Sequential Flow Injection Determination of Chlorine Species Using a Triiodide-selective Electrode Detector

Bahrudin SAAD,[†] Wan Tatt WAI, Abdussalam Salhin Mohd. ALI, and Muhammad Idiris SALEH

School of Chemical Sciences, Universiti Sains Malaysia, 11800 Penang, Malaysia

A flow injection analysis (FIA) method for the determination of four residual chlorine species, namely combined available chlorine (CAC), free available chlorine (FAC), total available chlorine (TAC) and chlorite (ClO_2^-) was developed using a flow-through triiodide-selective electrode as a detector. An important strategy of speciation studies utilized the kinetic discrimination of reactions between the CAC and FAC with Fe^{2+} , which was applied to the speciation of FAC, CAC and TAC. The speciation of available chlorine species and chlorite (an oxychlorine species) was achieved by using the same set-up, but using flow streams of different pH. The effects of the pH of the carrier stream, the flow rate and the sample volume were studied. The method exhibited linearity from 2.8×10^{-6} to 2.8×10^{-4} M active chlorine (expressed as OCl^-) with a detection limit of 1.4×10^{-6} M. The selectivity of the method was studied by examining the minimum pH for the oxidation of iodide by other oxidants, and also by assessing the potentiometric selectivity coefficients. The proposed method was successfully applied to the determination of chlorine species in tap water, and disinfecting formulations where good agreement occurred between the proposed and standard methods were found.

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There is a continuous interest in the development of analytical methods for the determination of residual chlorine, since chlorine has been used in many bleaching and disinfecting treatments for industrial and household utilities throughout the world. Residual chlorine is comprised several species with different chemical properties and germicidal effect.

The major component of the chlorine family is known as "available chlorine",¹ which comprised essentially a class of chemicals that yield hypochlorous acid (HOCl) when is dissolved in water. "Available chlorine" can be subdivided into two categories, namely free available chlorine (FAC) and combined available chlorine (CAC). FAC describes the oxidizing power attributable to chlorine in solutions as HOCl , hypochlorite (OCl^-), or in highly acidic solutions as free chlorine (Cl_2). CAC, which is frequently associated with inorganic chloramines (NH_2Cl , NHCl_2) and organic chloramines (RNHCl , $\text{R} = \text{alkyl}$), undergoes limited hydrolysis in water, permitting only small amounts of HOCl to be formed initially while the rest remains combined. Active chlorine, as determined by iodimetric titrations for FAC and CAC, is known as total available chlorine (TAC) ($\text{TAC} = \text{FAC} + \text{CAC}$).

Another component of residual chlorine, known as oxychlorines, is comprised chlorine dioxide (ClO_2), chlorite (ClO_2^-) and chlorate (ClO_3^-). The oxychlorine species do not produce HOCl , and their oxidizing power is also referred to as active chlorine or "equivalent available chlorine", and is determined by iodimetric titration. Since CAC is more stable than FAC in aqueous solution, it is more preferably used for disinfecting applications, although FAC gives a higher disinfecting capability than CAC (1). Therefore, the speciation of FAC and CAC is necessary to evaluate the stability, dissociation state and disinfecting strength of the solutions.

Chlorite is widely used in the cotton bleaching industry,^{1,2} and

also as an initial compound for chlorine dioxide generation. It is also a major by-product in effluents that had been disinfected with chlorine dioxide plants³ and kraft mills.⁴

Numerous methods, such as the polyaniline film electrode,⁵ chemiluminescent test strip,⁶ diffuse reflectance spectroscopy,⁷ and apart from the conventional colorimetric methods,⁸ potentiometric⁹ and amperometric^{10,11} methods, have been reported for the determination of FAC. Various flow injection analysis (FIA)-based methods have also been reported for the determination of FAC using such reagents as *N,N'*-diethyl-*p*-phenylenediamine (DPD),^{12,13} Methyl Orange (MO),¹⁴ *o*-toluidine,¹⁵ 4-nitrophenylhydrazine,¹⁶ *o*-dianisidine,^{17,18} Rhodamine 6G,¹⁹ bis(2,4,6-trichlorophenyl)oxalate²⁰ and 3,3'-dimethylnaphthidine.²¹ The quantification of CAC and TAC using syringaldazine, indigo carmine, *o*-dianisidine and 2,2'-azino-bis(3-ethylbenzothiazoline) (ABTS) in FIA mode were reported by our group.²³

The speciations of ClO_2^- , ClO_3^- and ClO^- utilizing their kinetic differences in reactions with $\text{Fe}^{2+}/\text{Fe}^{3+}$ buffer²⁵ and iodide²⁶⁻²⁸ at different pH values were reported. However, these methods cannot be used to determine CAC and FAC separately. Separation methods such as capillary electrophoresis²⁹ or ion chromatography,^{4,30-32} and differential pulse polarography^{33,34} were reported for the determination of chlorite. However, none of the separation methods achieved the speciation of FAC and CAC. Although manual spectrophotometric methods, such as those based on DPD⁸ and ABTS,³⁵ are widely used for the sequential speciation of FAC and CAC but these methods suffer selectivity and stability limitations.

