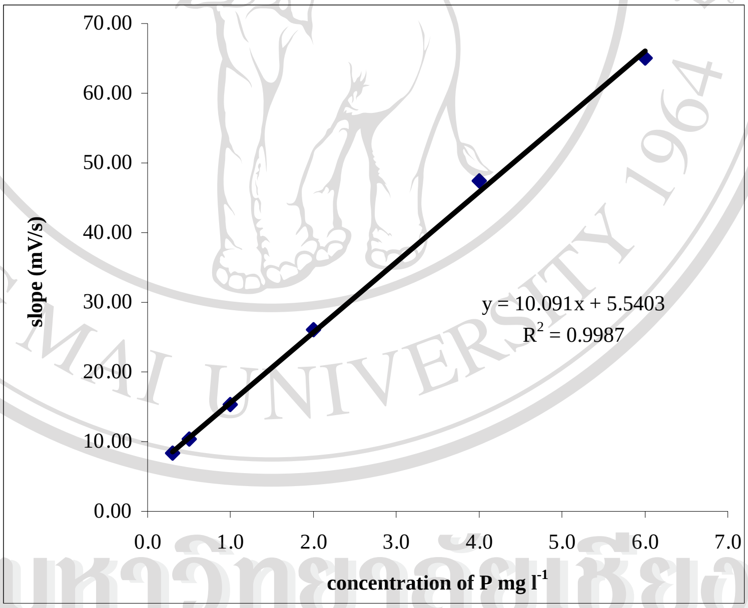

Figure 3.6 A calibration graph for determination of phosphate by stopped-FIA

The calibration graph in Figure 3.6 can be used to determine phosphate in soil samples. The sample must be analyzed using the same conditions as the standard.

3.2.5.2 Precision

A solution containing 2 mg P l^{-1} of the standard phosphate was used to study precision of the proposed method. The analysis of 10 replicates was done under the selected condition. The results are shown in Table 3.6.

Table 3.6 Precision of phosphate determination by stopped-FI method.

Number of injection	**Slope (mV/s)**
1	26.40
2	26.40
3	26.40
4	27.07
5	27.50
6	25.76
7	25.14
8	26.40
9	26.14
10	27.07
Mean	26.43
SD	0.68
%RSD	2.57

From the results, it was found that the relative standard deviation (RSD) obtained was 2.6%. This indicates that the proposed system has a good precision.

3.2.5.3 Accuracy and application of the method

Accuracy of the proposed method was determined by comparing results obtained from the stopped-FIA with those from a batch method (spectrophotometric method)[38]. Soil samples were extracted as mentioned in 2.4.1. Comparative analyses of the same samples were carried out on the same day and the results are shown in Table 3.7 and Figure 3.7.

Table 3.7 Comparison of the amount of available phosphate in soil extracted solution found by stopped-FI and batch methods.

Sample number	[P] in sample solution (mg/l)[a]		% Different [b]
	FIA method	Batch method	
1	4.47 ± 0.12	4.47 ± 0.00	0.0
2	4.45 ± 0.08	4.39 ± 0.06	1.4
3	5.33 ± 0.12	5.39 ± 0.06	-1.1
4	9.59 ± 0.48	9.63 ± 0.00	-0.4
5	6.07 ± 0.26	6.02 ± 0.06	0.8
6	2.96 ± 0.06	2.98 ± 0.02	-0.7
7	5.11 ± 0.24	5.04 ± 0.04	1.4
8	4.76 ± 0.20	4.72 ± 0.00	0.8
9	9.62 ± 0.18	9.59 ± 0.06	0.3
10	8.40 ± 0.10	8.50 ± 0.00	-1.2
11	4.95 ± 0.20	5.04 ± 0.00	-1.8
12	2.29 ± 0.06	2.29 ± 0.02	-0.0
13	9.38 ± 0.48	9.42 ± 0.06	-0.4
14	4.41 ± 0.18	4.36 ± 0.02	1.2
15	2.03 ± 0.10	1.99 ± 0.02	2.0
16	9.59 ± 0.48	9.67 ± 0.06	-0.8
17	8.64 ± 0.24	8.62 ± 0.00	0.2
18	5.80 ± 0.00	5.73 ± 0.00	1.2
19	1.19 ± 0.04	1.19 ± 0.00	0.0
20	2.00 ± 0.00	1.99 ± 0.02	0.5

[a] = means of triplicate results

[b] % different =

$$\frac{[\text{ FIA value} - \text{batch value}] \times 100}{\text{batch value}}$$

