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# A novel stopped flow injection—amperometric procedure for the determination of chlorate[☆]

Orawan Tue-Ngeun[a,1], Jaroon Jakmunee[a,b,*], Kate Grudpan[a,b]

[a] Department of Chemistry, Faculty of Science, Chiang Mai University, Chiang Mai 50200, Thailand
[b] Institute for Science and Technology Research and Development, Chiang Mai University, Chiang Mai 50200, Thailand

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**Abstract**

A novel stopped flow injection—amperometric (sFI-Amp) procedure for determination of chlorate has been developed. The reaction of chlorate with excess potassium iodide and hydrochloric acid, forming iodine/triiodide that is further electrochemically reduced at a glassy carbon electrode at +200 mV versus Ag/AgCl electrode is employed. In order to increase sensitivity without using of too high acid concentration, promoting of the reaction by increasing reaction time and temperature can be carried out. This can be done without increase of dispersion of the product zone by stopping the flow while the injected zone is being in a mixing coil which is immersed in a water bath of 55 ± 0.5 °C. In a closed system of FIA, a side reaction of oxygen with iodide is also minimized. Under a set of conditions, linear calibration graphs were in the ranges of $1.2 \times 10^{-6}$–$6.0 \times 10^{-5}$ mol l$^{-1}$and $6.0 \times 10^{-5}$–$6.0 \times 10^{-4}$ mol l$^{-1}$. A sample throughput of 25 h$^{-1}$ was accomplished. Relative standard deviation was 2% ($n = 21$, $1.2 \times 10^{-4}$ mol l$^{-1}$ chlorate). The proposed sFI-Amp procedure was successfully applied to the determination of chlorate in soil samples from longan plantation area.

*Keywords:* Stopped flow injection; Chlorate; Amperometry

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## 1. Introduction

One major source of chlorate discharge to the environment is pulp mill effluent where chlorine dioxide is used for bleaching [1]. Minor amounts of chlorate and chlorite are also produced when chlorine dioxide is used to disinfect supply water [2]. Potassium chlorate ($KClO_3$) is used as an oxidant in fireworks and matches [3]. Chlorate compounds have also been widely applied to soil in order to stimulate flowering of longan trees [4], especially at longan plantation in the north of Thailand [5]. Although chlorate is not very toxic to human, it has been shown to cause haemolytic anemia [6]. Chlorate is very toxic to marine brown algae, i.e. Macrocystis and Fucus, which are vital components of the coastal ecosystem [2].

Ion chromatography (IC) has been reported for simultaneous determination of chlorate and other species, such as, IC/mass spectrometry for bromate, chlorate, iodate, and chlorine dioxide determination [7], IC/spectrophotometry using post-column reaction with osmate-catalyzed for chlorate, chlorite, bromate, and nitrite determination by detection the triiodide at 288 nm [8]. A high capacity anion exchange column with suppressed conductivity detection was also used by the U.S. EPA in Method 300.1 for the determination of bromate, bromide, chlorite, and chlorate by direct injection [9]. However, this technique requires relatively expensive instrument and rather long analysis time, so it is not suitable for determination of only one single analyte, when only chlorate is needed.

The iodometric method employing the amplification reaction of chlorate with iodide ion and acidic medium ($ClO_3^- + 6I^- + 6H^+ \rightarrow 3I_2 + Cl^- + 3H_2O$) [10–12] has been commonly used for chlorate determination, but the reaction of chlorate ion with iodide ion is slow under mildly acidic condition. The rate law of the reaction, $-d[ClO_3^-]/dt = k[ClO_3^-][I^-]^{1.5}[H^+]^2$ [10] indicates that the reaction could be accelerated under a high acid concentration. However, under this condition a readily oxidation

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[*] Corresponding author. Tel.: +66 53941910; fax: +66 53222268.
*E-mail address:* scijjkmn@chiangmai.ac.th (J. Jakmunee).

[1] Permanent address: Department of Chemistry, Faculty of Science, Naresuan University, Phitsanulok 65000, Thailand.

