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Full Paper

Stopped-flow injection spectrophotometric method for determination of chlorate in soil

Sarawut Somnam[1], Kate Grudpan[1,2], and Jaroon Jakmunee[1,2,*]

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

* Corresponding author, e-mail: scijjkmn@chiangmai.ac.th

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Abstract: A stopped-flow injection (FI) spectrophotometric procedure based on iodometric reaction for the determination of chlorate has been developed. Standard/sample was injected into a stream of potassium iodide solution and then merged with a stream of hydrochloric acid solution to produce triiodide. By stopping the flow while the sample zone is being in a mixing coil, a slow reaction of chlorate with iodide in acidic medium was promoted to proceed with minimal dispersion of the triiodide product zone. When the flow started again, a concentrated product zone was pushed into a flow cell and a signal profile due to light absorption of the product was recorded. Employing a lab-built semi-automatic stopped-FI analyser, the analysis can be performed with higher degree of automation and low chemical consumption. Linear calibration graph in the range of 5-50 mg ClO_3^- L^{-1} was obtained, with detection limit of 1.4 mg ClO_3^- L^{-1}. Relative standard deviation of 2.2% (30 mg ClO_3^- L^{-1}, n=10) and sample throughput of about 20 h^{-1} were achieved. The system was applied to soil samples and validated by batch spectrophotometric and standard titrimetric methods.

Keywords: chlorate, stopped-flow injection, iodometry, soil

Introduction

Chlorate is utilised in the bleaching process in the pulp and paper industry [1]. In addition, chlorate has been employed in agriculture as a herbicide and as a defoliant especially between the years 1930 and 1950. Recently, especially in Thailand, chlorate compounds, e.g. potassium chlorate, have been popularly used for promoting flowering and fruiting of longan. The plant can absorb chlorate through both leaf and root [2]. However, there have been some reports on the effect of chlorate causing damage to plants. The intake of chlorate in high amounts caused falling of leaves and death in plants [2]. Chlorate may compete with nitrate as a substrate for the enzyme nitrate reductase [3-5], which can reduce chlorate to chlorite which is toxic to plants [2,6].

From the above instance, information on chlorate content in soil is therefore useful for controlling the effect of chlorate on plants and the environment. Various methods for determination of chlorate have been reported such as ion chromatography [4], infrared spectrophotometry [7], batch spectrophotometry [8], and flow injection (FI) [9-10]. Ion chromatography and infrared spectrophotometry can quantitate chlorate at low concentration levels, but they require relatively high operating costs and complicated instruments. Batch and FI spectrophotometric methods have gained interest. They are based on different chemical reactions such as iodometric reactions [11], complexation of chlorate with rhenium-α-furildioxime [12], and decolourisation of indigo carmine by chlorate [8]. Although those procedures may provide simplicity and rapidness of analysis, they suffer from interferences and low sensitivities. Stopped-FI procedure can increase sensitivity by increasing the reaction time in a stopping period, thereby promoting more product. It also reduces the main interference due to oxygen in air by allowing the reaction to occur in a closed tube. The stopped-flow injection method with amperometric detection system has been developed for determination of chlorate in soil [13]. However, it involves a complicated system employing a water bath of 55 ^{o}C to accelerate the reaction.

In this work, we propose a stopped-FI spectrophotometric procedure for the determination of chlorate utilising iodometric reactions which were reported for batchwise analysis [14]. The sample is injected into a stream of potassium iodide and merged with a stream of acidic solution. Then, the sample-reagent mixture zone is stopped in a mixing coil to promote the slow reaction of chlorate with iodide in acidic medium to produce triiodide while no dispersion of the product zone occurs during the stopping period. When the flow starts again, the product zone is pushed into a flow cell giving rise to a highly sensitive signal to be recorded as a peak. Since the reaction proceeds in a closed system the interfering effect of oxygen in the air which is usually observed in a batch method is minimised. The peak height obtained is proportional to the chlorate concentration. A calibration graph in the range of 5-50 mg ClO_3^- L^{-1} is achieved with a detection limit of 1.4 mg ClO_3^- L^{-1}. Stopped FI also reduces the consumption of reagent and consequently minimises waste. The whole analysis cycle takes about 160 s, with a consumption of 2.3 mL of each reagent.

