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Reversed flow injection spectrophotometric determination of chlorate

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ABSTRACT

An interfacing has been developed to connect a spectrophotometer with a personal computer and used as a readout system for development of a simple, rapid and sensitive reversed flow injection (rFI) procedure for chlorate determination. The method is based on the oxidation of indigo carmine by chlorate ions in an acidic solution (dil. HCl) leading to the decrease in absorbance at 610 nm. The decrease in absorbance is directly related to the chlorate concentration present in the sample solutions. Optimum conditions for chlorate were examined. A linear calibration graph over the range of 0.1–0.5 mg L^{-1} chlorate was established with the regression equation of $Y = 104.5X + 1.0$, $r^2 = 0.9961$ ($n = 6$). The detection limit (3σ) of 0.03 mg L^{-1}, the limit of quantitation (10σ) of 0.10 mg L^{-1} and the RSD of 3.2% for 0.3 mg L^{-1} chlorate ($n = 11$) together with a sample throughput of 92 h^{-1} were obtained. The recovery of the added chlorate in spiked water samples was 98.5 ± 3.1%. Major interferences for chlorate determination were found to be BrO_3^-, ClO_2^-, ClO^- and IO_3^- which were overcome by using SO_3^{2-} (as Na_2SO_3) as masking agent. The method has been successfully applied for the determination of chlorate in spiked water samples with the minimum reagent consumption of 14.0 mL h^{-1}. Good agreement between the proposed rFIA and the reference methods was found verified by Student's *t*-test at 95% confidence level.

1. Introduction

Contamination of chlorate in the environment arises from human's activities. It has historically been used for weed control in agriculture, at concentrations of 20–40 g L^{-1}, and are still used as a defoliant. Chlorate is being used increasingly as the raw material for the on-site production of chlorine dioxide used in bleaching of pulp and paper [1]. Chlorates are used in the manufacture of fire work, matches, explosives [2], dyes, printing fabrics, paper pulp processing, tanning, finishing of leather and as a weak antiseptic (2–3 percent solutions have been used as mount wash). Chlorates of alkali metals are approved for use in toothpaste at concentrations of 5 percent or less and for other use at 3 percent or less by the European Union. In addition, sodium chlorate is an active ingredient in a number of commercial herbicides [3]. Recently, alkali metal chlorates have been widely applied to soil to stimulate flowering of longan trees [4] particularly, at longan plantation in northern part of Thailand [5] when chloride dioxide is used to disinfect supply water small amounts of chlorate and chlorite are produced [6].

In general when chlorine (Cl_2) is introduced into water as disinfection agent, it is hydrolyzed to form hypochlorous acid (HClO) according to the reaction (1):

$$Cl_2(g) + H_2O \rightleftharpoons HClO + HCl \tag{1}$$

Initially some of the added chlorine reacts with organic matters and metal ions present in water which is not available for disinfection. Hence, the remaining HClO is acted as disinfecting agent in waters such as swimming pools. The HClO solution itself partially dissociate into hypochlorite ions (ClO^-) in water [7,8] as shown in reaction (2):

$$HClO \rightarrow ClO^- + H^+ \tag{2}$$

Chlorate ions in Cl_2 treated waters are arising from disproportionation reaction of a mixture containing HClO and ClO^- in the aqueous solution of chlorine according to reaction (3):

$$2HClO^- + ClO^- \rightarrow ClO_3^- + 2Cl^- + 2H^+ \tag{3}$$

In the presence of sunlight (solar radiation), hypochlorous acid decomposes into hydrochloric acid and oxygen, the reaction can be represent as

$$2Cl_2 + 2H_2O \rightleftharpoons 4HCl + O_2 \tag{4}$$

Since HClO is considered to be a stronger oxidant than Cl_2 and it reacts with HCl to form chlorine gas as indicated in reaction (5):

$$HClO + HCl \rightarrow H_2O + Cl_2 \tag{5}$$

Many hypochlorite compounds exist only in solution and are nonexistent in a pure form, such as HClO which is the least stable of

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the generalized chlorates or oxygen containing chlorine compounds or ions. Hypochlorite is unstable with respect to disproportionation. It tends to degrade by heat (under heating or heat from solar radiation) to a mixture of Cl^-, O_2 and other chlorates as shown in reactions (6) and (7), respectively:

$$2ClO^-(aq) \rightarrow 2Cl^-(aq) + O_2(g) \tag{6}$$

$$3ClO^-(aq) \rightarrow 2Cl^-(aq) + ClO_3{}^-(g) \tag{7}$$

Chlorite ($ClO_2{}^-$) and chlorate ($ClO_3{}^-$) are by-products of chlorine dioxide (ClO_2). Both of them have potential harmful effects [9]. The World Health Organization (WHO) proposed a guideline value of 200 $\mu g\,L^{-1}$ for chlorite but no value for chlorate due to the limited knowledge about its toxicity. Nevertheless, the WHO recommends to minimize the level of chlorate as much as possible as long as there is no reliable toxicological data. In Switzerland, the sum of chlorite and chlorate is limited to 300 $\mu g\,L^{-1}$ in drinking waters [10]. Recently, the new proposed tolerance limit in Switzerland is 200 $\mu g\,L^{-1}$ for both chlorite and chlorate [11]. Ingestion of chlorate causes irritation to the gastrointestinal tract. Symptoms may include weakness, vomiting and diarrhea. Additionally, it may cause abdominal pain, haemolysis, methemoglobinaemia, cyanosis, anuria, coma and convulsions together with liver and kidney damage. Death may occur from renal failure, generally in 4 days. Estimated lethal doses are from 15 to 30 g. Repeated ingestion of small amounts may cause loss of appetite and weight loss. Therefore, monitoring of chlorate residues in environmental samples is a necessary requirement. Various methods have been developed for the determination of chlorate such as titrimetry including iodometry [12–14], potentiometric titration [15], spectrophotometry including UV–Vis spectrophotometry [16–18], fluorescence [19] and chemiluminescence spectrophotometry [20]. In recent years, ion chromatography (IC) has been described for simultaneous determination of chlorate and other oxidants, for example IC–MS method for determining bromate, chlorate, iodate and chlorine dioxide [21]. IC/spectrophotometry employing osmate-catalyzed postcolumn reaction of chlorate with iode for determining chlorate in waters in presece of chlorite bromate and nitrite by measuring the resulting triiodide ($I_3{}^-$) at 288 nm [22]. The standard method [23] for bromate, bromide, chlorate and chlorite determinations by direct injection is also based on incorporating a high capacity anion exchange column with suppressed conductivity detection to the IC system. These hyphenated methods provide highly reliable results. However, they require expensive instrumentation with high maintenance cost and difficulty of operation. Furthermore, some of which are time-consuming with relatively large amounts of sample and reagent consumption together with rather large amounts of waste released. Additionally, some methods require various types of reagent that may enable unexpectedly greater toxicity to the environment. The above methods are not suitable for monitoring of only one analyte such as only chlorate. The more simple, rapid and cheaper means with low reagent/sample consumption and minimum waste released are therefore sought.

Flow injection with spectrophotometric and/or electrochemical detection seems promising to satisfy with these purposes. A number of flow injection methods have been described for chlorate determination in water samples. Using the FI system with either spectrophotometric or electrochemical detector, direct exposure of the analyte to air can be avoided. Previously reported FI spectrophotometric procedures for chlorate determination were based on measurements of the resulting triiodide at 370 nm using KI in 12 $mol\,L^{-1}$ HCl as reagent [24–27]. Recently the similar FI system has been adopted as a basis for the development of a FI method for determining hypochlorite and chlorate [28]. Hypochlorite reacts with iodide at room temperature whereas chlorate reacts under an elevated temperature. With respect to FI with electrochemical detectors, a few articles have been reported. A FI procedure with amperometric detection has been proposed for determining chlorate and hypochlorite based on the liberation chlorine by reaction with chloride in 8 $mol\,L^{-1}$ H_2SO_4 [13]. A potentiomentric flow injection method for quantitation of chlorate, chlorite and hypochlorite has also been developed using a redox electrode detection and a Fe(III)–Fe(II) potential buffer solution containing chloride [29]. More recently, a novel stopped flow injection amperometric procedure for determining chlorate has been described [30]. The method has been successfully applied for the determination of chlorate in soil samples collected from longan plantation area. To our present knowledge, no previously published article based on flow injection spectrophotometric determination of chlorate based on measurement of decoloration of indigo carmine in HCl medium. Only one published paper described a batch-wise spectrophotometric method for chlorate determination using indigo carmine as chromogenic reagent [18].

This article describes a very simple, rapid and relatively inexpensive reversed flow injection procedure for determination of chlorate in waters. An interfacing has been developed to connect the rFI manifold with a personal computer which is used as the readout and the data processing system.

2. Experimental

2.1. Instrumentation

A home-made single-channel reversed flow injection (rFI) system was designed and fabricated using easily available materials and equipment in the laboratory. Teflon tubings with different sizes (0.508, 0.864, 1.067 and 1.321 mm) were used as flow lines. A peristaltic pump, Microtube pump MF-3A (Tokyo Rikakikai Co. Ltd., Japan) was used to deliver the sample and/or standard solution into the rFI system. Disposable syringe (1 mL) (Nissho Nipro Corporation Ltd., Thailand) was used to inject the reagent via a six port valve, model V-451 (Upchurch Scientific, Hungary) into the rFI system which was mixed with the sample stream at a coiled reactor where the chemical reaction was taken place and the reaction product was then carried through the flow through cell (Hellma, Germany) of a spectrophotometer, Jenway model 6400 (Jenway Ltd., U.K.) where the absorption was detected. An interfacing was developed to connect the spectrophotometer with a personal computer that was used as a readout device and data processing system for the proposed rFI manifold.

A pH/mV meter model 5986-2S (Cole-Parmer, USA) was used for pH measurements.