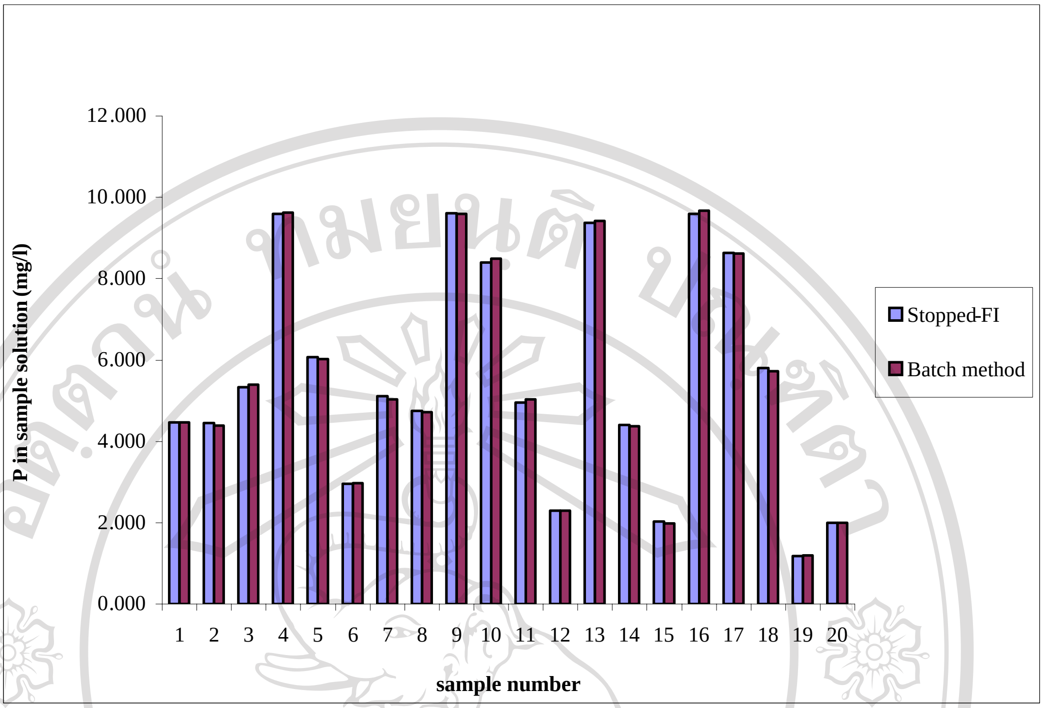

Figure 3.7 Comparison graph of available phosphate in soil samples by the proposed method and batch method.

From Table 3.7 and Figure 3.7, an available phosphate found in soil samples by using stopped-FI method agreed well with those found by the batch method. The correlation of the two methods is shown in Figure 3.8.

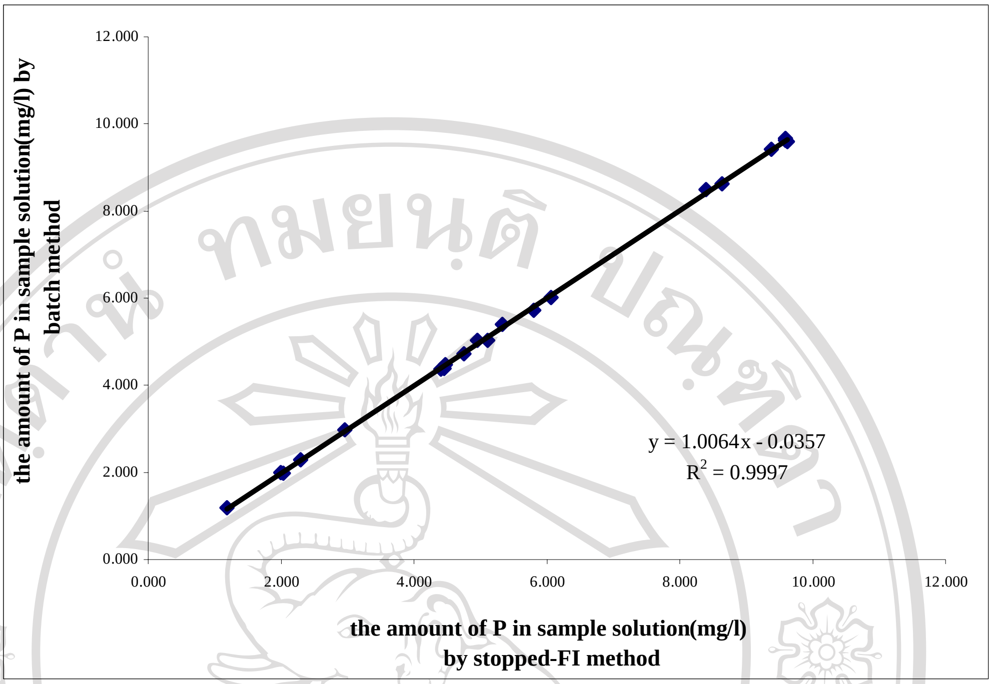

Figure 3.8 Correlation graph of available phosphate in soil samples by proposed method and batch method.

Slope, intercept and R^2 of the correlation graph are closed to 1, 0 and 1, respectively. In addition, according to paired t-test of results of 20 samples, no significant difference (95% confidence) between these methods was found. This indicates that both methods correlate well.

Apart from determination of phosphate in soil samples, soluble phosphate in fertilizers were also studied by the same system. The results are shown in Table 3.8(b).

Concentration of available phosphate in soils and soluble phosphate are summarized in Table 3.8(a) and (b).

Table 3.8 (a) Comparison of the amount of available phosphate in soil samples found by stopped-FIA and batch methods.