Materials and Methods

Chemicals

Deionised water (Milli RX, Millipore) was used throughout. All reagents were of analytical reagent grade unless otherwise stated. Potassium chlorate (99.5 %w/w, Merck) was used to prepare a stock standard solution of 1000 mg L^{-1} ClO_3^-, by dissolving 0.1474 g of the chemical in water, making up to 100 mL in a volumetric flask. Potassium iodide (iodate free, Carlo Erba) (4.1711 g) was dissolved in 250 mL of water to obtain a 0.1 M iodide solution. Hydrochloric acid (7 M) was prepared by diluting 150 mL of conc. hydrochloric acid (Carlo Erba) with water to the final volume of 250 mL.

Sample preparation

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

A portion (20 g) of each sample was extracted with water (20 mL) by shaking for 1 h. The mixture was then filtered through a filter paper (Whatman, No. 42), rinsed with water and the filtrate adjusted to a volume of 25.00 mL with water prior to analysis.

Stopped FI setup

The stopped FI system used is illustrated in Figure 1. A lab-built semi-automatic stopped-FI analyser as reported previously was employed. It consisted of a peristaltic pump (MP-3, Eyela, Japan), a 6-port injection valve (Upchurch, USA) and a microcontroller (Basic stamp II SX) for timing control of the pump and the valves. A detector was a simple spectrophotometer (Spectronic 21, Spectronic Instrument, USA), equipped with a 10 mm path-length flow-through cell (Hellma, Germany). All tubing used was of PTFE tubing of 0.5 mm inner diameter, except Tygon pump tubing (Saint-Gobain Performance Plastics, USA).

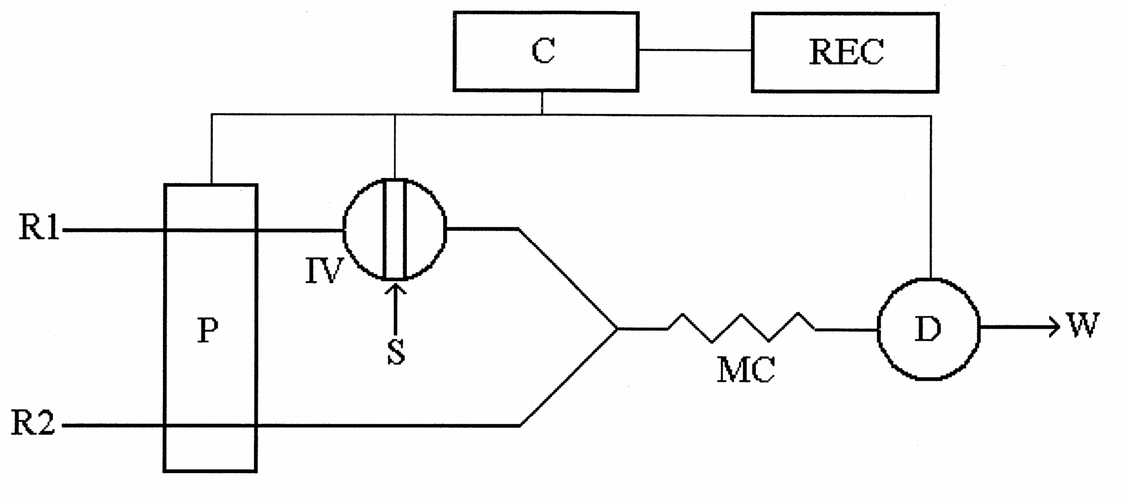

Figure 1. Stopped-FIA manifold for determination of chlorate: R1 = 0.1 M potassium iodide, R2 = 7 M hydrochloric acid, P = peristaltic pump, C = controller, IV = six-port injection valve, MC = mixing coil, D = detector, REC = recorder, S = standard/sample, W = waste