A blank polyvinyl chloride (PVC) membrane containing only 2-nitrophenyloctyl ether as a plasticizer has been reported concerning its selective response towards triiodide, and its response mechanism has been postulated.^{24,36} In the present work, we applied this membrane as a triiodide flow-through detector, which enabled the speciation of CAC, TAC, FAC and chlorite to be conducted. Although other triiodide selective

[†] To whom correspondence should be addressed.
E-mail: bahrud@usm.my

Fig. 1 FIA manifold used for the speciation of chlorine. Reagents 1 and 2 contain iodide in acetate buffer at pH 6.0 and 3.0, respectively. Carrier stream: iodide in acetate buffer, pH 6.0. 0.1 M KCl was used as the reference solution stream for the electrode. SV, selection valve; IV, injection valve; RC, reaction coil; PP, peristaltic pump.

electrodes using ionophores³⁷⁻⁴³ have been reported, the blank PVC membrane is preferred due to its simplicity in preparation and its economy.

The novelty of the proposed method lies in the speciation of CAC and FAC based on their different kinetic reactions with Fe^{2+} . The use of Fe^{2+} for the kinetic discrimination and speciation of FAC, CAC and TAC has not been reported. Additionally, the set-up can also be suited for the determination of chlorite in the presence of available chlorine when the reagent stream (0.01 M iodide in acetate buffer) is prepared at different pH values. The studies demonstrate other interesting approaches of speciation studies utilizing the triiodide-selective electrode.

Underlying Principles in Analytical Determination

Speciation of FAC, CAC and TAC

FAC in the form of OCl^- and CAC in the form of ammonia chloramines (NH_2Cl , NHCl_2) or organic chloramines (RNHCl) in aqueous solutions are known to react with iodide to liberate iodine in a slightly acidic solution.⁴⁵ The reaction is faster in more acidic solutions.

ClO_2^- can also produce iodine after reacting with iodide at a lower pH 2.

The liberated iodine in the presence of iodide is converted to triiodide (yellow color),⁴⁶ which is sensed by the electrode.

FAC and CAC react with iodide at the same rate even at a pH as high as 6.5. Therefore, there is no kinetic discrimination for both reactions, and thus the separate determination of FAC and CAC is not possible. The use of NO_2^- to destroy the FAC for the selective CAC measurement³⁵ is not practical in this case because NO_2^- is also an oxidizing agent for iodide.

The reaction of Fe^{2+} with OCl^- to form Fe^{3+} has been reported.²⁵

Fig. 2 (i) FIA peaks obtained from the injection of a sample mixture (FAC + CAC) using water (via SV1). After the first peak (due to TAC) was recorded, a Fe^{2+} stream was activated by SV1, and after injecting mixture, the CAC peak occurred. FAC could be obtained from the difference. Reagent 1 (via SV2) was flowed into the system throughout. (ii) FIA peaks obtained from a sample mixture (FAC + TAC) with the chlorite standard merged with reagent 1 stream (via SV2). After the first peak (due to TAC) was recorded, the reagent 2 stream was activated by SV2, and after injection of the sample mixture with the chlorite standard, the TAC and the chlorite peak appeared. Chlorite value could be obtained from the difference.

Also, by off-line investigations we have found that the reactions of Fe^{2+} with FAC and CAC occur at different rates. In acidic solutions, the reaction with FAC is instantaneous, while for CAC, about 1 min is required for the color formation of Fe^{3+} .