Sample number	Physical appearance	[P] in soil sample (ug/g) [a]		% Different [b]
		FIA method	Batch method	
1	Friable, wet	11.2 ± 0.3	11.2 ± 0.0	0.0
2	Friable, wet	11.1 ± 0.2	11.0 ± 0.2	0.9
3	Friable, wet	13.3 ± 0.3	13.5 ± 0.2	-1.5
4	Friable, wet	24.0 ± 1.2	24.1 ± 0.0	-0.4
5	Friable, wet	15.2 ± 0.7	15.0 ± 0.2	1.3
6	Laterite	7.39 ± 0.2	7.45 ± 0.1	-0.8
7	Friable, wet	12.8 ± 0.6	12.6 ± 0.1	1.6
8	Friable, wet	11.9 ± 0.5	11.8 ± 0.0	0.8
9	Black soil	120 ± 2.3	119 ± 0.8	0.8
10	Sand	42.0 ± 0.5	42.5 ± 0.0	-1.2
11	Friable, sand	12.4 ± 0.5	12.6 ± 0.0	-1.6
12	Friable, wet	5.73 ± 0.2	5.73 ± 0.1	0.0
13	Hard, dry	23.4 ± 1.2	23.6 ± 0.2	-0.8
14	Friable, wet	11.0 ± 0.5	10.9 ± 0.1	0.9
15	Friable, wet	5.08 ± 0.3	4.96 ± 0.1	2.0
16	Hard, dry	24.0 ± 2.4	24.2 ± 0.3	-0.8
17	Friable, wet	43.2 ± 0.6	43.1 ± 0.0	0.2
18	Friable, wet	14.5 ± 0.0	14.3 ± 0.0	1.4
19	Mud	2.97 ± 0.1	2.97 ± 0.0	0.0
20	Mud	4.99 ± 0.0	4.97 ± 0.1	0.5

[a] = means of triplicate results

[b] % different = $\dfrac{[\text{ FIA value} - \text{batch value}] \times 100}{\text{batch value}}$

Table 3.8 (b) Comparison of the amount of soluble phosphate in fertilizers sample found by stopped-FIA and batch methods.

Sample number	$[P_2O_5]$ in fertilizer sample (mg/g)		% Different
	FIA method	Batch method	
1	84.8 ± 6.5	82.6 ± 1.7	2.7
2	69.1 ± 3.7	62.3 ± 0.7	10
3	50.1 ± 1.1	36.5 ± 0.5	37.3
4	396 ± 4.6	321 ± 0.0	23
5	62.8 ± 2.1	52.8 ± 1.7	19
6	75.9 ± 4.0	67.4 ± 1.7	13
7	97.5 ± 5.4	90.2 ± 1.7	8.1
8	136 ± 5.4	125 ± 1.7	8.8
9	0.732 ± 0.0	0.995 ± 0.0	-26
10	0.811 ± 0.0	0.715± 0.0	13

[a] = means of triplicate results

[b] $$\% \text{ different} = \frac{[\text{ FIA value} - \text{batch value}] \text{ x } 100}{\text{batch value}}$$

Determination of phosphate in soil and fertilizer sample by stopped-FI method has more advantages than the batch method. This method can reduce effect of interferences, such as silicate or arsenate, because their reaction rates in the molybdenum blue reactions are different. By using the slope of FIAgram instead of peak height, effect due to coloring species in a sample was also decreased. In addition, stopped-FI technique is simple, inexpensive, rapid and high sensitive method. Very small amount of reagents consumption are also one advantage of this technique.

3.3 Preliminary conditions of the stopped-FI system for determination of chlorate

Stopped-FI method for determination of chlorate involves iodometric chemical reactions as shown in the following [30]:

$$ClO_3^- + 6I^- + 6H^+ \rightarrow 3I_2 + Cl^- + 3H_2O$$

$$I_2 + I^- \rightarrow I_3^-$$

Oxyacid , such as nitric acid and sulfuric acid, was not allowed to use in this reaction because it can be oxidised by chlorate. But nitrate or nitrite in soil was oxidised by chloride ion from hydrochloric acid, so the system was not interfered.

Triiodide from this reaction can be detected at 400 nm. In this work similar to section 3.1, the semi-automatic FI-analyzer was employed. The preliminary conditions used are summarized in Table 3.9. The injected solution was held in a mixing coil for increasing the reaction time during the stopped period (see section 2.5.2). Then the flow was started, the injected zone was propeled through the flow cell of a spectrophotometer, while the absorbance was continuously recorded versus time. Signal profiles are illustrated in Figure 3.9. Peak height was proportional to chlorate concentration. A calibration was plotted between peak height and concentration of chlorate.

Table 3.9 Preliminary conditions for determination of chlorate using the semi-autometic stopped-FI analyzer.

Condition	**Value**
Injection volume, µl	55
Mixing coil length, cm	50
Flow rate, ml min^{-1}	2.0
Travelling time, s	21.5
Stopping time, s	90.0
Washing time, s	60.0
Wavelength, nm	400