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of iodide ion by oxygen in air would occur. In a potentiometric titration using sodium thiosulfate as titrant [13], 6 M hydrochloric acid was employed with hexane as oxygen shielding agent. Utilizing a FI system, which prevents direct exposure to air, 12 M hydrochloric acid can be used to accelerate the reaction. This leads to more sensitive methods based on spectrophotometric detection of triiodide at 370 nm [11,12,14]. A similar FI system has been applied to the determination of hypochlorite and chlorate [15]. The former species can react with iodide at room temperature while the latter requires an elevated temperature. A potentiometric flow injection procedure for the determination of oxychlorine species such as chlorate, chlorite and hypochlorite using a redox electrode detection and a Fe(III)–Fe(II) potential buffer solution containing chloride has also been reported [16]. A FI-amperometric method for the determination of chlorate and hypochlorite based on formation of chlorine by the reaction of the analytes with chloride in 8 mol $l^{-1}$ sulfuric acid has also been described [17].

In this work, we developed a sFI-Amp procedure based on the reaction of chlorate with an excess iodide ion in an acidic condition to produce triiodide which is further electrochemically reduced at a glassy carbon electrode. In order to achieve high sensitivity without the use of too high acid concentration, a novel sFI procedure was introduced to promote the reaction by increasing a reaction time and a temperature. This can be done by stopping the flow while the injected zone was being in a mixing coil which was immersed in a water bath. In this way, dispersion of the product zone would be minimized. A simple homemade amperometric analyzer with a lab built flow through electrochemical cell can be used as a detector. A closed system of such a FI also minimizes any side reaction of oxygen with iodide. Moreover, the amperometric detection minimizes interferences from substances usually found in a soil sample which would interfere seriously in a spectrophotometric detection. Application of the proposed sFI-Amp procedure was demonstrated to the determination of chlorate in soil samples from longan plantation area.

## 2. Experimental

### 2.1. Apparatus

The sFI-Amp manifold for chlorate determination is illustrated in Fig. 1(a). It was a modified FIAstar system (5010 Analyzer, Tecator, Sweden), consisting of a peristaltic pump (P), a 6-port injection valve (I) and timing controlled unit. A