Thus, the difference in the kinetics of the reactions between FAC and CAC with Fe^{2+} has been exploited for the speciations of FAC, CAC and TAC. In the proposed FIA method, TAC is firstly determined by using a water stream (via SV1, Fig. 1), where both FAC and CAC are non-selectively reacted. The mixtures are then merged with reagent 1 (acetate buffer containing iodide, pH 6.0; via SV2) and fill up the loop of the injector (IV). The activation of IV will transfer the products to the surface of the electrode for detection. Secondly, CAC (slower reaction, Eq. (7)) in the presence of FAC is selectively determined by using a Fe^{2+} stream (via SV1), which is then merged with reagent 1 (via SV2). The Fe^{2+} will reduce FAC (Eq. (6)) and the Fe^{3+} formed is masked by F^- , so that it will not oxidize I^- (Fe^{3+} can oxidize I^- to triiodide under slightly acidic conditions).⁴⁶ CAC is then merged with reagent stream 1 (acetate buffer containing iodide, pH 6.0) before it is reduced by Fe^{2+} (Eq. (7)). After merging with the carrier stream (also acetate buffer containing iodide, pH 6.0), the products are injected into the flow system and detected by the electrode. The FAC can be obtained by the difference between the TAC and CAC values (Fig. 2). The use of excess iodide in the carrier stream is to avoid the degeneration of triiodide⁴⁶ on the way to the detector.

Determination of chlorite in the presence of available chlorine

Chlorite, a major by-product of chlorine dioxide disinfection, is normally present with other chlorine species. Since chlorite is unstable in the presence of FAC, both these species are unlikely to coexist together.⁴ On the other hand, chlorate, which is another common by-product together with chlorite, is not reactive to iodide unless at very low pH and in the presence of a catalyst. Therefore, chlorite can be determined in the presence of CAC if the pH of the acetate buffer is maintained at low

value (pH 3). For the selective determination of chlorite in the presence of available chlorine, a water stream (*via* SV1) and a reagent 2 stream (acetate buffer containing iodide, pH 3.0; *via* SV2) were directed into the flow system. NaF was used to complex any Fe^{3+} that was formed, and to prevent its reaction with iodide. Chlorine dioxide can also be determined by this method after undergoing reduction to form chlorite.³⁰

Experimental

Chemicals and reagents

Reagent-grade chemicals and distilled deionized water were used throughout. Acetate buffer was prepared by adding 0.01 M glacial acetic acid (BDH) in a 250 mL volumetric flask that contained sodium acetate (0.01 M) (Sigma). Then, 0.40 g of potassium iodide (Fluka) was added to the solution. The solution was adjusted to the appropriate pH (3.0 or 6.0). Ferrous sulfate (2×10^{-3} M) (Aldrich) and sodium fluoride (4.0×10^{-3} M) (Sigma) were prepared in deionized water. FAC and chlorite standard solutions were prepared from 11% (w/v) sodium hypochlorite (BDH) and sodium chlorite (Sigma), respectively, and were standardized iodimetrically every day before use. Syringaldazine (SYR) (Fluka) was prepared in methanol:water (1:1, v/v).²³ The DPD (Fluka) ammonium ferrous titration and iodimetric titration solutions were prepared according to the standard method.⁴⁴

Apparatus

Potentiometric measurements were performed at $25.0 \pm 0.2^\circ\text{C}$ using an Orion 701 A digital ion analyzer equipped with an Orion 90-02 Ag/AgCl reference electrode. A glass calomel electrode connected to an Orion research expandable ion analyzer (Model EA 940) was used to measure the pH of aqueous solutions.

Preparation of PVC membrane

A triiodide-selective membrane was prepared by dissolving 2-nitrophenyl octyl ether (Fluka) (0.2 g) and PVC powder (Sigma) (0.1 g) in 3 mL tetrahydrofuran (Merck). The mixture was stirred for 30 min, and four drops of the mixture were applied dropwise to the tip of a coated-wire platinum substrate and left to dry. The electrode was conditioned in an iodide solution for 2 h before use. Details of the flow cell and its use in the FIA mode have been described elsewhere.^{47,48}

FIA set-up

The FIA set-up is shown in Fig. 1. A flow-through cell of the wall-jet design with in-built reference electrode (Model FIP-3), supplied by Chemflow Devices (Thornbury, Victoria, Australia), was used. Solutions were propelled by a multichannel peristaltic pump (Gilson Miniplus 3) equipped with PTFE tubings (0.8 mm i.d.). A Rheodyne-type 500 four-way injection valve and two Rheodyne 500 selection valves were used for sample injection and buffer solution selection. The comparative FIA spectrophotometric method, based on SYR²³ for FAC determination, was carried out using a Hitachi spectrophotometer equipped with an Uvonic ultramicroflow cell of 20 μL and 1.0 mm pathlength. The compositions of the FI streams were: ferrous sulfate (2.0×10^{-3} M); NaF (4.0×10^{-3} M); reagent 1 (0.01 M iodide in acetate buffer, pH 6.0); reagent 2 (0.01 M iodide acetate in buffer, pH 3.0); carrier stream (same as reagent 1, *i.e.*, 0.01 M iodide in acetate buffer, pH 6.0); 0.1 M potassium chloride (Fluka) was used as the reference solution for the electrode.