2.2. Reagents

All reagents used in this work were of analytical reagent grade (unless otherwise stated) and used without any further purification. All reagent solutions were prepared and/or diluted with deionized reversed osmosis water (resistivity $\geq$10 $mol\,L^{-1}$ cm).

A standard stock solution of chlorate (100 $mg\,L^{-1}$) was prepared by dissolving 0.0734 g of potassium chlorate, $KClO_3$ (Merck, Germany) in water and diluting to 500 mL in a 500 mL volumetric flask. Standard chlorate solutions of lower concentrations were obtained by appropriate dilution of this stock solution.

A standard indigo carmine solution (5×10^{-5} $mol\,L^{-1}$) was prepared by dissolving 0.0027 g of indigo carmine in water 1 mL of concentrated hydrochloric acid, HCl (37.0%, Merck, Germany) was added followed by diluting to 100 mL with water in a 100 mL volumetric flask.

All possible interfering anions studied (Cl_2, Cl^-, $ClO_2{}^-$, ClO^-, $ClO_4{}^-$, $BrO_3{}^-$, $IO_3{}^-$, $NO_3{}^-$, $SO_4{}^{2-}$ and F^-) and cations (Fe^{3+}, Al^{3+},

Table 1
Optimization of experimental conditions for chlorate determination.

Variable	Range studied	Optimum value
Wavelength (nm)	580 to 630	610
HCl concentration (mol L^{-1})	3.0 to 5.0	4.0
pH	−0.4 to −0.85	−0.63
Indigo carmine in HCl (mol L^{-1})	3.0×10^{-5} to 9.0×10^{-5}	5.0×10^{-5}
Sample or standard flow rate (mL min^{-1})	2.5 to 4.5	2.0
Mixing tubing diameter (mm i.d.)	0.51 to 1.30	1.07
Mixing tubing length (cm)	100.0 to 250.0	200
Reagent injection volume (μL)	100.0 to 200.0	150
HCl in the dye (%, v/v)	0 to 4.0	1.0

Cu^{2+}, Zn^{2+} and Mg^{2+}) were prepared as their aqueous solutions with appropriate concentrations depending on the interfering ions concern. The following compounds were employed for the preparation of interfering ions: Cl^- as KCl (Merck, Germany), ClO_2^- as $NaClO_2$ (BDH, England), ClO^- as NaOCl (BDH, England), ClO_4^- as $KClO_4$ (BDH, England), BrO_3^- as $KBrO_3$ (Merck, Germany), IO_3^- as KIO_3 (Merck, Germany), NO_3^- as KNO_3 (Merck, Germany), SO_4^{2-} as K_2SO_4 (Merck, Germany) and F^- as KF (E. Merck, Germany). For cations the following compounds were employed: Fe^{3+} as $FeCl_3{\cdot}6H_2O$ (Merck, Germany), Al^{3+} as $AlCl_3{\cdot}6H_2O$ (BDH, England), Cu^{2+} as $CuSO_4{\cdot}5H_2O$ (J.T. Baker Inc., Philipsberg, USA), Zn^{2+} as $ZnSO_4{\cdot}7H_2O$ (BDH, England) and Mg^{2+} as $MgSO_4{\cdot}7H_2O$ (BDH, England). EDTA as Na_2EDTA (Fluka, Switzerland) and SO_3^{2-} as Na_2SO_3 GR grade (E. Merck Germany).

2.3. Sample collection and pretreatment

Four natural surface waters were collected from Lamphun Province (S_1–S_4). The samples with sample codes S_1–S_3 were collected from water resources along longan orchards Lamphun Province and sample S_4 was collected from Mae Kuang River, Lamphun Provice. Ground water samples were collected from Chiang Mai. Tap water samples were collected from Laboratories at Chemistry Department and swimming pool water samples were collected from Chiang Mai University. Additionally, 4 water samples (S_8–S_{11}) were collected from the water resources along the longan orchards situated between Chiang Mai and Lamphun Provinces where the majority of the beyond season of longan fruits were produced. The water samples were filtered through a 0.45 μm membrane filter at the selected sampling sites, stored in polyethylene containers and analyzed in the laboratory immediately.

2.4. Procedure

2.4.1. FIA method

The FI and the chemical conditions (see Table 1) were optimized using univariate method. Under optimum experimental conditions, a 150 μL of 5.0×10^{-5} mol L^{-1} indigo carmine in 1.0% (v/v) HCl solution is injected into the flowing sample or standard stream containing chlorate in 4.0 mol L^{-1} HCl with a constant flow rate of 3.2 mL min^{-1} via a rotary valve. After the reaction mixture passed through the mixing coil where the redox reaction is taking place, the reaction product reaches the detector, the absorbance of the dye is detected at 610 nm and displayed by the PC throughout the whole experiments. Calibration graph is obtained by plotting the decreases in peak heights against various concentrations of chlorate.