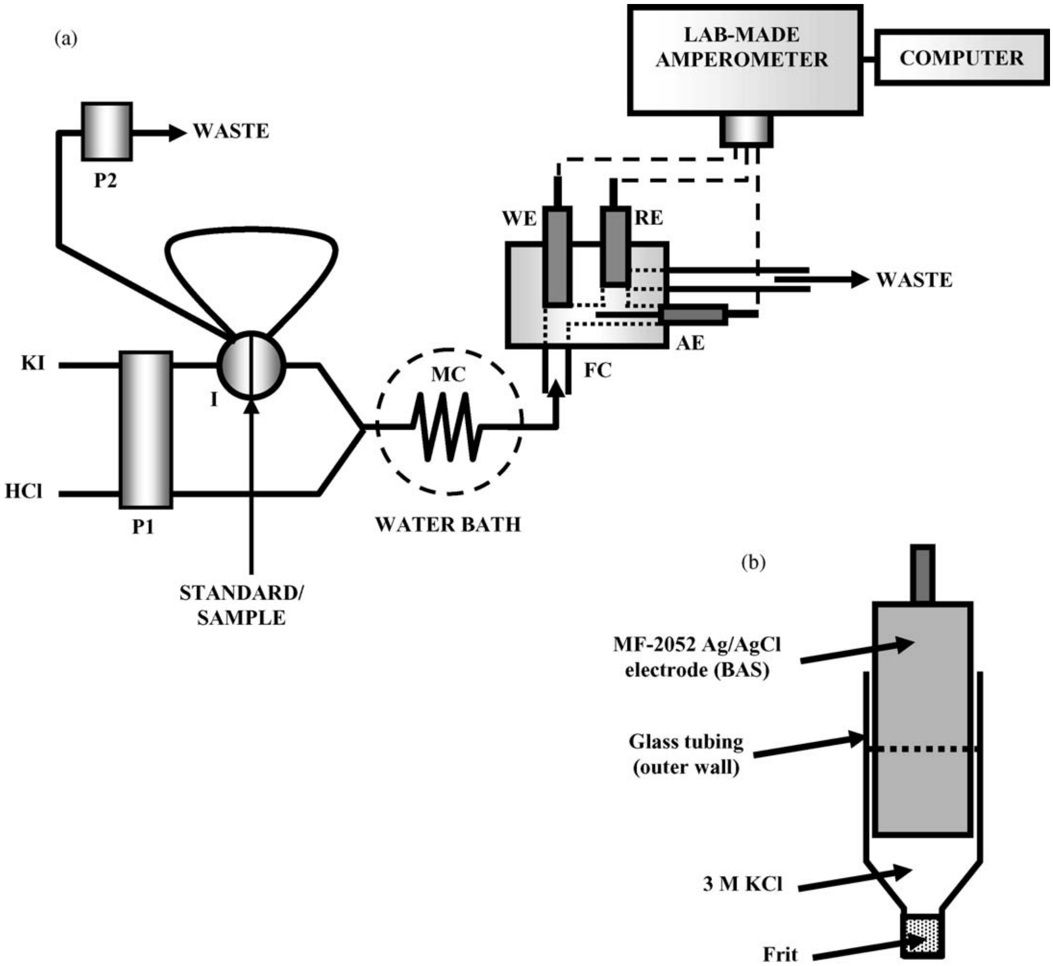

Fig. 1. (a) The sFI-Amp manifold used for determination of chlorate: P1 and P2: peristaltic pump 1 and 2; I: injection valve; MC: mixing coil; AE: auxiliary electrode; WE: working electrode; and RE: reference electrode. (b) A double junction design reference electrode.

lab-made amperometric analyzer with lab built flow through electrochemical cell (FC) was used as a detector. A personal computer with an in-house built software with Basic Stamp 2SX interface unit (Parallex, USA) was employed for recording data. Temperature was controlled by using a water bath (Gallenkamp, England).

A wall jet FC was assembled as shown in Fig. 1(a) (as side view). A Perspex plastic block was drilled to insert electrodes with *o*-ring sealing. Electrolyte carrier solution was entered the cell from the bottom and passed sequentially through a glassy carbon (MF-2012, 3.0 mm diameter, Bioanalytical System (BAS), USA) working electrode (WE), a platinum wire (MW-1032, BAS, USA) auxiliary electrode (AE) and an Ag/AgCl (MF-2052, BAS, USA) reference electrode (RE), respectively. A double junction design of RE (Fig. 1(b)) was used in order to prolong the lifetime of the MF-2052 RE.

All tubings for assembling the FI system were Teflon tube of 0.8 mm i.d., except pump tubes.

### *2.2. Reagents*

Potassium iodide (AnalaR, BDH) and hydrochloric acid (Reagenti, CARLO ERBA) were used to prepare reagent solutions of concentration 0.07 mol $l^{-1}$ and 7.0 mol $l^{-1}$, respectively. The potassium iodide solution was freshly prepared by dissolving 2.92 g KI in 250 ml water and kept in a dark bottle.

Potassium chlorate (99.5 %, w/w, AJAK), after standardization by standard iodometric procedures [18], was used to prepare stock standard solution of $12 \times 10^{-3}$ mol $l^{-1}$ chlorate. A stock solution was stored in a cool and dark place. Working standard solutions were daily prepared by appropriate dilution of the stock solution with water.

All solutions were prepared using Ultrapure water (Milli-Q, Millipore).

### *2.3. Collection and preparation of soil sample*

Soil samples were collected from the longan plantation field in Chiang Mai, northern of Thailand. A soil sample was taken from 15 points at around the rim of the longan tree, at the depth of 15 cm. The sample was dried and ground before a portion of about 100 g was taken for further treatment.