Selectivity studies

Selectivity coefficients were studied using the FIA conditions that were used for TAC determination (*i.e.*, water stream *via* SV1 and reagent 1 stream *via* SV2). Foreign ions (Fe^{3+} , Zn^{2+} , CO_3^{2-} ; F^- , NH_4^+ ; Fe^{2+} , ClO_3^- , Mn^{2+} , CrO_4^{2-} , Ca^{2+} , K^+ ; BrO_3^- , Mg^{2+}), except for Cu^{2+} (5.9×10^{-5} M), were arbitrarily prepared at 2.4×10^{-4} M. The peak heights of these foreign ions and Cu^{2+} when injected into the FIA unit (mV) were recorded as H_i . The peak height when injected with the OCl^- standard solution (C_{OCl^-}) (7.4×10^{-5} M) was recorded as H_{OCl^-} . The selectivity coefficients, $K_{\text{OCl}^-,i}^{\text{pot}}$, were determined by the separate solutions method²⁴ using the following expression:

$$K_{\text{OCl}^-,i}^{\text{pot}} = \left(\frac{C_{\text{OCl}^-}}{C_i^{-1/z_i}} \right) \exp \left(\frac{H_i - H_{\text{OCl}^-}}{S_{\text{ex}}} \right),$$

where S_{ex} represents the calibration slope of OCl^- and z_i is the charge.

Acetic acid (0.01 M) and/or sodium acetate (0.01 M) were used to adjust the pH.

Analysis of real samples

Four brands of disinfecting solutions containing FAC and CAC, which were diluted to different working concentrations, as well as tap water, were used to validate the method. Standard DPD ammonium ferrous titration and iodimetric methods⁴⁴ were used as reference methods for TAC determination. The DPD method was chosen, since it can detect < 1 ppm OCl^- , while the iodimetric method can only detect $\text{OCl}^- > 1$ ppm.⁴⁴ The FIA method based on syringaldazine,²³ was employed as a comparative method for the evaluation of CAC. A recovery test for chlorite was performed by adding the chlorite standard at three different concentrations to diluted disinfecting solutions that had been treated with excess ammonium sulfate (to convert all of the FAC in the solutions to CAC).

Results and Discussion

Effect of the pH and FI variables

The effect of the pH of the carrier stream from 1.7 to 7.2 on the triiodide membrane response was studied. It was found that pH 3.0 produced the most intense peak (Fig. 3). The reduction in the signal at higher pH values was due to a slow reaction between chlorine and iodide, especially when the pH is more than 7. A too much acidic carrier stream had to be avoided because this would enhance the reaction of oxidants, such as Fe^{3+} , Cu^{2+} , MnO_4^- and IO_3^- , with iodide other than chlorine itself. A carrier stream of pH 6, however, was used because only a few oxidants can oxidize iodide at this pH. Thus, when measurements of only FAC and CAC are intended, the pH of the reagent stream 1 was maintained at pH 6.0.

The effect of the injected volume was studied by injecting 1.96×10^{-4} M OCl^- from 25 μL to 150 μL and where a gradual increase in the peak height until 100 μL (Fig. 4) was found. The effect of the carrier flow rate (0.6 to 2.5 mL min^{-1}) also shows increasing sensitivity until about 1.25 mL min^{-1} , where minimum potential changes were found thereafter (Fig. 5). The response time for a larger sample volume was longer, while the higher flow rate increased the time for the peak to reach its baseline. Therefore, pH 6.0 for the reagent 1 stream, 25 μL of the sample volume and 1.25 min^{-1} of the carrier flow rate were adopted for the system. The lengths of reaction coils RC1 and RC2 were not critical due to the fast reaction involved, and thus 10 cm of the coil was sufficient for satisfactory results.

The speciation procedure stated above is not feasible for

Fig. 3 (A) Effect of the pH of the carrier stream on potential signals when injected with the 1.96×10^{-4} M OCl^- standard. Carrier flow rate, 1.25 mL min^{-1} ; injected volume, $25 \mu\text{L}$. The water stream (via SV1) and the reagent 1 stream (via SV2) were flowed into the system. (B) Effect of pH of reagent stream on the potential signal when injected with chlorite standard (9.9×10^{-5} M). Carrier stream flow rate, 1.25 mL min^{-1} ; sample volume, $25 \mu\text{L}$; pH of carrier stream, 6.