2.4.2. Standard method for chlorate determination [14]

In order to validate the proposed rFI procedure. The iodometric method was used as standard method for chlorate determination. This procedure is based on the oxidation of iodide to iodine by chlorate in the presence of concentrated hydrochloric acid according to reaction (8):

$$ClO_3^- + 6I^- + 6H^+ \rightarrow Cl^- + 3I_2 + 3H_2O \qquad (8)$$

The liberated iodine is titrated with standard sodium thiosulphate solution using starch solution as the indicator.

$$I_2 + 2S_2O_3^{2-} \rightarrow 2I^- + S_4O_6^{2-} \qquad (9)$$

A 10 mL of concentrated hydrochloric acid was added to 25 mL of the water sample in a 250 mL conical flask, followed by 0.30 g of sodium bicarbonate to remove air. Immediately 1 g of solid potassium iodide (accurately weighed) was added. The reaction mixture was shaken, and allowed to stand for 5–10 min. The solution was titrated with standard 0.01 mol L^{-1} sodium thiosulphate, until just prior to the end point. When the intense yellow color began to fade, a 3.00 mL of starch solution was added to form an intensely blue color complex followed by titration the solution with standard 0.01 mol L^{-1} sodium thiosulphate until the end point was attained, the solution changed from deep blue color to colorless solution.

3. Results and discussion

A simple, rapid and sensitive procedure was developed and applied for the determination of chlorate ions in water samples. Chlorate was determined based on the decolorization of indigo carmine in 4.0 mol L^{-1} hydrochloric acid at 610 nm. The intensity of the color formed or decolorization is related directly to the amount of analyte (ClO_3^-) present.

3.1. Analytical chemistry of indigo carmine

The redox reaction depends very much on the experimental conditions. Therefore, it is very important to optimize the reaction conditions [31]. Various parameters influencing the sensitivity of the method were optimized using the univariate method. Indigo carmine is a dye and is used as a redox indicator [32]. The dye is stable and water soluble between pH 0 and 9, but it decomposes to the semiquinone form at pH >9 [18]. The dye, which has a high absorbance in the reduced form at 610 nm, is colorless in the oxidized form with no absorbance peak above 400 nm. Several studies

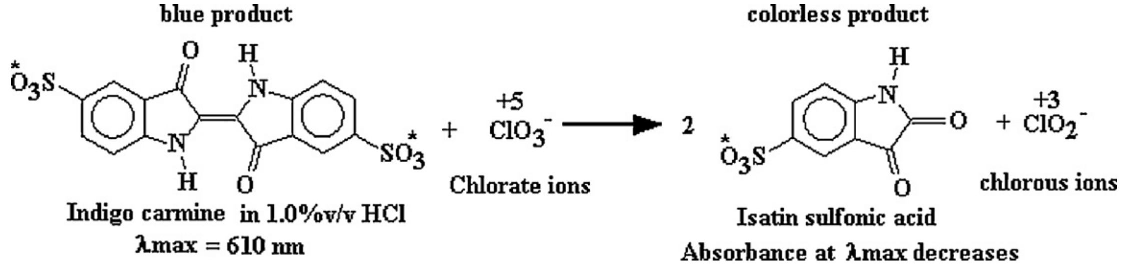

Fig. 1. Chemical reaction between indigo carmine and chlorate ion in hydrochloric acid.

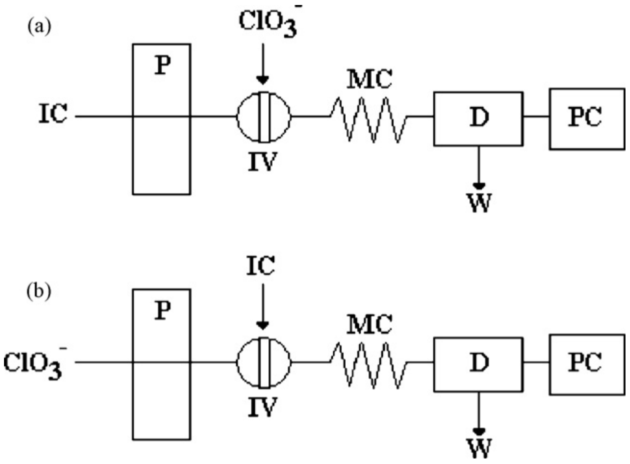

Fig. 2. Two types of FIA manifold. (a) FIA manifold and (b) rFIA manifold, P, peristaltic pump; IC, indigo carmine solution; IV, injection valve; MC, mixing coil; D, detector; PC, personal computer; W, waste.

have been made on the oxidation of indigo carmine using peroxydisulphate [33], hypohalites [34], N-haloarenesulfonamides [35], ozone [36], hydrogen peroxide [37], chlorite and chlorate [18]. The chemical reaction of indigo carmine by chlorate ion in acid solution is shown in Fig. 1.

This work, describes a reversed FIA (rFIA) spectrophotometric procedure for chlorate determination based on the decolorization of indigo carmine by chlorate in acidic media and the decrease in absorbance of the system at 610 nm is a measure of chlorate concentration in the sample. Chlorate reacts with indigo carmine only at very low pH (approximately 0.1) and the stoichiometry of indigo carmine:chlorate is 3:2 [18]. Therefore, the absorbance of indigo carmine at 610 nm will decrease as chlorate concentration increase.