Procedure

A standard or sample (55 μl) was injected into a stream of 0.1 M KI, before merging with a stream of 7 M HCl and flowing to a mixing coil (see Figure 1). This design prevents the contact of concentrated acid with the injection valve, which may cause corrosion of the valve. The flow rate of each stream was 2.0 mL min^{-1}. The operation cycle and peak profiles are illustrated in Figure 2. After injection for 9.5 s, the sample zone was halted for 90 s in the mixing coil by stopping the pump via the control unit of the stopped flow analyser. Then the flow was restarted again to push the zone through the detecting flow cell where absorbance at 400 nm was continuously recorded. The last step would take 60 s. A calibration graph was a plot of peak height versus chlorate concentration. Concentration of chlorate in an unknown sample was then evaluated from the calibration graph.

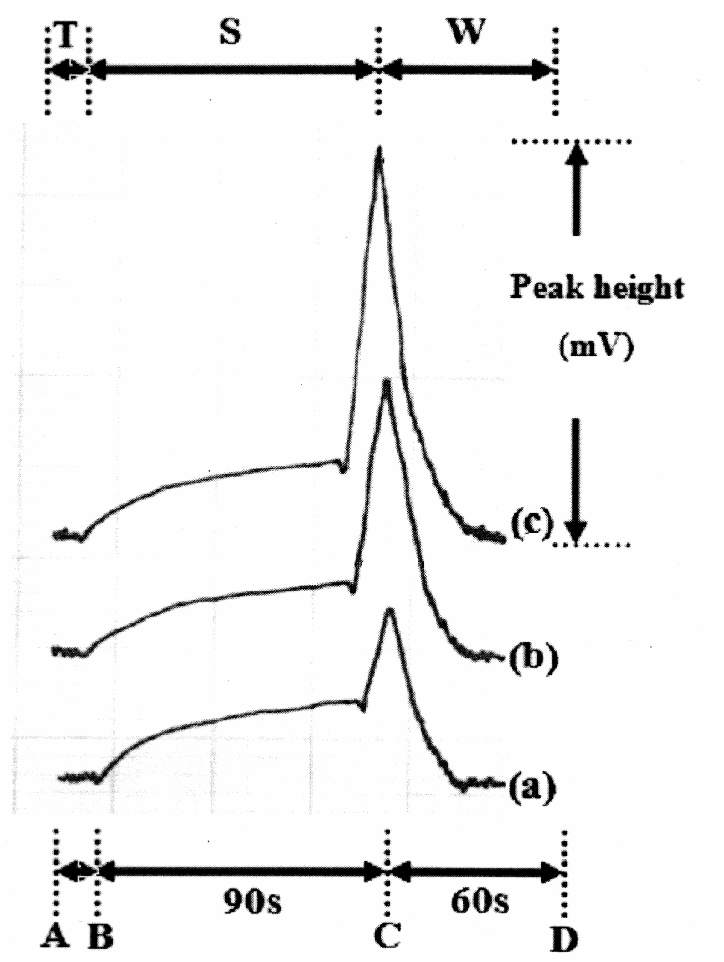

Figure 2. Stopped-FI signal profiles obtained for chlorate concentration of (a) 5 (b) 10 and (c) 20 mg ClO_3^- L^- (T = travelling time: a period from the injection to the stopping point, S = stopping period: a period during which the flow is halted, W = washing time: a period from the restarting of the flow to the end of the analysis, A = sample injecting point, B = point of stopping the flow, C = point of restarting the flow, D = end point of operation cycle)

Results and Discussion

The stopped-FI method for determination of chlorate involves iodometric chemical reactions as follows [14]:

$$ClO_3^- + 6I^- + 6H^+ \rightarrow 3I_2 + Cl^- + 3H_2O \qquad (1)$$

$$I_2 + I^- \rightarrow I_3^- \qquad (2)$$

The triiodide from this reaction can be detected spectrophotometrically at 400 nm. Hydrochloric acid is appropriate for this reaction. An oxy acid such as nitric acid and sulphuric acid is to be avoided in this reaction because it can be oxidised by chlorate.