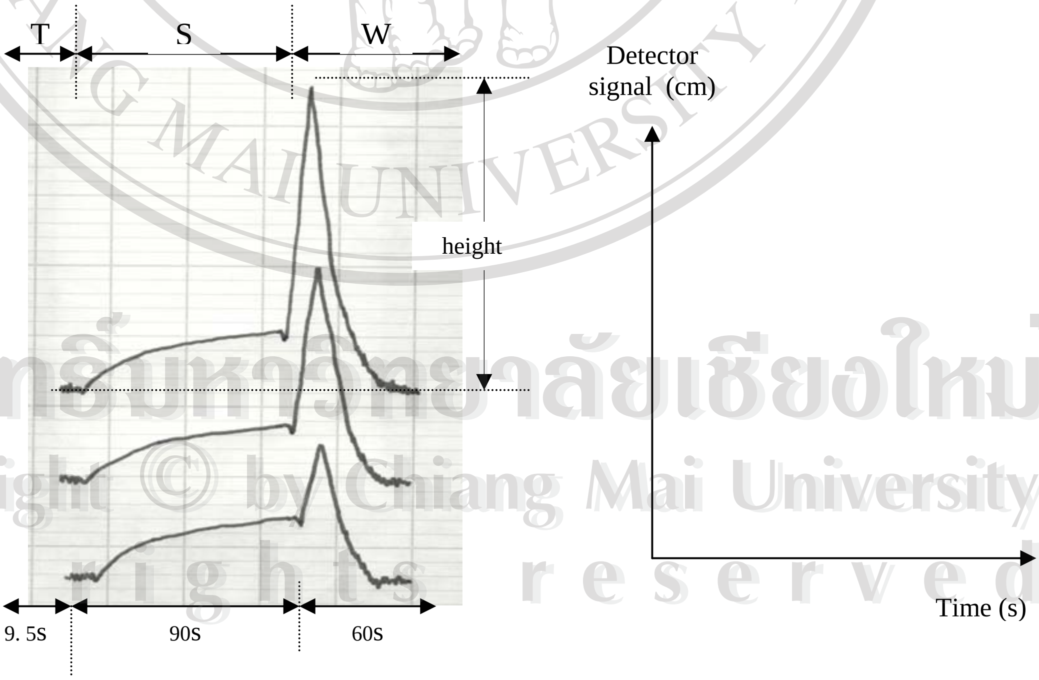

Figure 3.9 Examples of stopped-FI signal profiles obtained for chlorate determination

From Figure 3.9, an increase of signal in the stopping period was due to air oxidation of iodide in the strongly acidic solution. This effect may be reduced by purging nitrogen gas to the solution before used. However, it is not necessary to remove oxygen, since the signal from oxygen oxidation is quite constant.

3.4 Determination of chlorate by stopped-FI method

3.4.1 Effect of stopping time

The time for stopping a pump was studied and varied at 15, 30, 60 and 90 s. Concentration of potassium iodide and hydrochloric acid were 0.3 and 3 M, respectively. A series of standard chlorate solutions (100, 300 and 500 mg ClO_3^- l^{-1}) was injected to make a calibration graph. Slope of each calibration graph is shown in Table 3.10 and Figure 3.10.

Table 3.10 Slope of calibration graph of variation of stopping time

Stopping time (s)	**Calibration graph data**		
	Slope	**Y-intercept**	**R^2**
15	0.0069	0.1858	0.9987
30	0.0101	0.4583	0.9992
60	0.0163	1.0933	0.9942
90	0.0217	1.9992	0.9973

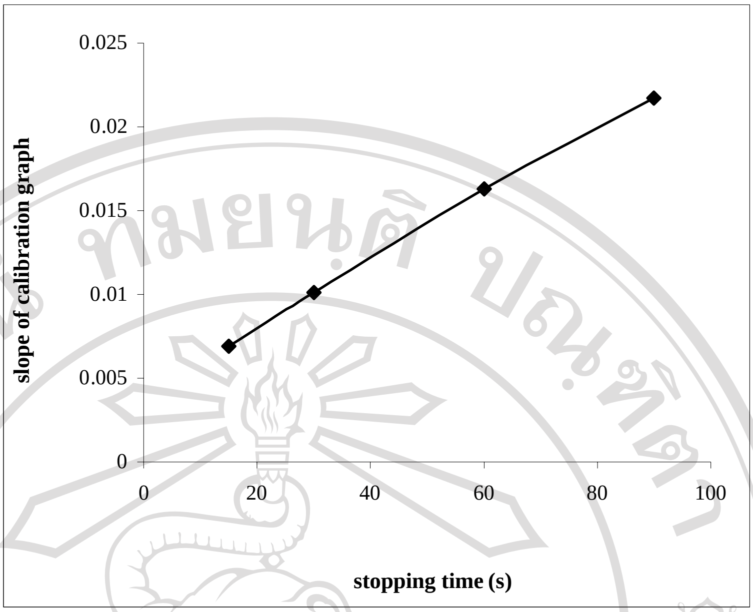

Figure 3.10 Effect of stopping time.

From this graph , the higher stopping time the higher slope was obtained. Although, the sensitivity can be increased further by increasing the stopping time, the stopping time of 90 s was chosen. Because it cannot be set more than 99 s due to limitation of the instrument.

3.4.2 Effect of potassium iodide and hydrochloric acid concentration

Effect of potassium iodide and hydrochloric acid was studied simultaneously. The range of variation of potassium iodide and hydrochloric acid concentration was varied from 0.1 to 0.3 M and 5 to 7 M, respectively. A series of standard chlorate solutions (5-50 mg ClO_3^- l^{-1}) was injected to make a calibration graph as mentioned in 2.6.2. Slope of each calibration graph is shown in Table 3.11 and Figure 3.11.

Table 3.11 Slopes and R^2 of calibration graphs of variation of potassium iodide concentration at 5, 6 and 7 M hydrochloric acid.