3.2. Preliminary investigation

Two types of FI manifolds were designed and tested for chlorate determination as shown in Fig. 2. Manifold-(a) exhibited a single line nFIA, in which chlorate standard solution was injected into the stream of indigo carmine solution whereas manifold-(b) was a single line rFIA, in which indigo carmine solution was injected into the chlorate standard solution stream. It was found to be more satisfactory to inject the indigo carmine solution into the stream of sample or standard solution containing chlorate ions (manifold-(b)) because its exhibited the greater sensitivity than that obtained by manifold-(a). Thus, the manifold-(b) was chosen for chlorate.

3.3. Optimization of experimental conditions

Preliminary studies revealed that it was found to be more satisfactory to inject the indigo carmine solution into the stream of sample or standard solution (Fig. 2b). To take full advantage of the procedure, various experimental parameters were studied in order to obtain the optimized system. Table 1 shows the optimal conditions for ClO_3^- determination.

3.3.1. Effect of wavelength

The depression of absorbance of indigo carmine due to the presence of chlorate at various wavelengths were recorded over the range of 580–630 nm. It was shown that the highest sensitivity was obtained at 610 nm which correspond with the previously reported one [18]. Therefore, this wavelength (610 nm) was chosen for the determination of chlorate through out further studies.

3.3.2. Effect of HCl concentration

Normally, the pH has more or less effect on the redox potentials of the dye and oxidant. Chlorate is a strong oxidizing agent at low pH. Therefore, it is essential to investigate the effect of pH by varying the concentration of hydrochloric acid from 2.5 to 5.0 mo L^{-1}. The results showed that this reaction was strongly dependent on the hydrochloric acid concentration. At 2.5 mol L^{-1} HCl, indigo carmine was rarely decolorized by chlorate. By increasing the hydrochloric acid concentration from 3.0 to 4.0 mol L^{-1} the sensitivity increased, whereas a greater HCl concentration caused slightly decrease in sensitivity (Table 2). Thus, a 4.0 mol L^{-1} HCl was selected as the optimum hydrochloric acid concentration for subsequent studies.

3.3.3. Effect of indigo carmine concentration

The effect of indigo carmine concentration on chlorate determination was investigated by varying indigo carmine concentrations over the range of 3.0×10^{-5} to 9.0×10^{-5} mol L^{-1}. It was indicated that the sensitivity increased with increasing indigo carmine concentration up to 5.0×10^{-5} mol L^{-1}. When the concentration was greater than 5.0×10^{-5} mol L^{-1} the sensitivity decreased rapidly up to 6.0×10^{-5} mol L^{-1} after that the sensitivity decreased slightly. Therefore, a 5.0×10^{-5} mol L^{-1} indigo carmine solution was chosen as optimum for further experiments.

3.3.4. Influence of HCl concentrations present in indigo carmine solution

The influence of HCl concentration (%, v/v) present in indigo carmine solution was studied by varying the HCl concentration over the range 0–4%. It was found that the highest sensitivity obtained when the HCl concentration was 1% above which the sensitive decreased rapidly up to 3% in HCl and reached the minimum sensitivity at 4% in HCl. So, a 1% (v/v) HCl was selected as optimum and used throughout the experiments.

3.3.5. Effect of reagent flow rate

The flow rate of standard chlorate and/or sample solution plays an important role in the FIA system. Therefore, it is necessary to investigate the optimum flow rate in order to obtain the maximum sensitivity. The effect of flow rate on oxidation reaction of indigo

Table 2
Effect of hydrochloric acid concentration on peak heights.

	Peak height (mV)[a] obtained from the HCl acid concentration (mol L^{-1})					
	2.5	3.0	[Chlorate] (ppm)	4.0	4.5	5.0
0.20	ND	2.7	5.3	6.3	5.3	4.7
0.40	ND	4.7	11.3	12.3	10.7	9.3
0.60	ND	6.7	17.3	18.3	16.3	15.7
0.80	ND	7.7	22.3	23.3	21.0	18.3
1.00	ND	8.7	27.0	29.3	26.0	23.7
Slope (mV/ppm)		7.50	27.20	28.50	25.85	23.50
Correlation coefficient (r^2)		0.9698	0.9967	0.991	0.9989	0.9885

ND is not detected.

[a] Average of triplicate results.

Table 3
Effect of pump flow rate on peak heights.

