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Author(s)	JIN, Jiye; SUZUKI, Yasutada; ISHIKAWA, Naoyoshi; TAKEUCHI, Toyohide
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# A Miniaturized FIA System for the Determination of Residual Chlorine in Environmental Water Samples

Jiye JIN,<sup>\*†</sup> Yasutada SUZUKI,<sup>\*\*</sup> Naoyoshi ISHIKAWA,<sup>\*\*\*</sup> and Toyohide TAKEUCHI<sup>\*\*\*</sup>

<sup>\*</sup>*Department of Chemistry, Faculty of Science, Shinshu University,  
3-1-1 Asahi, Matsumoto, Nagano 390-8621, Japan*

<sup>\*\*</sup>*Department of Material Science and Technology, Interdisciplinary Graduate School of  
Medicine and Engineering, University of Yamanashi, 4-4-37 Takeda, Kofu, Yamanashi 400-8510, Japan*

<sup>\*\*\*</sup>*Department of Chemistry, Faculty of Engineering, Gifu University, 1-1 Yanagido, Gifu 501-1193, Japan*

The present study was aimed at developing a portable miniaturized FIA system with a two-electrode based amperometric detector for on-site monitoring of residual chlorine in environmental samples. The electrode potential control and current data collection were conducted with a home-designed potentiostat with a size of 150 × 100 × 40 mm and the weight of 350 g. It was confirmed that the amperometric response increased in proportion to the chlorine concentration up to 5 µg/ml, and the detection limit for chlorine was 0.05 µg/ml. Besides a drastic reduction in the size of the analytical system, such miniaturization achieved the advantages of increased speed, minimal mobile-phase consumption, and high sensitivity. The proposed method was successfully applied to the determination of residual chlorine in samples of pool water and tap water. The results were well agreed with those obtained by the *N,N*-diethyl-*p*-phenylenediamine (DPD) photometric method.

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## Introduction

Chlorine in aqueous solutions is used for a number of purposes, such as disinfection and bleaching, and also as a powerful oxidizing agent in various manufacturing processes. It is known that chlorine is highly toxic, and additionally it can further react with other substances, such as phenols, in environment to produce chlorophenols, which are suspected to be carcinogens. Furthermore, chlorine provides strong and persistent odor, even at low concentrations. Thus, the development of the new methods and devices for the reliable and continuous measurement of residual chlorine at trace levels is really required for environmental monitoring. Several analytical methods, such as iodometric titrations, photometric methods using *N,N*-diethyl-*p*-phenylenediamine (DPD),<sup>1</sup> and the amperometric-based electrochemical sensors,<sup>2</sup> have been used to detect residual chlorine (generally in the form of HOCl or OCl<sup>-</sup>). In recent years the electrochemical sensors have been becoming very attractive because they are free of any reagent and provide sufficient sensitivity. On the other hand, however, these sensors have proved to be unreliable because the measured currents depend on the mass-transfer coefficient established on electrode surface by the particular hydrodynamics prevailing in the measuring cell. Furthermore, long-term stability of electrode surface has been another major drawback in any continuous measurement. A promising approach to overcome these shortcomings is the application of flow injection methodologies, in which the flow rate is

controlled and the electrode surface is not easily contaminated. Then, the improvement of the signal reproducibility, rapidity for the measurement and sample handling in the determination of residual chlorine have been achieved by flow injection analysis (FIA) coupled with amperometric detection.<sup>3-5</sup>

Chlorine usually dissipates from the water sample very quickly as a result of exposure to light, increased temperature, and agitation. A laboratory analysis is not recommended for the determination real samples due to the short storage time for stable sample preservation. Such needs have led to the development of portable FIA system for the purpose of on-site determinations. The electrochemical detection offers several advantages in microfluidic analysis system, including simple instrumentation with remarkable sensitivity, ease of implementation, low cost and low-power requirements. In contrast to most optical detection methods, the detector is easily miniaturized without any loss in sensitivity because the extremely slow flow rate leads to an improvement in the electrolysis efficiency.<sup>6</sup> The present work reports on the development of a miniaturized portable FIA system with an amperometric detector that can be used for on-site monitoring of residual chlorine in environmental samples.