Concentration of KI (M)	[HCl] (M)								
	5			6			7		
	Slope	Y-intercept	R^2	Slope	Y-intercept	R^2	Slope	Y-intercept	R^2
0.1	0.0182	-0.364	0.5000	0.0555	-0.451	0.9927	0.1663	-0.761	0.9936
0.3	0.0315	-0.521	0.7349	0.0869	-1.059	0.9827	0.1367	-1.091	0.9894
0.6	0.0281	0.191	0.5688	0.1018	-0.234	0.8651	0.1427	-0.767	0.9658

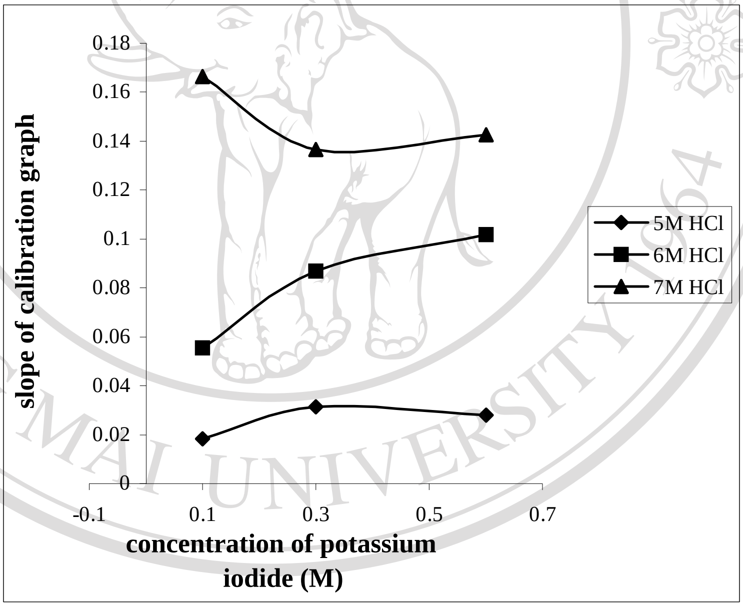

Figure 3.11 Effect of potassium iodide concentration at 5, 6 and 7 M hydrochloric acid.

Increasing of either iodide or hydrochloric acid concentration, higher slopes of the calibration graphs (sensitivity) was obtained. This may due to the suitable acidity of the solution. At 5 and 6 M hydrochlric acid solution, acidity was not strong enough for the reaction and gave a lower peak height.

At 7 M hydrochloric acid, the reaction was unable to occur at the concentration lower than 0.1 M iodide. But at the higher concentration of iodide, reaction proceeded quickly and gave closely peak height. So, there was an effect in decreasing of slope of the calibration graph.

3.4.3 Summary of the selected conditions

The selected concentrations of reagents; potassium iodide and hydrochloric acid, for determination of chlorate in the range of 5-50 mg l^{-1} are 0.1 M and 7 M respectively. Other conditions are the same as shown in Table 3.9.

3.4.4 Determination of chlorate in soil samples

3.4.4.1 Calibration graph

Peak height and calibration graph obtained in the range of 5-50 mg ClO_3^- l^{-1} are shown in Table 3.12 and Figure 3.12, respectively. Detection limit calculated from the calibration data was found to be 1.38 mg ClO_3^- l^{-1}. In general, chlorate in soil sample from longan garden is about 10-250 mg ClO_3^- l^{-1}. So it was not necessary to make the range of calibration data lower than 5 mg ClO_3^- l^{-1}.

Table 3.12 Calibration data of 5-50 mg ClO_3^- l^{-1}

Concentration of chlorate (mg l^{-1})	**Peak height (cm)**
5	0.59
10	1.20
20	2.73
30	4.14
40	5.24
50	6.37

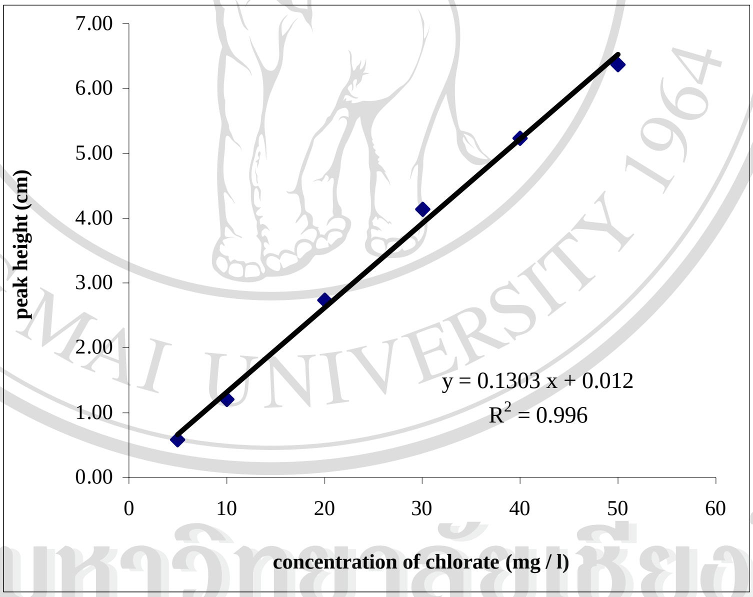

Figure 3.12 A calibration graph for determination of chlorate obtained from stopped-FI method.

3.4.4.2 Precision

A standard solution containing 30 mg l^{-1} chlorate was used to study precision of the proposed method. The analysis of 10 replicates was done under the selected condition. The results are shown in Table 3.13.