The first reaction is slow, depending on concentration of ClO_3^-, I^- and H^+. By increasing the concentration of either H^+ or I^- the reaction can be accelerated. Use of elevated temperature also helps [13,15]. However, at high temperature and/or high concentration of H^+, iodide is quantitatively oxidised by oxygen, so the determination cannot be easily carried out in a batch method. Employing a FI manifold, the reaction product can be enhanced during the stopping period designed to extend the reaction time in a closed system of the mixing coil before spectrophotometric measurement is taken [13,16]. This novel approach is different from the conventional stopped-FI in that the reaction zone is halted in the flow cell so that a change in absorbance can be monitored [17-18]. A calibration graph was plotted as peak height versus concentration of chlorate. Various parameters affecting the procedure were then studied.

Effect of stopping time

With concentration of potassium iodide and hydrochloric acid being kept constant at 0.3 and 3 M respectively, stopping time was varied: 15, 30, 60 and 90 s. A series of standard chlorate solutions (100-500 mg ClO_3^- L^{-1}) was injected. It was found that higher sensitivity was obtained the longer the stopping time. The stopping time of 90 s was chosen due to the limitation of the instrument for which a maximum stopping time of 99 s can be set and this period provided enough sensitivity for chlorate determination in soil sample.

Effect of iodide and hydrochloric acid concentration

Effects of concentration of potassium iodide and hydrochloric acid solution were studied in the ranges of 0.1-0.6 M and 5-7 M respectively. With the stopping time of 90 s, a series of standard chlorate solutions (5-50 mg ClO_3^- L^{-1}) were injected in order to construct a calibration graph for each condition. The slopes of the calibration graphs are shown in Figure 3. A higher slope of the calibration graph (higher sensitivity) was obtained with using of higher concentrations of either iodide or hydrochloric acid, except at 7 M hydrochloric acid wherein a higher concentration of potassium iodide led to a lower slope of the calibration graph. This may be due to the oxidation of the iodide ion by air or iodate impurity in potassium iodide chemical, which is more pronounced at high content of acid [13] causing high blank signal and low slope. However, the reaction was minimised at lower iodide concentration (0.1 M) because of inadequate quantity of iodide and/or iodate ion for this reaction. Potassium iodide and hydrochloric acid at 0.1 M and 7 M respectively were selected for further study.

