A direct analysis of nanomolar metal ions in environmental water samples with Nafion-coated microelectrodes

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Abstract

Square Wave Anodic Stripping Voltammetry (SWASV) was combined with microfabricated microelectrodes to analyze metal ions in aqueous solution and showed excellent performance such as short analysis time about 1 min per experiment, simultaneous detection of several ions and very low detection limit as low as several nanomoles per liter (i.e. sub-ppb in mass) without any of supporting electrolyte and stirring during analysis. Nafion, a famous ion-exchanging polymer, was introduced to protect the electrode surface from obstructing materials. The Nafion-coated microelectrode was free from disturbing impurities and was capable of analyzing natural water samples directly. Results from the direct water analysis showed similar performance to those from pre-treated samples in both sensitivity and analysis time. To secure the reproducibility of Nafion-coated electrode, a simple electrochemical cleaning method with potential sweep was used and the electrode remained reliable to continued experiments. Nafion-coated microelectrodes were further examined via the comparison with ICP–MS data.
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1. Introduction

As industry develops, the demand for a rapid detection of water pollution is gradually increasing. Among the pollution problems, water pollution is one of the most serious subjects since water is essential for the life. Especially heavy metal ions can threaten an ecosystem or human itself with only infinitesimal amount and monitoring of heavy metal ion in trace concentration is desired. Traditionally, most water analyses have been done in the laboratory with the sample previously obtained from the investigation spot. Water samples are collected and physically transported to laboratories, so there is a time gap between sampling and actual analysis [1]. In a number of applications, the time delays in this transportation are unacceptable. In addition, the analyzing instrument generally requires an experienced operator.

In order to improve on these weak points, electrochemical water analysis with microelectrode was taken to be a candidate for a novel analyzing system [1–9]. Meanwhile, microelectrodes have some advantages against conventional electrodes and have attracted attention as an analytic sensor for a decade [1,2,4–8]. As previously reported, an electrochemical analysis method for detection of metal ions in aqueous solution [5], square wave anodic stripping voltammetry (SWASV) combined with microfabricated microelectrodes showed excellent performance such as short analysis time, simultaneous detection of several ions and very low detection limit as low as sub-ppb without any of supporting electrolyte and stirring.

Yet there still remains an important problem to realize a direct analysis of natural water samples. Pre-treatments including filtering and acidification are required because most natural samples contain various floating matters and organic/inorganic compounds, which readily disturb and even spoil the experiments [10–12]. Some strategies have been

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developed for eliminating these interferences, including mineralization [10], ultrasonication [13], and coating of the working electrode with a permselective membrane [15,16].

Nafion, an ion-exchanging polymer, was used to protect the electrode surface from obstructing materials. Results from the direct water analysis are reported in this article and they were further examined via the comparison with ICP–MS data.

2. Experimental

2.1. Reagents

All chemicals such as $Cd(NO_3)_2$, $Pb(NO_3)_2$, $Hg(CH_3COO)_2$, HNO_3, double-distilled $HClO_4$ and a 5 wt.% Nafion solution were purchased from Aldrich Chemical Co. and used as received. A 0.45 μm nylon filter (Pall life sciences corp., USA) was used for the treatment of environmental samples.

Aqueous solutions were prepared with triply distilled water from Modulab water system (US filter corp.). All the experiments were carried out at room temperature.

2.2. Instrumentation

The BAS 100B PC-controlled electrochemical analyzer (BioAnalytical Systems Inc.) with three-electrode system was used for all electrochemical measurements. RE-5B Ag/AgCl reference electrode and platinum wire counter electrode were also purchased from BioAnalytical Systems Inc. and used. All reported potentials are referenced to Ag/AgCl electrode.

The HP 4500 induced coupled plasma mass spectrometer (Hewlett Packard Co.) was used to get ICP–MS data.

2.3. Fabrication of electrode

The fabrication processes of working electrode are performed as reported before [5] and shown in Fig. 1. Thermal oxide is grown on silicon substrate to the thickness of 5000 Å and a 2000 Å Pt layer is patterned by lift-off method (a). The gold signal lines and contact pads are patterned by lift-off, too (b). Next, the silicon nitride layer is deposited with plasma enhanced chemical vapor deposition (PECVD) and the areas to be electrodes and contact pads are etched by reactive ion etching (RIE) (c). The geometry and dimension of electrodes can be controlled easily by applying various photomask patterns. Platinum disk electrodes with diameter of 10 μm were fabricated and used in this report.