Fig. 4 Effect of the volume of the injected OCl^- standard (1.96×10^{-4} M) on the electrode signals. Carrier stream flow rate, 1.25 mL min^{-1} ; injected volume, $25 \mu\text{L}$. The water stream (via SV1) and reagent 1 stream (via SV2) were flowed into the system.

Fig. 5 Effect of the carrier flow rate on the potential peaks when injected with the 1.96×10^{-4} M OCl^- standard. Sample volume, $25 \mu\text{L}$; reagent and carrier pH 6. The water stream (via SV1) and the reagent 1 stream (via SV2) were flowed into the system.

Fig. 6 Calibration plot obtained from the injections of different concentrations of OCl^- on the potential change (carrier flow rate, 1.25 mL min^{-1} ; sample volume, $25 \mu\text{L}$; carrier and reagent stream, pH 6.0; the water stream via SV1 and the reagent 1 stream via SV2 were flowed into the system).

Table 1 Selectivity coefficients of foreign ions

	$\log K_{\text{OCl}^-,1}^{\text{pot}}$		$\log K_{\text{OCl}^-,1}^{\text{pot}}$
Fe^{3+}	-0.50	ClO_3^-	-0.53
NH_4^+	-1.60	Mn^{2+}	-0.50
Cu^{2+}	-0.02	CrO_4^-	-0.52
Zn^{2+}	-0.40	BrO_3^-	-0.55
CO_3^{2-}	-0.42	K^+	-0.73
Mg^{2+}	-0.32	Ca^{2+}	-0.52
Fe^{2+}	-0.38		

Table 2 Minimum pH for the oxidation of iodide by various species

Oxidant	pH	Oxidants	pH
BrO_3^-	4.0	ClO_3^-	1.0
NO_2^-	5.0	CrO_4^-	2.0
Fe^{3+}	6.5	Cu^{2+}	6.5
IO_3^-	6.5	MnO_4^-	6.5

Table 3 Comparison of the results for the determination of TAC

Sample	TAC, $\times 10^{-6}$ M	
	FIA	Standard method ^a
Tap water	18.72 ± 0.03	8.40 ± 0.02
Tap water	25.84 ± 0.02	5.60 ± 0.03
Diluted bleach 1	10.2 ± 0.08	9.84 ± 0.07
Diluted bleach 2	15.8 ± 0.07	16.8 ± 0.09
Diluted bleach 3	17.6 ± 0.07	16.8 ± 0.08
Diluted bleach 4	48.7 ± 0.1	56.0 ± 0.2
Diluted bleach 5	13.7 ± 0.07	14.8 ± 0.09

a. $n = 4$. Based on manual DPD ferrous ammonium titrations.⁴⁴

manual iodimetric titration⁴⁴ because of non-selective reactions between CAC and FAC with I^- under the equilibrium conditions. F^- is used effectively for the masking of Fe^{3+} , since it does not complex Fe^{2+} .⁴⁶ The correct concentration of the Fe^{2+} solution used is important concerning the success of the FIA system. The Fe^{2+} concentration should be in the range of 3×10^{-4} – 3×10^{-3} M to ensure a complete reaction of the FAC that is present in the working concentration range. An Fe^{2+} concentration exceeding the range above will accelerate the reduction of CAC, thus causing an error in the determination.

Determination of chlorite (ClO_2^-)

Chlorite undergoes reduction by iodide (Eq. (4)) only at a lower pH value than that of the available chlorine species. Because chlorite is unstable in the presence of FAC and Fe^{3+} ,^{1,4} it is unlikely for FAC and chlorite to coexist together in a solution. Also, the reduction of chlorite by iodide and Fe^{2+} is very slow at pH 6. Thus, chlorite is not expected to interfere in the determination of FAC and CAC under the adopted experimental conditions. However, if the determination of chlorite is intended, the same manifold can be used by changing the pH of the reagent stream (from pH 6.0 to 3.0) to facilitate the reaction of chlorite and iodide to form triiodide. The effect of the pH of the reagent stream on the chlorite peaks is shown in Fig. 3. It is clear that the reaction between chlorite gives a superior sensitivity at pH 3 or less. If the speciation of chlorite and available chlorine species is intended, the value of chlorite

Table 4 Comparison of the results for the determination of the chlorine species ($\times 10^{-4}$ M)