[Chlorate] (ppm)	Peak height (mV)[a] obtained from the pump flow rate (mL min^{-1})				
	2.5	3.0	3.5	4.0	4.5
0.10	4.7	6.0	6.4	6.0	4.6
0.20	10.7	13.7	14.4	13.4	9.6
0.30	16.3	22.0	23.0	21.7	13.6
0.40	22.7	28.7	30.7	28.0	16.6
0.50	30.7	37.3	41.0	36.7	21.0
Slope (mV/ppm)	64.0	77.6	85.5	76.0	39.8
Correlation coefficient (r^2)	0.9950	0.9989	0.9976	0.9983	0.9937
t_{base} (s)	57	50.0	41.0	36.0	33.0
Sample through put (h^{-1})	63	72	87	100	109

[a] Average of triplicate results.

carmine by chlorate was investigated by varying the flow rate from 2.5 to 4.5 mL min^{-1}. The results (Table 3) showed that the sensitivity increased with increasing flow rate up to 3.5 mL min^{-1}. When the flow rate exceeded 3.5 mL min^{-1} the sensitivity decreased because at high flow rate gave rise to a shorter reaction time and caused decrease in bleaching of indigo carmine. A flow rate of 3.5 mL min^{-1} was chosen as optimum flow rate with a reasonable high sensitivity (86 mV/ppm) of a compromise between sensitivity and sample throughput (87 h^{-1}).

3.3.6. *Influence of the mixing tubing size*

The influences of the inner diameters of mixing tubings on the peak heights of various concentrations of chlorate were studied by varying over the range 0.508–1.321 mm. It was indicated that the inner diameter of 1.07 mm was the most appropriate because it gave the best sensitivity and the better linearity of calibration curve.

3.3.7. *Effect of the mixing tubing length*

In order to achieve maximum sensitivity and the sample throughput, the effect of mixing tubing length was studied. Teflon tubing with a fixed inner diameter (1.07 mm i.d.) but with different lengths (1.00, 1.50, 2.00 and 2.50) were used as a mixing coil. The effect of the mixing tubing length was studied by varying the tubing length from 1.00 to 2.50 m. The optimum length of the mixing tubing chosen for this experiment was 2.00 m because it provided the highest sensitivity and adequate sample throughput (92 h^{-1}).

3.3.8. *Effect of reagent injection volume*

The effect of reagent injection volume was studied by varying a loop length to give an injection volume over the range 100–200 μL. It was seen that the most suitable injection volume was 150 μL which give the best sensitivity and appropriate sampling rate of 92 h^{-1}.

3.4. *Analytical figures of merit*

The calibration curve for the determination of chlorate was linear over the range 0.05–0.80 mg L^{-1} chlorate with regression equation of $Y = 104.5X + 1.4$ and correlation coefficient of 0.9961 ($n = 5$). The precision of the flow injection system (repeatability) and the proposed method (reproducibility) have been determined which were 3.2% and 3.8%, respectively. The detection limit (3σ) was 0.03 mg L^{-1} chlorate together with the limit of quantitation (10σ) of 0.10 mg L^{-1} and the mean percentage recovery of the added chlorate of 98.5 ± 3.1% was obtained ($n = 11$). The simple throughput of 92 h^{-1} and the reagent consumption of 14.0 mL h^{-1} were achieved. The above analytical figures of merit were obtained using the laboratory developed software to connect the rFI manifold with a PC which used as a data display device in order to obtain the more fully automated method. Comparative determination of the same water samples and standard solutions using the same rFI manifold coupled with a chart recorder as readout device. It was found that results obtained with the former rFI manifold (with a PC) were enhanced up to 10-fold of those obtained by using the latter rFI manifold (with a chart recorder). Although the sample throughput was not clearly improved by using PC as readout device, a slightly improved precision was observed with the PC. Apart form improvement in sensitivity, the former rFI manifold was superior to the latter rFI manifold in that, it provided a fully automated means for analysis of real samples because it was capable of automatically displaying the FI signal data processing, calculation, and printing out the results, etc.

3.5. *Interferences*

To study the selectivity of the proposed method, the effects of various cations (Fe^{3+}, Al^{3+}, Cu^{2+}, Zn^{2+} and Mg^{2+}) and anions (Cl^-, ClO_2^-, ClO_4^-, ClO^- BrO_3^-, IO_3^-, NO_3^-, SO_4^{2-} and F^-) were investigated. Interference effects of the above possible ions on chlorate determination were initially studied by varying the weight ratio of interfering ion to chlorate up to 50:1. It was found that Al^{3+}, Zn^{2+}, Fe^{3+}, Cu^{2+}, Mg^{2+}, Cl^-, NO_3^-, F^- and SO_4^{2-} did not interfere. Further increment of the ion:ClO_3^- ratio up to 500. It was obvious that the maximum tolerable ion:ClO_3^- ratios for the presence of selected interfering ions varied from 225 to 50 depending on certain interfering ions concern. The decresing order of maximum tolerable ion : ClO_3^- ratio was as follows : for Fe^{3+} + (225), >F^- (150), >Mg^{2+} (100), >Cu^{2+} (90), >SO_4^{2-} (50) and >ClO_4^- (20). IO_3^-, ClO_2^-, ClO^-, Cl_2 and BrO_3^- interfered seriously (Table 4). It was clear that the presence of all cations studied (Al^{3+}, Zn^{2+}, Fe^{3+}, Mg^{2+} and Cu^{2+}) gave rise to the depression of FI signals (as peak height). The reason for these may be due to the fact that cations form stable complexes with the reagent (indigo carmine) and/or chlorate ions leading to decreases in peak heights. Cations interferences were successfully overcome by using EDTA (Na_2–EDTA) as masking agent. Regarding to anion interferences (Cl^-, NO_3^-, IO_3^-, ClO_2^-, ClO^-, BrO_3^-, ClO_4^-, F^- and SO_4^{2-} together with Cl_2), it was found that Cl^-, NO_3^-,

Table 4
Analysis of spiked water samples.