3. Results and discussion

3.1. Analysis of metal ions in aqueous solution

Metal ions in aqueous solution were analyzed as previously reported [5]. Briefly, mercury is electrodeposited to the
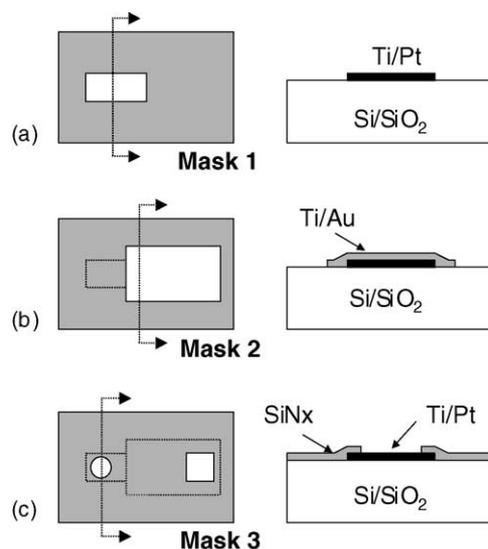

Fig. 1. Fabrication process of the microelectrode: (a) patterning of electrode metal; (b) patterning of pad and signal line; (c) opening the areas for electrodes and pads.

surface of platinum microelectrode to form a hanging mercury drop microelectrode with hemispherical geometry. This mercury-coated electrode is used as a working electrode for metal analysis. With SWASV technique, we could simultaneously sense several metal ions without any additional supporting electrolytes. Since the mass transfer is sufficiently fast and the quantity of reduced metal ion is so small [14], there is no need of stirring sample solution, which is indispensable in SWASV with conventional electrode. The SWASV was carried out with $E_{SW} = 25$ mV, $\Delta E_S = 5$ mV, $f = 120$ Hz and preconcentration step was at -800 mV for 60 s. Fig. 2 is the result of SWASV for successive additions of Cd^{2+} and Pb^{2+} ions to distilled water. As shown in figure, we could analyze trace metal ions as little as some nanomoles per liter within 70 s. The detection limit ($S/N = 3$) was about 1.5 nM for each ion, in other words about 0.3 ppb for lead and 0.14 ppb for cadmium, respectively. The linear relationship between peak currents and ion concentrations is also clearly shown. The currents are proportional to concentrations in the range of 1–150 nM with these experimental conditions.

3.2. Analysis of real environmental samples

To demonstrate the capability of this method as a metal ion sensor, SWASV was performed on tab water and pond water. The former was obtained at our laboratory and the latter was taken from a small pond in the campus, which is stagnant and full of life such as waterweed, fish, tortoise and even ducks. Each sample was analyzed at the same manner as described in previous section. Fig. 3 shows the result of experiments in tab water samples. The presence of lead ion is clearly shown. By the standard addition method, five individual experiments have shown that tab water contains about 12.7 $\pm$ 1.5 nM (2.5 $\pm$ 0.3 ppb) Pb^{2+} and no Cd^{2+}. Every metal ion concentrations given in this article are acquired five times and averaged. If
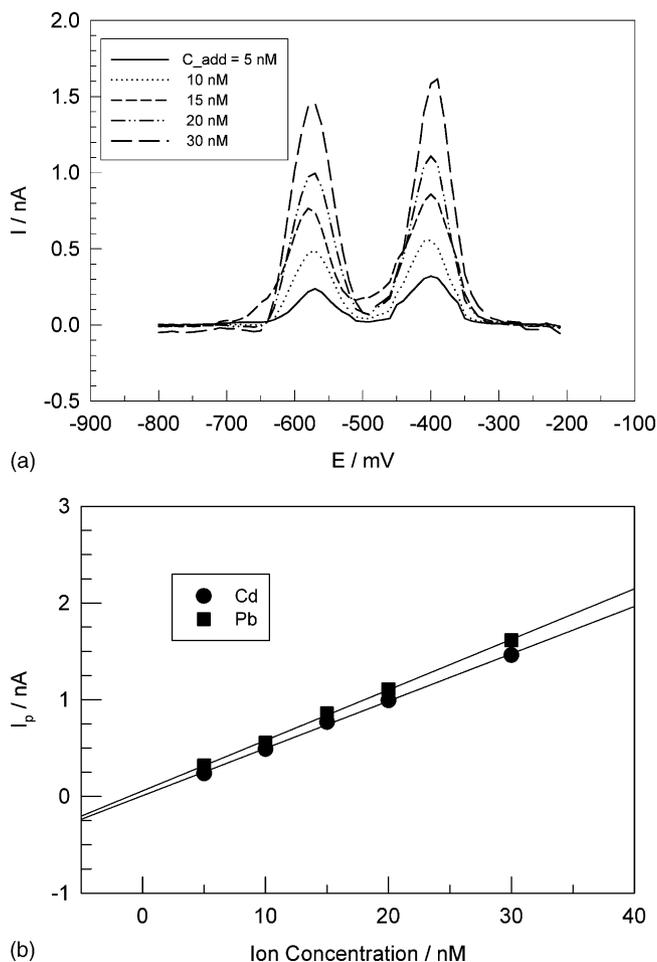
Fig. 2. SWASV for addition of Cd^{2+} and Pb^{2+} ions into distilled water: (a) voltammograms and; (b) linear relationship between peak currents and ion concentrations.