A 25 g of dried-soil sample was extracted by shaking for 2 h with 50 ml of water. It was filtered with filter paper (Whatman, No. 42) and rinsed with water. The filtrate was made up to 100 ml in a volumetric flask with water.

### *2.4. sFI-Amp manifold and procedure*

The sFI-Amp manifold (Fig. 1(a)) was designed to inject a standard or sample (100 μl) into a 0.07 mol $l^{-1}$ potassium iodide stream before merging with 7.0 mol $l^{-1}$ hydrochloric acid stream. This would prevent high concentration of hydrochloric acid entering/destroying the injection valve. The closed FI system also helps to reduce an oxidation of iodide ion by oxygen in air which is an extremely fast reaction in high concentration of hydrochloric acid ($4I^- + 4H^+ + O_2 \rightarrow 3I_2 + 2H_2O$) [10]. A period (called "travelling time") after injection was made until the pump was stopped was set to be 12 s. By doing this, the sample zone was being inside a mixing coil (MC), which was immersed into a water bath of $55 \pm 0.5\,^{\circ}C$. This temperature would promote the reaction of chlorate with iodide and acid to form triiodide. After a period of stopping (called "stopping time") of 90–120 s, the sample zone was flowed further through a FC and the reduction current of the triiodide was monitored by applying a constant potential of +200 mV at a glassy carbon working electrode versus Ag/AgCl reference electrode. The current was converted to potential by the amperometric analyzer and then recorded by the computer as a FI peak. A calibration graph was plotted between the peak height (mV) and chlorate concentration. Chlorate concentrations in sample was calculated using the calibration equation.

## 3. Results and discussion

### *3.1. Optimization of the FI-Amp system for the determination of chlorate*

#### *3.1.1. Amperometric instrument parameters*

The sFI-Amp procedure for determination of chlorate is based on the conversion of chlorate to triiodide by reacting with an excess iodide and hydrochloric acid. A previous report on the detection of triiodide by amperometry based on the reduction of triiodide at a glassy carbon working electrode with an applied potential of +200 mV versus Ag/AgCl reference electrode was followed [19]. The home-made FC was designed to allow the solution passing to WE, AE and RE, respectively, in order to prevent the reaction product at AE to pass over the WE, so this kind of interference could be avoided.

#### *3.1.2. Effect of concentration of potassium iodide*

Concentrations of potassium iodide were studied. From the preliminary study, it was found that HCl concentration of at least 7 mol $l^{-1}$and a temperature of 45 °C should be used in order obtained a signal of chlorate in concentration range of $6.0 \times 10^{-5}$–$6.0 \times 10^{-4}$ mol $l^{-1}$. The concentrations of KI in range of 0.01–0.3 mol $l^{-1}$ was investigated, while the following conditions were selected and kept constant: injection volume, 100 μl; MC length, 300 cm; flow rate of both of potassium iodide and hydrochloric acid streams, 2.9 ml $min^{-1}$; water bath temperature, 45 °C; travelling time, 12 s; and stopping time, 120 s. A series of chlorate standard solutions ($6.0 \times 10^{-5}$–$6.0 \times 10^{-4}$ mol $l^{-1}$) was injected into the system. The obtained peak heights (mV) were plotted versus chlorate concentration (mol $l^{-1}$) yielding a calibration graph. Linear calibration graph was obtained for each concentration of KI used. A plot of the slopes of the calibration graphs versus KI concentrations is depicted in Fig. 2. It should be noted that at a higher concentration of KI, higher baseline signals were obtained which might be due to air oxidation of iodide or some iodate impurity presented in KI and this may lead to decrease of sensitivity (slope). Too low concentration of KI is not sufficient