Chlorate concentration (mg L^{-1})		Recovery (%)
Standard added	Found	
0.00	–	–
0.10	0.097	97
0.15	0.147	98
0.20	0.200	100
0.30	0.297	99
Σx	394	
Average x	98.5	
SD	1.29	
RSD (%)	1.31	

IO_3^-, ClO_2^-, ClO^-, BrO_3^- and Cl_2 exhibited increment of FI signal whereas F^-, SO_4^{2-} and ClO_4^- gave the depression of peak heights. The explanation for these may be due to the fact that Cl^-, NO_3^-, IO_3^-, ClO_2^-, ClO^-, BrO_3^- and Cl_2 are stronger oxidants than the analyte (ClO_3^-), they act as oxidizing agent in the same manner to chlorate resulting in the increment of FI signals. With respect to the presence of F^-, SO_4^{2-} and ClO_4^- in the sample solution containing ClO_3^-, the depression of FI signals was observed probably owing to the stronger oxidizing power of ClO_3^- ions than those of F^-, SO_4^{2-} and ClO_4^- which may be oxidized by ClO_3^-. This caused a decrease in ClO_3^- concentration giving rise to the reduction of FI signals. However, anions interferences such as ClO^-, ClO_2^-, ClO_4^-, IO_3^-, BrO_3^- and Cl_2 could be avoided by using SO_3^{2-} (as Na_2SO_3) as masking agent. Chlorate ions were not masked because the selective masking agent for chlorate was $S_2O_3^{2-}$. Alternatively, both cation and anion interferences can be eliminated by using on-line ion-exchange microcolumn coupled with the FI system which will be published later. It was shown that the major interferences for chlorate determination were BrO_3^-, ClO_2^-, ClO^- and IO_3^- which gave positive error (increment of the FI signal). The interferences effect might be due to the stronger oxidizing power of these ions than ClO_3^- resulting in the decolorization of indigo carmine. Interfering effects of the other cations and anions were negligible (Table 4).

Table 6
Comparative determination of chlorate by the proposed FI method and standard method (Titration).

Sample	Sampling site	Chlorate concentration (mg L^{-1})	
		FIA	Titration
S_1	Natural water from longan orchard, Lamphun	ND	ND
S_2	Natural water from longan orchard, Lamphun	ND	ND
S_3	Natural water from longan orchard, Lamphun	ND	ND
S_4	Natural water from Kuang River, Lamphun	ND	ND
S_5	Ground water	ND	ND
S_6	Tap water from laboratory	ND	ND
S_7	Swimming pool water, Chiang Mai University	22.5	22.5
S_8	Natural water from longan orchard Chiang Mai	0.12	ND
S_9	Natural water from longan orchard Chiang Mai	0.15	ND
S_{10}	Natural water from longan orchard between Chiang Mai and Lamphun	0.17	ND
S_{11}	Natural water from longan orchard between Chiang Mai and Lamphun	0.15	ND

ND represent not detected.

3.6. Application

The proposed rFI procedure has been satisfactorily applied to the determination of chlorate in spiked water samples (Table 5). Comparative determination of chlorate in water samples by the proposed method and standard method (Titration) was also carried out. Water samples were collected from 11 selected sampling sites. Sample codes S_1–S_{11} were collected from water resources from longan orchards in Lamphun and Chiang Mai Provinces where chlorate was applied to the longan trees to accelerate them to bud and blossom beyond season. S_4 and S_5 are reference sampling sites. S_6 and S_7 are sampling sites, which may be contaminated with chlorate. Water samples with sample codes S_8–S_{11} were water samples collected from water resources along longan trees planting areas located between Chiang Mai and Lamphun Provinces. Results were shown in Table 6. It was seen that high chlorate contents were found in the swimming pool water samples (S_7) while chlorate contents in the water samples (S_1–S_6) were not detected. The absence of chlorate in the waters with water sample codes S_1–S_3 might be due to the fact that the chlorate residues were lower the detection limit and that some of which reacted with metal ions and organic materials present in the water samples and they also decomposed to other species with very low oxidizing power. In order to test the sensitivity of the proposed method for analyzing OCl_3^- in real samples, the ClO_3^- residues were investigated in the water samples (S_8–S_{11}) collected from the water resources along the longan trees planting areas between Chiang Mai and Lamphun Province where the majority of beyond season longans were produced. It was shown that small amounts of chlorate residues were found in the water samples (S_8–S_{11}) using the proposed rFI method whereas the chlorate contents in the same water samples were not detected using the titration method because the titration method was not sensitive enough for analysis of real samples.