the data set on standard addition is provided, this method is capable of sensing the amount of several metal ions directly.

Although the SWASV technique with microelectrodes work well in relatively clean samples such as distilled water
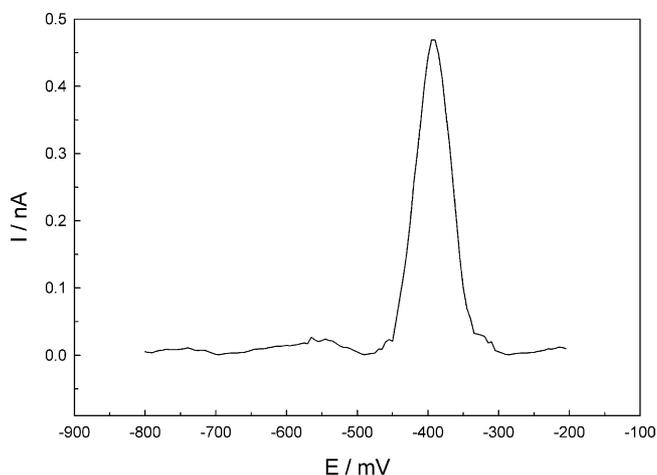

Fig. 3. Direct analysis of tab water with SWASV.

and tab water, it shows different results in rather dirty samples. Fig. 4(a) is the result of same experiments for pond water. Voltammograms with distorted baseline and overlapped oxidation peaks appear. These phenomena are known to occur mainly due to the deactivation of electrode by adsorption of compounds into the mercury surface [10,11]. So it should be eliminated—disturbing materials including floating matters and various compounds. The elimination step was performed as conventional methods [17,18]. First, floating matters are removed by means of filtration with nylon filter having 0.45 μm pore size. Secondly, samples are acidified to remove or deactivate organic compounds. A strong, oxidizing acid of 0.1 M concentration is used usually. Double-distilled perchloric acid was used in this report. The result of metal ion analysis with pretreated pond water samples is shown in Fig. 4(b). The distortion in Fig. 4(a) has disappeared. Also, there is proof of lead ion. Calculated $[Pb^{2+}]$ and $[Cd^{2+}]$ are 16.2 ± 1.7 nM (3.2 ± 0.3 ppb) and 0.0 nM, respectively.

3.3. Direct detection of metal ions with Nafion-coated electrode

Since the pretreatment of samples is a difficulty in realizing direct metal ion analysis, we have tried several methods and materials to perform analysis without pretreatments. Among those trials, Nafion, a well-known cation-exchanging polymer, showed excellent properties so it was chosen. Due to its cation-exchanging nature, the Nafion layer blocks most anions, while it shows some permeability to cations [19].

The Nafion-coated mercury microelectrode was constructed with dip coating method. First, the microelectrode was dipped into a 5 wt.% Nafion solution. Then the Nafion-coated electrode was placed in a fume hood and dried for a day. Lastly, dried electrode was thermally cured at 120 °C for 1 or 2 h in an oven to ensure the surface toughness [20].