Table 3.13 Precision of chlorate determination by stopped-FI method.

Number of injection	**Peak heigth (cm)**
1	4.30
2	4.10
3	4.25
4	4.25
5	4.20
6	4.30
7	4.00
8	4.20
9	4.20
10	4.15
Mean	4.20
SD	0.09
%RSD	2.21

From the results, it was found that the relative standard deviation (RSD) obtained was 2.2%. This indicates that the proposed system has a good precision.

3.4.4.3 Accuracy and application of the method

Accuracy of the proposed method was determined by comparing results from stopped-FI with those from a batch spectrophotometric method[39] and titrimetric standard method[12]. The results are shown in Tables 3.14-3.16 and Figures 3.13-3.15.

Table 3.14 Comparison of the amount of chlorate found by stopped-FI method and batch method.

Sample Number	Appearent	Chlorate in soil sample (ug/g)		%Different[b]
		Stopped-FI[a]	Batch method	
1	Fine, gray	194 ± 4.7	196	-1
2	Fine, gray	258 ± 2.5	226	14
3	Fine, gray	107 ± 3.9	101	5
4	Rough, gray	36.5 ± 0.4	33.7	8.3
5	Fine, brown	49.5 ± 0.0	47.8	3.6
6	Fine, gray	68.9 ± 1.0	75.7	-9.0
7	Fine, brown	167 ± 2.3	142	18
8	Fine, faded red	57.8 ± 0.9	28.9	100
9	Fine, red	37.8 ± 0.3	32.3	17
10	Rough, black	101 ± 3.6	91.2	11
11	Sand, faded brown	127 ± 4.4	91.7	38
12	Rough, black	9.77 ± 0.4	10.8	-95
13	Sand, faded brown	50.4 ± 0.5	43.1	16
14	Rough, black	106 ± 1.3	119	-11
15	Rough, black	214 ± 3.8	163	31
16	Rough, faded black	30.0 ± 0.6	22.7	32
17	Sand, brown	10.6 ± 0.2	6.44	65
18	Fine, black	12.6 ± 0.2	6.15	104
19	Fine, black	ND.	0.91	-
20	Sand, faded brown	ND.	1.53	-

[a] = means of triplicate results

[b] $$\% \text{ different} = \frac{[\text{FIA value} - \text{batch value}] \times 100}{\text{batch value}}$$

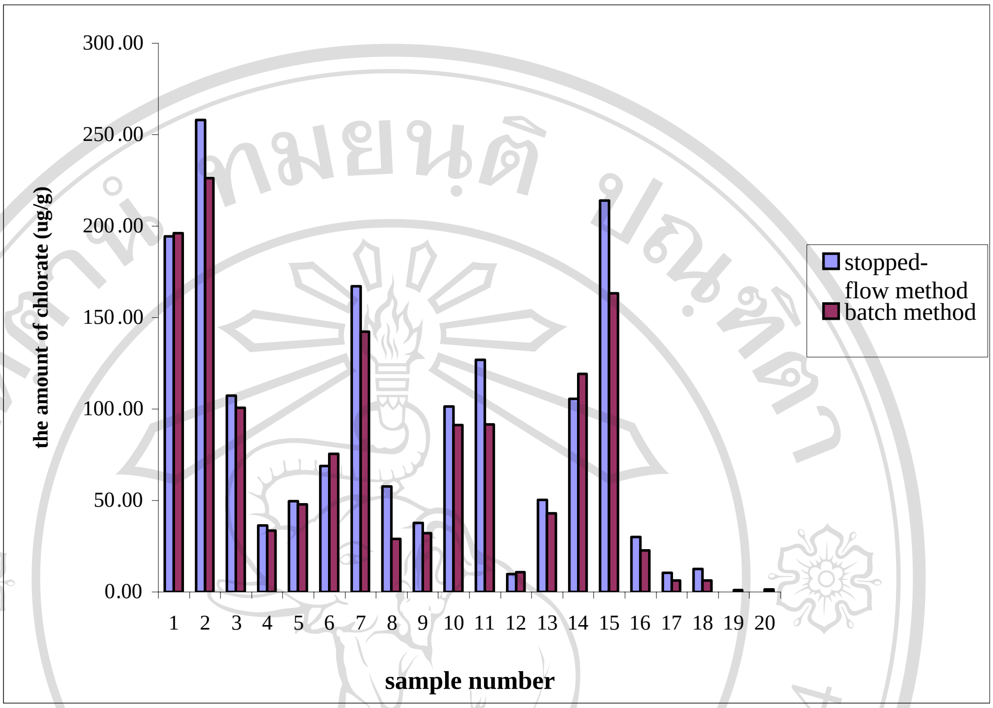

Figure 3.13 Comparison graph of chlorate in soil samples by proposed method and batch method.

Table 3.15 Comparison of the amount of chlorate found by stopped-flow method and titrimetric standard method.