Sample	Proposed FIA method		Reported method ^a		Standard iodimetry ⁴⁴
	CAC	TAC	CAC	TAC	TAC
Diluted bleach 6	2.13 $\pm$ 0.02	2.94 $\pm$ 0.03	2.12 $\pm$ 0.05	2.77 $\pm$ 0.06	2.83 $\pm$ 0.07
Diluted bleach 7	1.41 $\pm$ 0.01	1.85 $\pm$ 0.02	1.40 $\pm$ 0.02	1.74 $\pm$ 0.04	1.68 $\pm$ 0.05
Diluted bleach 8	2.13 $\pm$ 0.02	2.57 $\pm$ 0.03	2.10 $\pm$ 0.04	2.66 $\pm$ 0.05	2.60 $\pm$ 0.06
Diluted bleach 9	1.96 $\pm$ 0.01	2.45 $\pm$ 0.02	2.10 $\pm$ 0.04	2.41 $\pm$ 0.05	2.24 $\pm$ 0.05

a. $n = 4$, FIA based on syringaldazine reagent.²³

can be calculated from the difference in the peak height of TAC (Fig. 2(ii)).

Analytical characteristics

Under the adopted experimental conditions, the calibration graph (Fig. 6) showed a linear range of OCl^- from 2.8×10^{-6} to 2.8×10^{-4} M (validated by standard iodimetric titration). The detection limit ($S/N = 3$) is about 1.4×10^{-6} M and the linear-regression equation of the calibration is $y = 37.80x + 215.5$ with a correlation coefficient of 0.996. The linear range of the proposed method is similar to that of the reported FIA DPD colorimetric method but longer than the Pb-ISE potentiometric methods (2.8×10^{-6} – 2.8×10^{-5} M).²² The reproducibility when expressed as the relative standard deviation of four repeated injections of 2.24×10^{-4} M OCl^- standard is $\pm 1.1\%$. The sample throughput, calculated from repeated injections of the OCl^- standard at the lowest linear range, was 75 samples per hour. The electrode remained functional for at least one week of normal use without any noticeable reduction in the sensitivity or the response time.

Selectivity of the method

Ortuno *et al.* reported on a blank PVC triiodide membrane for the determination chlorine.²⁴ Common anions, such as PO_4^{3-} , Cl^- , $\text{S}_2\text{O}_3^{2-}$, SO_4^{2-} , NO_3^- , Br^- and I^- , were tested for their potentiometric selectivity coefficient. It was found that the selectivity was better than that of the other triiodide selective membranes that contained ionophores.²⁴ The selectivity of the triiodide electrode was further tested for several oxidants that are known to oxidize iodide, such as ClO_3^- , BrO_3^- , CrO_4^{2-} , Cu^{2+} , Fe^{3+} and MnO_4^- , as well as other ions that are known to be present in municipal water (*e.g.*, Mg^{2+} , Zn^{2+} , Mn^{2+} , Ca^{2+} , K^+ , NH_4^+ and CO_3^{2-}). Data indicate that the electrode is more selective towards the analyte over all of the foreign ions tested (Table 1). The effects of cations such as Fe^{3+} and Cu^{2+} can be masked by adding F^- or EDTA.

The carrier acetate buffer was prepared at pH 6.0 for the determination of TAC. The possibility of a few oxidants to cause interference under the experimental condition was investigated by manually mixing equal volumes of oxidant (0.01 M) with iodide (0.01 M) solutions. Acetic acid (0.01 M) was added dropwise while the solution was continuously stirred until the appearance of a yellow solution due to the formation of triiodide. The pH of the solution at this point was measured, and the results are given in Table 2. IO_3^- , MnO_4^- , Fe^{3+} and Cu^{2+} interfered under the tested condition.

Applications

The proposed method was applied to the determination of TAC in tap water and several diluted disinfecting solutions. For the determination of TAC at less than 2.8×10^{-5} M (equivalent to 2.8×10^{-5} M active chlorine), DPD ammonium ferrous titration⁴⁴ was employed as a reference method (Table 3). A

paired student *t*-test was performed at the 95% confidence level, and it was found that there was no significant difference in the means of the results obtained from the proposed FIA and the manual DPD ferrous ammonium titration method⁴⁴ (calculated *t*, 0.995; tabulated *t*, 2.447).⁴⁹

For the determination of CAC and TAC in the bleach solutions with the chlorine content being more than 2.8×10^{-5} M, the FIA spectrophotometric method based on syringaldazine²³ was used (Table 4). The TAC levels were also determined using the iodimetric titration.⁴⁴ The calculated *t* value based on the results between the TAC of the proposed method and standard iodimetric titration is 2.19 (tabulated *t* value, 3.182), while calculated *t* value between the CAC of proposed method and reported method is 0.4737 (tabulated *t* value is 3.182), showing no significant difference between the proposed method and the comparative methods at the 95% confidence level. Typical FIA peak signals are shown in Fig. 7.