## Experimental

A schematic drawing of the miniaturized FIA system and its picture are shown in Fig. 1. It consists of a syringe pump (BAS Bee pump; Bioanalytical Systems, USA), a 7520 internal sample chamber micro-scale injector with a 0.5-µl injection volume (Rheodyne, Cotati, CA, USA) and a house-made flow-through electrochemical detector. The amperometric detector

<sup>†</sup> To whom correspondence should be addressed.  
E-mail: jin@gipac.shinshu-u.ac.jp

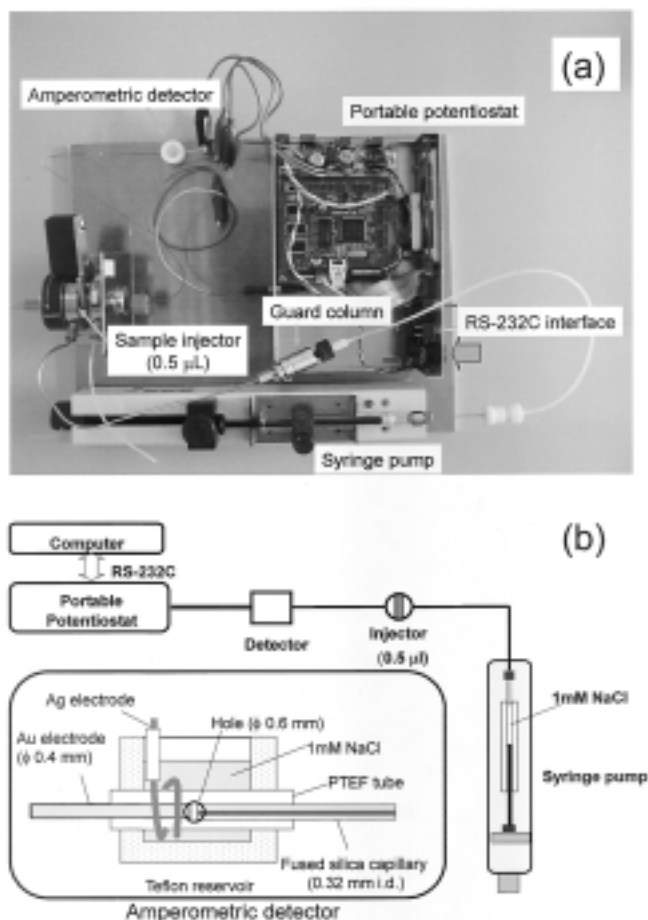


Fig. 1 Picture (a) and a schematic drawing (b) of the miniaturized FIA system.

was constructed by a two-electrode configuration consisting of a gold working electrode and a silver wire as counter/reference electrode, respectively. As can be seen in Fig. 1b, a gold wire ( $\phi$  0.4 mm) and fused-silica tubing (0.32 mm i.d.  $\times$  0.45 mm o.d.) were inserted face to face into a PTFE tube, after being softened over a micro-flame heater. Both the gold electrode and the fused-silica tubing can be tightly sealed in the PTFE tube after cooling, and the working electrode was positioned in front of the end of a fused-silica tubing to form an end-column detection configuration. The amperometric detector was placed in a Teflon reservoir filled with a 10 mM NaCl solution. Two holes ( $\phi$  0.6 mm) drilled in PTFE served as drain channels connecting to the reservoir. The detector with a two-electrode configuration was well suited to be used as a detector in the FIA system.

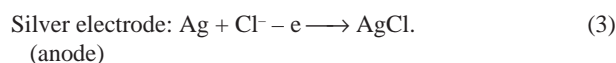
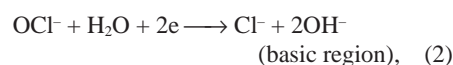
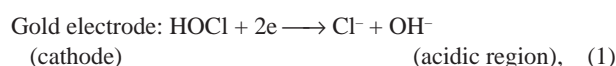
Potentiostats are important measuring instruments in the field of electrochemistry. As for the purpose of on-site determination, miniaturization of the potentiostat along with a reduction in the complexity of the chip, low power consumption and a high dynamic range was developed in the current work. The potentiostat was built using an embedded controller microprocessor (Renesas Technology H8/3067F, 16bit, 20 MHz), an A/D converter (Analog Devices AD7893BN-10), a D/A converter (Analog Devices AD7233AN), and operational amplifiers (Analog Devices OP77FJ, OP07CZ and National Semiconductor LM356H). It is available operated by a battery for a video camcorder (Sony NP-F550, 7.2 V, 1500 mA/H). The size of the potentiostat is 150  $\times$  100  $\times$  40 mm and weight is

only 350 g. The electrochemical measurements were controlled by a notebook computer and a laboratory-written software package *via* an RS-232C interface. The software was developed in Visual C language and provides the modules for (a) cyclic voltammetry; (b) square-wave voltammetry and (c) i-t amperometry.

The chlorine standard solution was prepared by adding 1 ml of 5% aqueous sodium hypochlorite solution (stock hypochlorite) into 25 ml of Milli-Q water and was titrated to a starch-iodide endpoint using a sodium thiosulfate titrant. A 10 mM NaCl solution (pH = 5.5) was used as mobile-phase. Standard solutions with low concentrations were prepared by dilution immediately with mobile phase solution prior to measurements. If not otherwise stated, a flow rate of 5  $\mu$ l/min was used.