Sample number	Appearent	Chlorate in soil sample (ug/g)		%Different[b]
		Stopped-FI[a]	Std. Method[a]	
1	Fine, gray	194 ± 4.7	189 ± 1.1	4
2	Fine, gray	258 ± 2.5	245 ± 0.8	5.3
3	Fine, gray	107 ± 3.9	103 ± 1.7	4
4	Rough, gray	36.5 ± 0.4	39.8 ± 1.6	-8.3
5	Fine, brown	49.5 ± 0.0	50.0 ± 1.4	-1
6	Fine, gray	68.9 ± 1.0	61.6 ± 2.1	11
7	Fine, brown	167 ± 2.3	155 ± 2.1	7.7
8	Fine, faded red	57.8 ± 0.9	45.9 ± 1.8	25.9
9	Fine, red	37.8 ± 0.3	35.7 ± 1.6	5.9
10	Rough, black	101 ± 3.6	102 ± 0.8	-1
11	Sand, faded brown	127 ± 4.4	122 ± 1.1	4
12	Rough, black	9.77 ± 0.4	8.80 ± 0.8	11
13	Sand, faded brown	50.4 ± 0.5	45.6 ± 1.4	10
14	Rough, black	106 ± 1.3	96.1 ± 1.4	9.3
15	Rough, black	214 ± 3.8	201 ± 1.6	6.5
16	Rough, faded black	30.0 ± 0.6	27.1 ± 0.7	11
17	Sand, brown	10.6 ± 0.2	9.04 ± 0.7	17.2
18	Fine, black	12.6 ± 0.2	11.1 ± 0.0	11
19	Fine, black	ND.	ND.	-
20	Sand, faded brown	ND.	ND.	-

[a] = means of triplicate results

[b] $$\% \text{ different} = \frac{[\text{FIA value} - \text{batch value}] \times 100}{\text{batch value}}$$

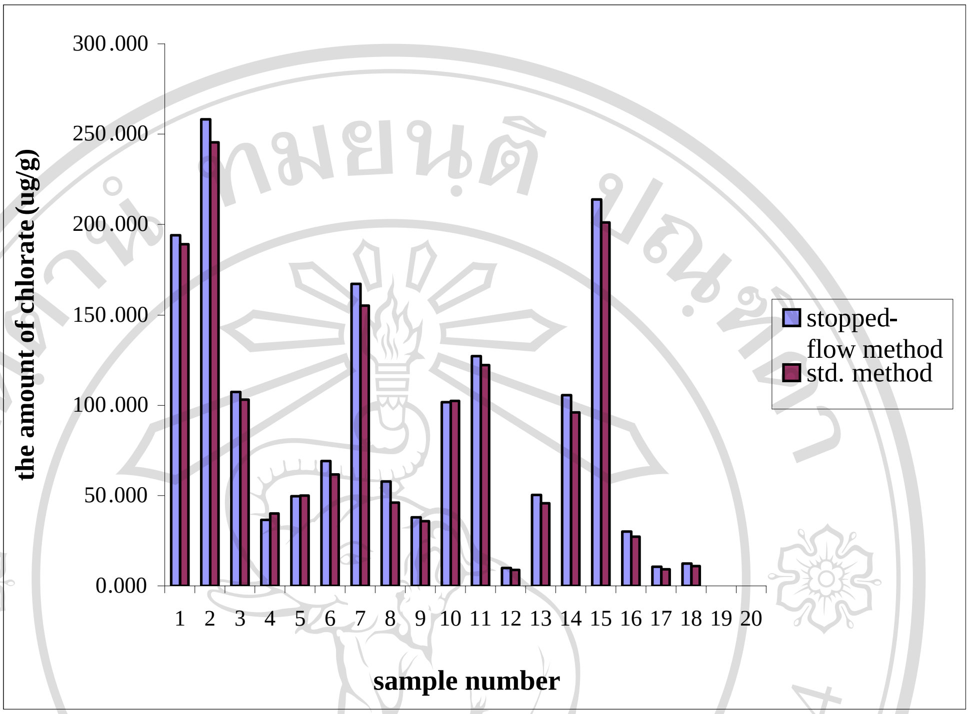

Figure 3.14 Comparison graph of chlorate in soil samples by proposed method and titrimetric standard method.

Table 3.16 Comparison of the amount of chlorate found by batch method and titrimetric standard method.

Sample number	Appearent	Chlorate in soil sample (ug/g)		%Different[b]
		Batch method	Std. method[a]	
1	Fine, gray	196	189 ± 1.1	4
2	Fine, gray	226	245 ± 0.8	-8.1
3	Fine, gray	101	103 ± 1.7	-2
4	Rough, gray	33.7	39.8 ± 1.6	-15
5	Fine, brown	47.8	50.0 ± 1.4	-4.4
6	Fine, gray	75.7	61.6 ± 2.1	22.9
7	Fine, brown	142	155 ± 2.1	-8.4
8	Fine, faded red	28.9	45.9 ± 1.8	-37
9	Fine, red	32.3	35.7 ± 1.6	-9.5
10	Rough, black	91.2	102 ± 0.8	-10
11	Sand, faded brown	91.7	122 ± 1.1	-25
12	Rough, black	10.8	8.80 ± 0.8	23
13	Sand, faded brown	50.4	45.6 ± 1.4	-5.5
14	Rough, black	106	96.1 ± 1.4	23.8
15	Rough, black	214	201 ± 1.6	-19
16	Rough, faded black	30.0	27.1 ± 0.7	-16
17	Sand, brown	10.6	9.04 ± 0.7	-29
18	Fine, black	12.6	11.1 ± 0.0	-44
19	Fine, black	0.91	ND.	-
20	Sand, faded brown	1.53	ND.	-