The recovery for chlorite (Table 5) was tested using three different bleach solutions that had been treated with excess ammonium sulfate to convert all of the FAC to CAC (chlorite not stable in the presence FAC), before a known amount of chlorite was added to the solutions. The values of chlorite were obtained by the difference between the TAC peaks before and after the addition of chlorite. Good recoveries were obtained from the tested samples (Table 5).

The FIA methods can be readily extended to the determination of chlorate ($\text{ClO}_3^- + \text{I}^- \xrightarrow{\text{OsO}_4 \text{ catalyst}} \text{I}_3^-$)³⁵ or chlorine dioxide ($\text{ClO}_2 \xrightarrow{\text{reducing agent}} \text{ClO}_2^-$).³⁵

Conclusion

A flow injection system based on a triiodide-selective membrane electrode was successfully developed for the speciation of FAC, CAC and TAC using the kinetic difference between the reactions of FAC and CAC with Fe^{2+} . The proposed method enables the on-line conversion of CAC and TAC to triiodide. An advantage of the on-line conversion is preventing the degeneration of triiodide (I_3^- is unstable when exposed to air).¹ The speciation of available chlorine and chlorite was achieved by changing the pH of the reagent stream. Good agreement between the results of the chlorine species and the reference method was found.

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References

1. J. S. Sconece, "Chlorine: Its Manufacture, Properties, and

Table 5 Recoveries of chlorite from bleach solutions determined using the proposed FIA ($n = 4$)

Sample	$\text{ClO}_2^- \times 10^{-5} \text{ M}$			Recovery, %
	Original bleach	ClO_2^- spiked	ClO_2^- recovered	
10	3.08 ± 0.1	1.08	1.13 ± 0.09	105.0 ± 0.3
11	9.80 ± 0.3	1.08	1.04 ± 0.09	96.4 ± 0.2
12	9.71 ± 0.2	1.08	1.03 ± 0.08	95.6 ± 0.3

Uses", 1972, Huntington, New York.