## Results and Discussion

Residual chlorine in water is generally present in the form of hypochlorous acid (HOCl), or its conjugated base, the hypochlorite ion (ClO<sup>-</sup>). Since pK<sub>a</sub> of HOCl is assumed to be 7.48 at 25°C, HOCl is dominant in the acidic region (pH < 5.5), while nearly all the chlorine is present as OCl<sup>-</sup> at higher pH values (pH > 8.5). Both HOCl and ClO<sup>-</sup> are electroactive and can be electrochemically reduced at the electrode surface. It was confirmed by square-wave voltammetry that gold electrode exhibited very large reductive currents as well as good stability compared with platinum and glassy carbon electrodes in the pH range of 4–8. At pH 5.5, the reduction peak was found at around +0.4 V *vs.* Ag/AgCl, which was not interfered by the other common co-existing species in water. When a constant potential was applied between the working electrode and the counter electrode, the electrical current was generated by the reduction of HOCl and/or OCl<sup>-</sup> at the gold electrode. The process consumes the electrons which come from the oxidation of silver electrode, and amperometric detection was based on measuring the current generated between the two electrodes by following equations:



The current resulting from the electrode reaction was found to be directly proportional to the concentration of chlorine in the solution.

Figure 2 shows the amperometric responses of chlorine in a miniaturized-FIA system. The electrode potential applied between two electrodes was +200 mV. The detector provided a linear response up to 5  $\mu$ g/ml. The relative standard deviations ( $n = 5$ ) were about 2–3%. A low detection limit of 0.05  $\mu$ g/ml was achieved as an estimated based on a signal-to-noise ratio  $\geq 3$ . The amperometric sensor was very stable when used as a flow-cell detector. Using a 0.5-ml syringe pump, the system can continuously work for more than 1.5 h.

The effects of several co-existing ions on the determination of 1  $\mu$ g/ml hypochlorite were examined by a standard procedure. An error 5% was considered to be tolerable. The anions, like NO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, Cl<sup>-</sup> and Br<sup>-</sup>, did not interfere at concentrations up

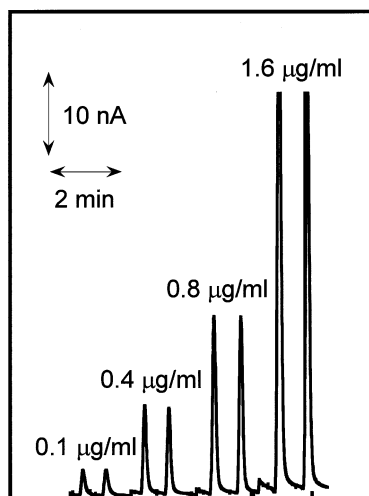


Fig. 2 Typical FIA responses to trace chlorine. Mobile phase, 10 mM NaCl (pH = 5.5); flow rate, 5  $\mu\text{l}/\text{min}$ ; detection potential, +200 mV vs. Ag.

to 50 mM.  $\text{BrO}_3^-$  and  $\text{NO}_2^-$  at a concentration level of 1 mM gave positive errors, probably because their reductive characteristics at the gold electrode.

Finally, the miniaturized FIA system was applied to the determination of free chlorine in samples of tap water, swimming pool water and bleach. The samples were prepared by adding a suitable amount of NaCl so as to give a concentration of 10 mM NaCl, or by dilution with a mobile-phase solution. They were then syringe-filtered through 0.2  $\mu\text{m}$  nylon filters before the measurements. The results (Table 1) were in good agreement with those provided by standard DPD method using a HI-93711 free chlorine colorimeter (Hanna Instruments).

## Conclusion

An amperometric detection with a two-electrode configuration was demonstrated to be well suited for the determination of chlorine in a miniaturized FIA system. Besides a drastic reduction in the size of the analytical system, such miniaturization achieved the advantages of increased speed and minimal mobile-phase consumption. Thus, the miniaturized

Table 1 Comparative results for the concentrations of chlorine, determined by the miniaturized FIA system and the conventional DPD method

Sample	This method <sup>a</sup> / $\mu\text{g ml}^{-1}$	DPD method <sup>a</sup> / $\mu\text{g ml}^{-1}$
1. Tap water 1 (Shinshu University)	0.240	0.248
2. Tap water 2 (Matsumoto City)	0.292	0.300
3. Swimming pool water (Sawamura pool, Matsumoto)	0.453	0.448
4. Pipe cleaner (Unicharm)	24000 (w/v 2.40%)	25000 (w/v 2.5%)

a. Mean value for three replicate analyses.

FIA system with amperometric detection can be used as an on-site monitoring instrument for residual chlorine in environmental samples. The work is continuing toward an improvement in the detection limits with fast-scan square-wave voltammetric detection as well as the use of chemically modified electrode for the analysis of other substances in environmental samples.

## Acknowledgements

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