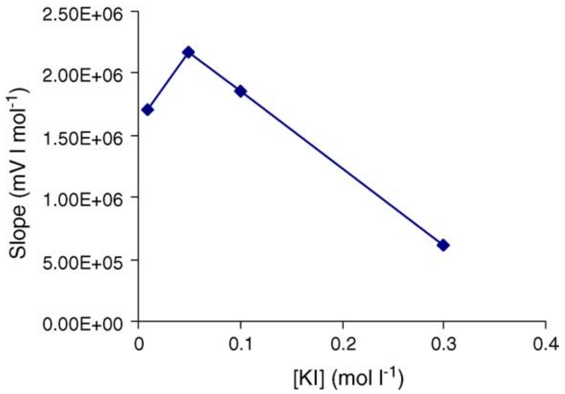

Fig. 2. Effect of concentration of potassium iodide (stopping time = 120 s, temperature = 45 °C, HCl concentration = 7 mol $l^{-1}$, other conditions see text).

in the reaction with the selected concentration range of chlorate and lead to a less sensitivity as well. KI of concentration 0.07 mol $l^{-1}$ was chosen for further study.

### *3.1.3. Effect of stopping time and temperature*

The stopping time in a range of 0–300 s was studied while the above selected condition, with 0.07 mol $l^{-1}$ KI and temperature of 45 °C was used. The results in Fig. 3 show that the slope of calibration graph increased linearly with the increasing of the stopping time. The stopping time of 90–120 s was chosen in order to compromise between sensitivity and rapidity of the analysis.

With a 120 s stopping time, the effect of temperature was then studied. A plot of slope of calibration graph versus temperature is shown in Fig. 4. It can be noticed that sensitivity increased linearly with the increase of temperature in a range of 40–60 °C. The temperature of 55 °C was selected in order to avoid the evolution of bubble in the line when using a higher temperature. It should be noted that although the longer stopping time or higher temperature lead to high sensitivity, the higher peak height of blank solution was also observed. This may be due to the air oxidation of iodide which can be minimized by purging the reagent and sample solutions with oxygen-free nitrogen gas.

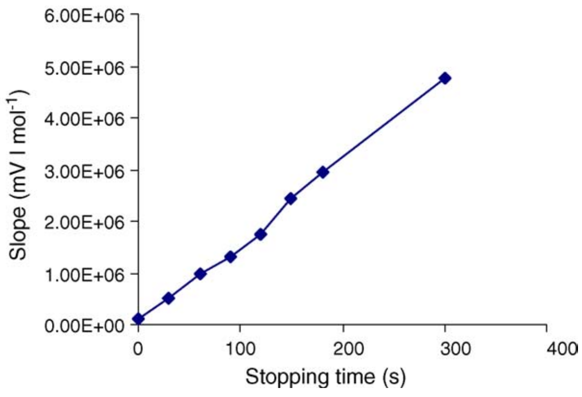

Fig. 3. Effect of stopped time (temperature = 45 °C, HCl concentration = 7 mol $l^{-1}$, KI concentration = 0.07 mol $l^{-1}$, other conditions see text).

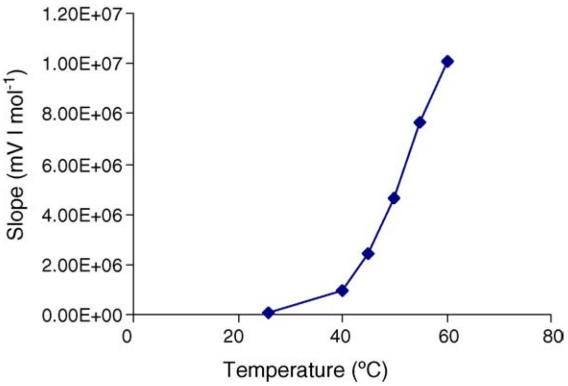

Fig. 4. Effect of temperature (stopping time = 120 s, HCl concentration = 7 M, KI concentration = 0.07 mol $l^{-1}$, other conditions see text).

### *3.1.4. Effect of HCl concentration*

Attempts have been made to reduce concentration of the HCl used. Under the above selected conditions, it was found that sensitivity rapidly decreased when a concentration of HCl was reduced less than 7 mol $l^{-1}$. So 7 mol $l^{-1}$ HCl should be recommended. However, a lower acid concentration may be employed but a longer stopping time should be applied so that a desired sensitivity would be obtained. This would then affect the sample throughput.