2. W. J. Williams, "Handbook of Anion Determination", 1979, Butterworth, London.
3. E. Veschetti, B. Cittadini, D. Maresca, G. Citti, and M. Ottaviani, *Microchem. J.*, **2005**, 79, 165.
4. J. Sullivan and M. Douek, *J. Chromatogr., A*, **1998**, 804, 113.
5. X. L. Xiao, J. Ming, and W. L. Xing, *Sens. Actuators, B*, **2004**, 97, 144.
6. J. J. Claver, M. C. V. Miron, and L. F. C. Vallvey, *Anal. Chim. Acta*, **2004**, 522, 267.
7. S. G. Dmitritrienko, O. A. Sviridova, L. N. Pyatkova, V. A. Zhukova, and Y. A. Zolotov, *Anal. Chim. Acta*, **2000**, 405, 231.
8. "Standard Methods for the Examination of Water and Wastewater", 16th ed., 1986, American Public Health Association, American Works Association, Water Pollution Control Federation, A. P. H. A, Washington, D.C.
9. L. P. Rigdon, G. J. Moody, and J. W. Frazer, *Anal. Chem.*, **1978**, 50, 465.
10. W. Matuszewski and M. E. Meyerhoff, *Anal. Chim. Acta*, **1991**, 248, 391.
11. W. Matuszewski and M. Trajanowicz, *Anal. Chim. Acta*, **1988**, 207, 59.
12. K. Carlsson, L. Moberg, and B. Karlberg, *Water Res.*, **1999**, 33, 375.
13. G. Gordon, D. L. Sweetin, K. Smith, and G. E. Pacey, *Talanta*, **1991**, 38, 145.
14. D. L. Legget, N. H. Chen, and D. S. Mahadevappa, *Analyst*, **1982**, 107, 433.
15. J. G. March, M. Gual, and B. M. Simonet, *Talanta*, **2002**, 58, 995.
16. K. K. Verma, A. Jain, and A. Townshend, *Anal. Chim. Acta*, **1992**, 261, 233.
17. M. C. Icardo, J. V. C. Mateo, and J. M. Catalayud, *Anal. Chim. Acta*, **2001**, 443, 153.
18. M. C. Icardo, J. V. C. Mateo, and J. M. Catalayud, *Analyst*, **2001**, 126, 2087.
19. G. P. Irons and G. M. Greenway, *Analyst*, **1995**, 114, 477.
20. M. Nakamura, N. Coichev, J. M. Lin, and M. Yamada, *Anal. Chim. Acta*, **2003**, 484, 101.
21. E. Pobozy, K. Pyrzynska, B. Szostek, and M. Trojanowicz, *Microchem. J.*, **1995**, 51, 379.
22. A. Sakai, A. Hemmi, H. Hachiya, F. Kobayashi, S. Ito, Y. Assano, T. Imato, Y. Fushinuki, and I. Taniguchi, *Talanta*, **1998**, 45, 575.
23. B. Saad, T. W. Wan, M. S. Jab, S. W. N. Wan, M. I. Saleh, and J. M. Slater, *Anal. Chim. Acta*, **2005**, 537, 197.
24. J. A. Ortuno, C. S. Padreno, J. Hernandez, and D. J. Oliva, *Talanta*, **2005**, 65, 1190.
25. H. Ohura, T. Imato, and S. Yamasaki, *Talanta*, **1999**, 49, 1003.
26. D. G. Themelis, D. W. Wood, and G. Gordon, *Anal. Chim. Acta*, **1989**, 225, 437.
27. G. E. Pacey, D. A. Hollowell, K. G. Miller, M. R. Strake, and G. Gordon, *Anal. Chim. Acta*, **1986**, 179, 259.
28. G. Gordon, K. Yoshino, D. G. Themelis, D. Wood, and G. E. Pacey, *Anal. Chim. Acta*, **1989**, 224, 383.
29. P. Praus, *Talanta*, **2004**, 62, 977.
30. G. Schminks and A. Seubert, *J. Chromatogr., A*, **2000**, 890, 295.
31. B. Nowack and U. V. Gunten, *J. Chromatogr., A*, **1999**, 849, 209.
32. A. K. Bhindi and B. Chiswell, *Anal. Chim. Acta*, **1992**, 265, 117.
33. S. Nakaveseisoon, S. Tachiyashik, J. Benga, G. E. Pacey, and G. Gordon, *Anal. Chim. Acta*, **1988**, 204, 169.
34. W. J. Masschelein, M. Denis, and R. Udent, *Anal. Chim. Acta*, **1979**, 107, 383.
35. U. Pinkernell, B. Nowack, H. Gallard, and U. V. Gunten, *Water Res.*, **2000**, 34, 4343.
36. C. S. Padreno, J. A. Ortuno, and J. Hernandez, *Anal. Chim. Acta*, **1996**, 333, 107.
37. M. R. Ganjahi, M. Emami, M. Javanbakht, M. S. Niasari, M. Shamsipur, and M. Yosefi, *Sens. Actuators, B*, **2005**, 105, 127.
38. H. Suzuki, H. Nakagawa, M. Miguna, and Y. Saito, *Anal. Sci.*, **1993**, 9, 351.
39. A. Pouhollahi and M. Shamsipur, *Anal. Chem.*, **1999**, 71, 1350.
40. K. Farhadi, H. Shaikhloei, R. Maleki, H. Shargi, and M. Shamsipur, *Bull. Korean Chem. Soc.*, **2002**, 23, 1635.
41. K. Farhadi and R. Maleki, *Anal. Sci.*, **2002**, 18, 133.
42. K. Farhadi, H. Shaikhloei, R. Maleki, M. Shamsipur, and H. Shaghi, *J. Chim. Chem. Soc.*, **2001**, 49, 861.
43. K. Farhadi, R. Maleki, and M. Shamsipur, *Electroanalysis*, **2002**, 11, 760.
44. "Official Standardised and Recommended Methods of Analysis", 2nd ed., 1973, Heffers, London.
45. J. R. Soderberg, C. Baer, J. D. Johnson, D. Rosenlatt, R. L. Jolley, W. A. Brungs, and R. B. Cumming (ed.), "Water Chlorination: Environmental Impact and Health Effects", 1980, Vol. 3, Ann Arbor Science, Ann Arbor.
46. I. M. Kolthoff, E. B. Sandell, E. J. Meehan, and S. Bruckenstein, "Quantitative Chemical Analysis", 4th ed., 1969, Macmillan, London.
47. B. Saad, M. Ariffin, and M. I. Saleh, *Talanta*, **1998**, 47, 1231.
48. B. Saad, B. L. Yeoh, and M. I. Saleh, *Lab. Robotics Automation*, **2000**, 12, 133.
49. G. D. Christian, "Analytical Chemistry", 6th ed., 2003, John Wiley & Sons, USA.

Fig. 7 Typical FIA peaks of the standard and samples (A, 7×10^{-6} ; B, 5.04×10^{-5} ; C, 1.42×10^{-5} ; D, $2.60 \times 10^{-4} \text{ mol L}^{-1} \text{ OCl}^-$; E, tap water 1; F, diluted bleach 4).