[a] = means of triplicate results

[b] % different = $\frac{[\text{FIA value} - \text{batch value}] \times 100}{\text{batch value}}$

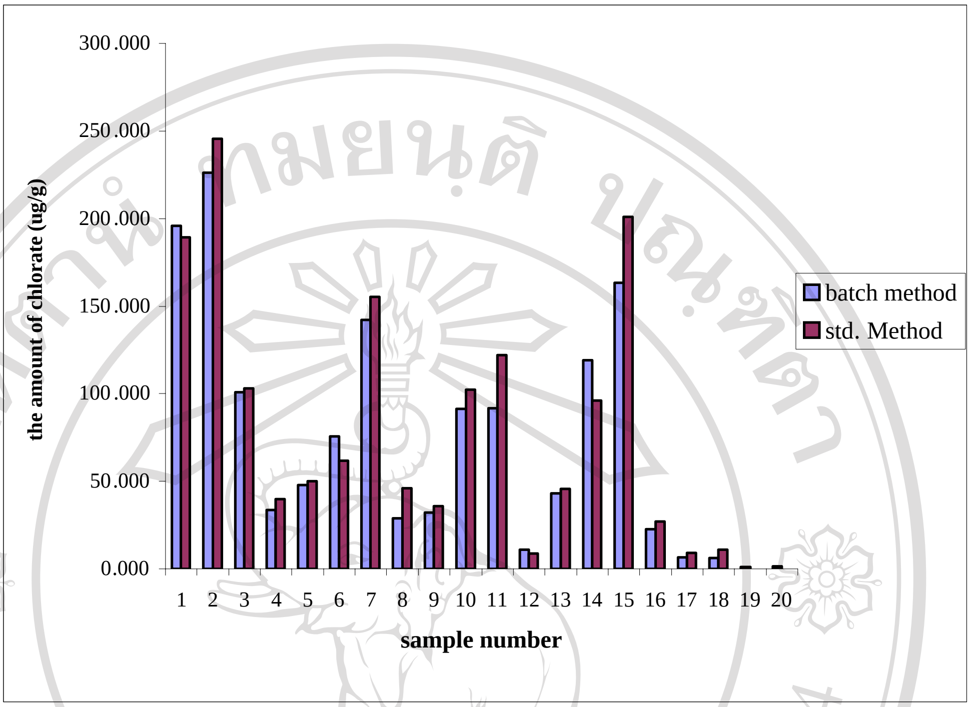

Figure 3.15 Comparison graph of chlorate in soil samples by batch method and titrimetric standard method.

From Table 3.15 and Figure 3.14, chlorate contents found in soil samples by using stopped-FI method agreed with those found by the standard method. The correlation of the two methods is shown in Figure 3.16.

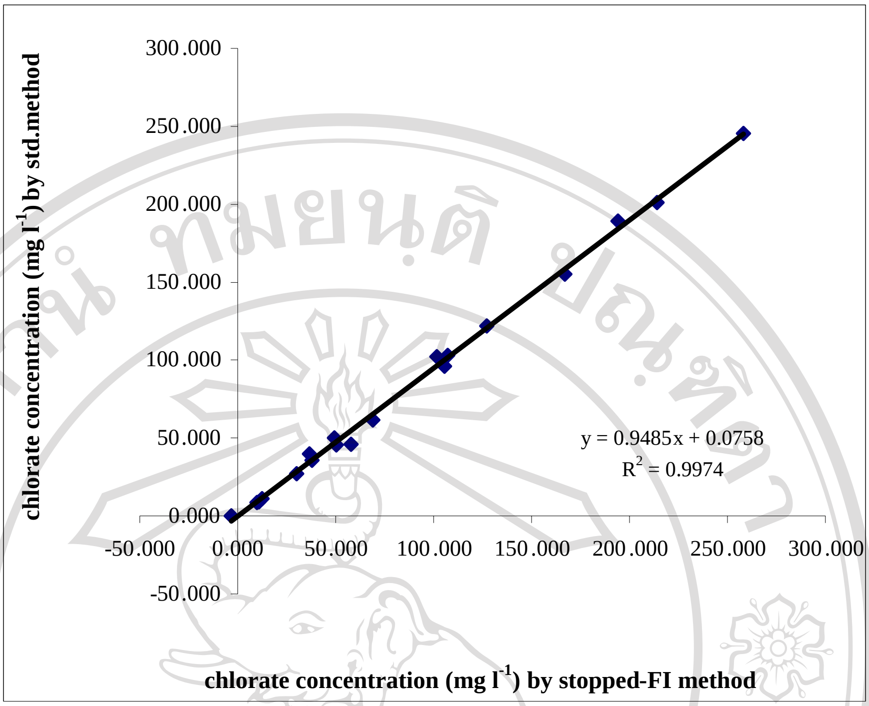

Figure 3.16 Correlation graph of chlorate in soil samples by proposed method and titrimetric standard method.

Slope, intercept and R^2 of the correlation graphs of soil samples are closed to 1, 0 and 1, respectively. The results of 20 samples determined by the proposed method were compared to batch method and titrimetric standard method and found that all agreed well with each others (the t-test at 95 % confidence).This indicates that these methods correlate each other well.

Stopped-FI method for chlorate determination has more advantages than batch spectrophotometric and titrimetric methods. Chemical reagents were used in very small amounts. In addition, this technique is simple, low cost, rapid and provides high sensitivity.