## *3.2. Analytical characteristics*

Employing the above selected conditions as shown in Table 1, a series of concentration of chlorate standard solution was injected into the system. FI peaks similar to those of normal FI were obtained as shown in Fig. 5. A calibration graph was constructed by plotting peak height (mV) versus chlorate concentration (mol $l^{-1}$). Calibration graphs were linear in the ranges of $1.2 \times 10^{-6}$–$6.0 \times 10^{-5}$ mol $l^{-1}$ ($y = (1.217 \times 10^{7})x + 14.3$, $r^2 = 0.9977$) and $6.0 \times 10^{-5}$–$6.0 \times 10^{-4}$ mol $l^{-1}$ chlorate ($y = (6.421 \times 10^{6})x + 451.5$, $r^2 = 0.9964$). With a 120 s stopping time, a detection limit of $1.2 \times 10^{-6}$ mol $l^{-1}$ chlorate was

Table 1
Selected conditions of the proposed sFI-Amp procedure

| Parameter | Analytical characteristics |
|---|---|
| Injection volume (μl) | 100 |
| Mixing coil length (cm) | 300 |
| Reagent concentration (mol $l^{-1}$) | |
| KI | 0.07 |
| HCl | 7 |
| Flow rate (ml $min^{-1}$) | |
| KI | 2.9 |
| HCl | 2.9 |
| Travelling time (s)[a] | 12 |
| Stopping time (s)[b] | 90–120 |
| Temperture of water bath (°C) | 55 ± 0.5 |

[a] Travelling time: the period between the point of injection to the point at which the flow is stopped.

[b] Stopping time: the period during the flow is stopped.

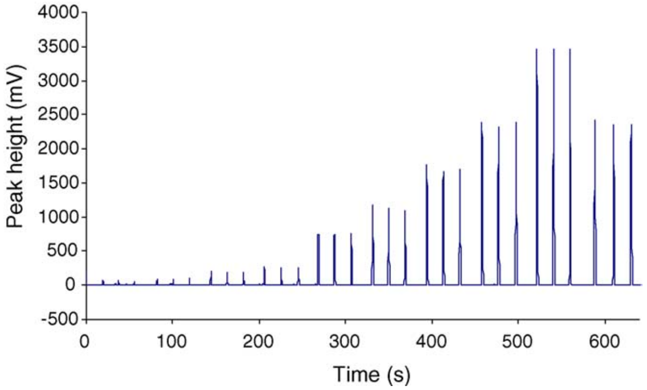

Fig. 5. FIgram obtained from sFI-Amp system for chlorate determination: peaks from left to right were blank, 1.2, 6.0, 12, 60, 120, 240, 360 and 600 μmol $l^{-1}$ of chlorate standard and sample 1, respectively. Conditions as in Table 1 were employed, with stopping time 120 s. Signal was recorded only at the period after the flow was restarted to push the reaction product into the detector.

obtained. A sample throughput was 25 $h^{-1}$. Relative standard deviation was 2% ($1.2 \times 10^{-4}$ mol $l^{-1}$ chlorate, $n = 21$).

Another merit of sFI is the less consumption of reagent, especially when a high concentration of reagent solution is concerned. In this procedure, the consumption of about 1.5 ml each of 7 mol $l^{-1}$ HCl and 0.07 mol $l^{-1}$ KI per injection should be noted.

### 3.3. *Interference study*

The species that can react easily with iodide ion to produce triiodide, e.g. iodate, hypochlorite, chlorite, could be seriously interfere in this system. These ions could be determined first by employing low acid concentration and room temperature and chlorate concentration could be obtained later using elevated conditions [15]. However, these ions are expected to present in some selected soil samples with concentrations of much lower than that of chlorate.