Table 5
Summary of the interference effects of possible ions on the peak height obtained from 0.30 mg L^{-1} chlorate ion.

Interfering ion	Tolerable concentration ratio[a] (mg L^{-1} of chlorate ions)	Types of interference effects	
		Increment	Suppression
Cl^-, NO_3^-, Al^{3+}, Zn^{2+}	450	Cl^-, NO_3^-	Al^{3+}, Zn^{2+}
Fe^{3+}	225	–	Fe^{3+}
F^-	150	–	F^-
Mg^{2+}	100	–	Mg^{2+}
Cu^{2+}	90	–	Cu^{2+}
SO_4^{2-}	50	–	SO_4^{2-}
ClO_4^-	20	–	ClO_4^-
IO_3^-, Cl_2	5	IO_3^-, Cl_2	–
ClO_2^-, ClO^-	2	ClO_2^-, ClO^-	–
BrO_3^-	0.75	BrO_3^-	–

[a] The concentration of an ion is considered to be interfering when causing a relative error of more than ±10% with request to the signal ClO_3^- alone.

With regard to the ClO_3^- contents found in the swimming pool water in Chiang Mai University (22.5 mg L^{-1}), the ClO_3^- ions may arise from treatment of the water with chlorine or chlorine dioxide as mentioned earlier in the introduction section according to reaction (3). Chlorate ions in Cl_2 treated water are also produced by photochemical reaction (solar radiation). In general, under weak or without solar radiation swimming pool waters contain Cl_2, Cl^-, ClO_2^- ClO^- and other species which can act as oxidizing agent in a similar manner as ClO_3^-. The effects of such species were also examined (Table 4).

Recently, it has been reported that at the initial chlorite (ClO_2^-) concentration of 100 mg L^{-1} under UV illumination, complete photodecomposition of chlorite was taken place yielding the flowing products including chloride (73.9 mol%), chlorate (26.1 mol%) and trace level of perchlorate (2.2×10^{-3} mol%) whereas the dark control contained chlorite (80.6 mol%), chloride (18.9 mol%) and chlorate (0.5 mol%). They also reported that, the irradiated samples under solar radiation produced very similar results as those obtained under the UV lamp. Under irradiation of the 100 mg L^{-1} chlorate solution with solar radiation, complete photodecomposition of ClO_2^- to 80.8 mol% Cl^-, 19.2 mol% ClO_3^- and small amounts of ClO_4^- (1.3×10^{-3} mol%) while the dark control showed the residual ClO_2^- of 76.4 mol%, part of ClO_2^- decomposed to 23.1 mol% Cl^-, and 0.5 mol% ClO_3^- [38]. It is clear that the swimming pool waters under the very bright and hot sunshine as in Thailand contain rather large amounts of Cl^-, moderately amounts of ClO_3^- and very low amounts of other species. The ClO^- ions are not existed because they are the least stable of all chlorates. Fortunately, Cl^-, NO_3^-, Al^{3+}

and Zn^{2+} did not interfere with ClO_3^- determination even in presence of the weight ratio of ions:ClO_3^- 450. However cation and anion interferences can be overcome by using selected masking agents as described earlier.

The proposed computerized rFI manifold is not only useful for water analysis but also useful for analysis of various analytes in a variety of sample matrices continuously whenever expensive reagents are required. In this case, the samples should be non-toxic, inexpensive and easily to collect in large quantity.

4. Conclusions

The use of a personal computer as a readout device using the proposed interfacing/software was feasible. The developed, simple rFI manifold was successfully used for determining chlorate by reverse flow injection spectrometry (Fig. 1) optimum conditions for chlorate determination were achieved (Table 1). A linear calibration graph over the range of 0.1–0.5 mg L^{-1} was obtained with the regression equation $Y = 104.5X + 1.37$ ($r^2 = 0.9961$). The procedure was found to be very sensitive as little as 0.03 mg L^{-1} chlorate could be detected (3σ) while the quantitation limit (10σ) was 0.10 mg L^{-1}. The inter-day and intra-day precisions together with the accuracy of the method were found to be 3.2–3.8% ($n = 11$) and 98.5 ± 31% respectively. The method has been applied for the determination of chlorate in natural water samples collected from 11 selected sampling sites with a sample throughput of 92 h^{-1}. Results obtained by the rFI method were in good agreement with those obtained by conventional titrimetry verified by Student's *t*-test at 95% confidential level. Major interfering ions for this method were BrO_3^-, ClO_2^-, ClO^- and IO_3^-. Upon comparison between the FI signals obtained using the chart recorder as readout device, a 10-fold enhancement of the FI signals was obtained amplification of the signals. Although the speed was not improved with the computer readout, it provided the more completely automated means for analysis of real samples. With suitably slight modification the rFI manifold could be applied to determination of a wide range of samples continuously with very low reagent consumption.

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