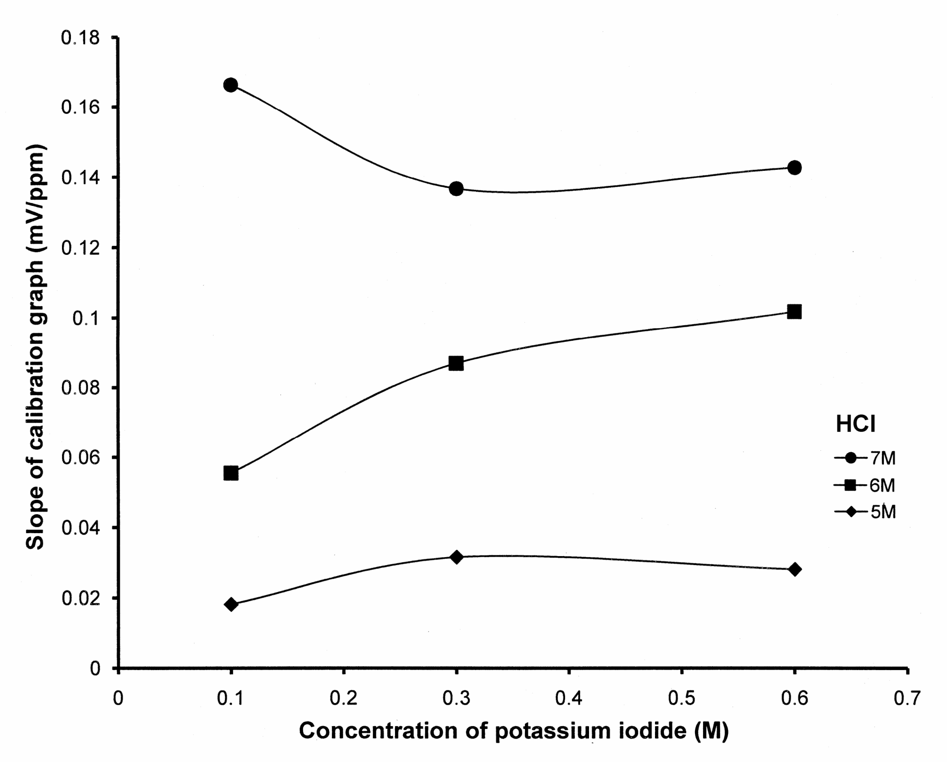

Figure 3. Effect of potassium iodide concentration on sensitivity (slope of the calibration graph of chlorate in concentration range of 5-50 mg ClO_3^- L^{-1}) at different concentrations (5, 6 and 7 M) of hydrochloric acid

Analytical characteristics

A linear calibration graph in the range of 5-50 mg ClO_3^- L^{-1} ($y=0.130x + 0.012$, $R^2=0.996$) was obtained. The detection limit calculated from the calibration data was found to be 1.4 mg ClO_3^- L^{-1}. The relative standard deviation was 2.2% for 10 replicated injections of 30 mg ClO_3^- L^{-1}. With the stopped-FI, the consumption of reagent and consequently the production of waste could be reduced. Each analysis cycle consumed about 2.3 mL each of 0.1 M KI and 7 M HCl solutions.

Analysis of soil samples

Soil samples were analysed for chlorate content by the proposed method. They were also analysed by a batch spectrophotometric method [8] and the titrimetric standard method [14]. The results are summarised in Table 1. Chlorate content found by stopped-FI method (x) agrees well with that found by the standard titrimetric method (y), as indicated by the slope, intercept and R^2 of the correlation graph of the two methods being closed to 1, 0 and 1 respectively ($y=0.95x + 0.08$, $R^2=0.997$). According to the t-test at 95% confidence level [19], there is no significant difference of the results from the three methods.

Table 1. Chlorate content in soil samples obtained by stopped-FI, standard titrimetric and batch spectrophotometric method

Sample number	Chlorate content found (μg g^{-1}) by		
	Stopped-FI*	Titrimetry [14]*	Batch spectrophotometry[8]
1	194 ± 5	189 ± 1	196
2	258 ± 2	245 ± 1	226
3	107 ± 4	103 ± 7	101
4	36.5 ± 0.4	40 ± 2	33.7
5	49.5 ± 0.1	50 ± 1	47.8
6	69 ± 1	62 ± 2	75.7
7	167 ± 2	155 ± 2	142
8	57.8 ± 0.9	46 ± 2	28.9
9	37.8 ± 0.3	36 ± 2	32.3
10	101 ± 4	102 ± 1	91.2
11	127 ± 4	122 ± 1	91.7
12	9.8 ± 0.4	9 ± 1	10.8
13	50.4 ± 0.5	46 ± 1	43.1
14	106 ± 1	96 ± 1	119
15	214 ± 4	201 ± 2	163
16	30.0 ± 0.6	27 ± 1	22.7
17	10.6 ± 0.2	9 ± 1	6.4
18	12.6 ± 0.2	11 ± 0	6.2

*mean of triplicate results

Conclusions

A novel stopped-FI method is proposed, in which there is a stopping of the flow to hold an injected zone of standard/sample in a mixing coil for promoting the reaction to take place without dispersion of the resulting product. It is applied to a slow reaction of chlorate with acidic iodide for the determination of chlorate. The procedure provides a suitable sensitivity for analysis of soil from longan plantation fields where chlorate is used to promote fruiting of the longan trees. With a simple instrument set-up employing a lab-built semi-automatic stopped-FI analyser, the determination can be done with high degree of automation and low reagent consumption.

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