The common ions ($CO_3{}^{2-}$, $NO_3{}^{-}$, $SiO_3{}^{2-}$, $Ca^{2+}$, $Cu^{2+}$, $Fe^{3+}$, $Mn^{2+}$and $Zn^{2+}$), which may be found in soil sample, were studied. The effects of these ions were investigated, by adding the ions to the $1.2 \times 10^{-4}$ mol $l^{-1}$ chlorate standard solution. The relative error in concentration of the standard chlorate solution of less than 5% was obtained for the interfering ion/chlorate mole ratios of 3 for $Cu^{2+}$, 4 for $Fe^{3+}$, and 50 for $CO_3{}^{2-}$, $NO_3{}^{-}$, $SiO_3{}^{2-}$, $Ca^{2+}$, $Mn^{2+}$ and $Zn^{2+}$. $Cu^{2+}$and $Fe^{3+}$ exhibited positive interference because the $Cu^{2+}$and $Fe^{3+}$ can reduce the iodide ion. Fortunately, copper and iron in soil-extracted solution (using water) were at very low concentrations (less than $2.4 \times 10^{-5}$ mol $l^{-1}$ of both ions, determined by flame-atomic absorption spectrophotometry) and did not interfere in this system.

### 3.4. *Analysis of soil samples*

The developed sFI-Amp procedure was applied to the determination of chlorate in soil samples from longan orchards in Chiang Mai, Thailand. Potassium/sodium chlorates are applied to the soil to stimulate flowering of the fruit. Due to a good solubility of the chlorate compounds in water, the soil was extracted with deionized water to have a chlorate concentration in the extract in a suitable range of the calibration graphs ($1.2 \times 10^{-6}$–$6.0 \times 10^{-5}$ and $6.0 \times 10^{-5}$–$6.0 \times 10^{-4}$ mol $l^{-1}$ chlorate). The extracted solution was injected into the system and chlorate content was obtained from the calibration graphs as presented in Table 2. The iodometric titration [18] was performed for comparison. The results of the batch titration method were slightly different from the sFI-Amp method, which may come from interfering of oxygen in air and slow reaction of chlorate with iodide and hydrochloric acid, which was difficult to control in batch titration method. However, the results obtained from both methods are in agreement (*t*-test, 95% confidence).

Table 2
Chlorate contents in soil samples from longan orchards determined by the proposed sFI-Amp procedure and the iodometric titration method [18] (triplicate results)

| Sample number[a] | Chlorate (μg/g) of dried soil | |
|---|---|---|
| | sFI-Amp | Iodometric titration |
| 1 | 335 ± 3 | 341 ± 6 |
| 2 | 108 ± 6 | 118 ± 5 |
| 3 | 88 ± 5 | 100 ± 4 |
| 4 | 20 ± 4 | 16 ± 5 |
| 5 | 27 ± 1 | 34 ± 7 |
| 6 | 15.1 ± 0.4 | 11 ± 5 |
| 7 | 3.9 ± 0.4 | ND[b] |
| 8 | 28 ± 1 | 21 ± 4 |
| 9 | 15 ± 2 | 10 ± 4 |
| 10 | 5.9 ± 0.4 | ND |
| 11 | 140 ± 1 | 147 ± 6 |

[a] Dried soil samples were obtained from Assoc. Prof. Dr. Somchai Ongprasert, Department of Soil Resource and Environment, Faculty of Agricultural Production, Maejo University, Chiang Mai, Thailand.

[b] ND: not detected.

## 4. Conclusion

A novel stopped flow injection amperometric procedure was developed for the determination of chlorate in soil sample. Chlorate in micro-molar concentration can be easily determined with this simple procedure even using a home-made amperometric analyzer and a home-made flow through electrochemical cell. High sensitivity can be obtained without conditions employing too high acid concentration, by promoting the reaction using longer reaction time and higher temperature by stopping the flow while the reaction zone being in a mixing coil which is immersed in a water bath. In a closed FI system, air oxidation of iodide reagent is also minimized. The amperometric detection also reduced the interferences from the substances (e.g. colored species) usually found in soil sample which may interfere very much in spectrophotometric detection. The proposed system provided a sample throughput of 25–35 $h^{-1}$ with less reagent consumption and successfully demonstrated for application to soil samples.

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