The result of SWASV analysis in untreated pond water sample is shown in Fig. 5. With a Nafion-coated electrode, almost same result as in pretreated samples has been acquired. The only difference between bare mercury electrode in pretreated sample and Nafion-coated electrode in untreated sample is that the levels of peak current from Nafion-coated electrode are a bit lower than those from bare mercury electrode. The relationship between peak currents and the exposure time of Nafion-coated electrode to sample solution is shown in Fig. 6. The peak current from oxidation of lead in amalgam form is shown, and it gradually increases with the exposure time to the solution. Result from Fig. 6 insists that adequate amount of time is needed for the movement of metal ions into mercury placed beneath the Nafion layer [15]. Unlike other samples, a long-time exposure to the pond water (i.e. 1 h) causes decrease in peak currents. It is due to adsorption of interfering materials onto the outer surface of the membrane [13] and will be discussed in next section. In this report, a 5 wt.% Nafion solution was used for the dip coating to get a physical strength of Nafion layer, and the exposure time was set to 10 min. Calculated $[Pb^{2+}]$ and $[Cd^{2+}]$ are $17.7 \pm$
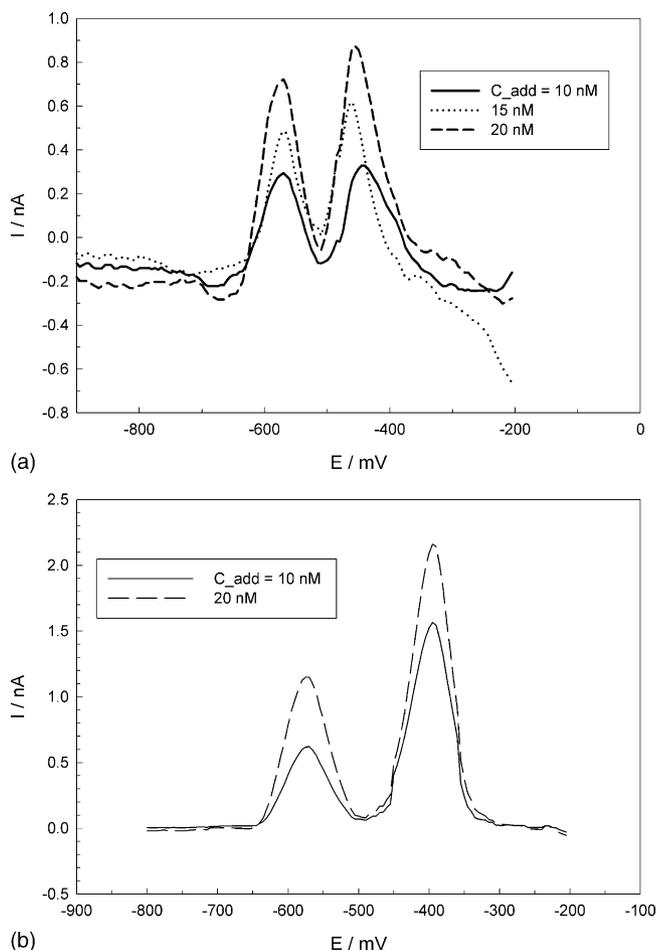
Fig. 4. SWASV for addition of Cd^{2+} and Pb^{2+} ions into pond water, (a) before and (b) after pretreatments.

1.6 nM (3.5 ± 0.3 ppb) and 0.0 nM, respectively. And they correspond well to the result of pretreated samples.

Tab water samples were also analyzed with the Nafion-coated electrode (not shown). The result of five separate tab water analyses shows that there are 12.6 ± 1.4 nM (2.5 ± 0.3 ppb) of Pb^{2+} and no Cd^{2+}. This result well matches with that from bare mercury electrode, too. To confirm the ability of direct sensing, we analyzed two more environmental samples, one from local river and the other from abandoned copper mine. Again the Nafion-coated electrode could handle the direct analysis of metal ions. Results from direct analysis showed that the river water contains 7.6 ± 1.1 nM (1.5 ± 0.2 ppb) of Pb^{2+} and no Cd^{2+}, while the mine water contains 54.1 ± 4.5 nM (11.2 ± 0.9 ppb) of Pb^{2+} and 58.7 ± 4.4 nM (6.6 ± 0.5 ppb) of Cd^{2+}.

Recently, many reports concerning the determination of toxic materials in environmental water samples have been published [21–27]. Various analytical techniques including UV–vis photometry [22], atomic absorption spectrometry (AAS) [23,24], high performance liquid chromatography (HPLC) [25], inductively coupled plasma mass spectrometry (ICP–MS) [26] and atomic emission spectrometry (ICP–AES) [27] have been applied for years with many cre-
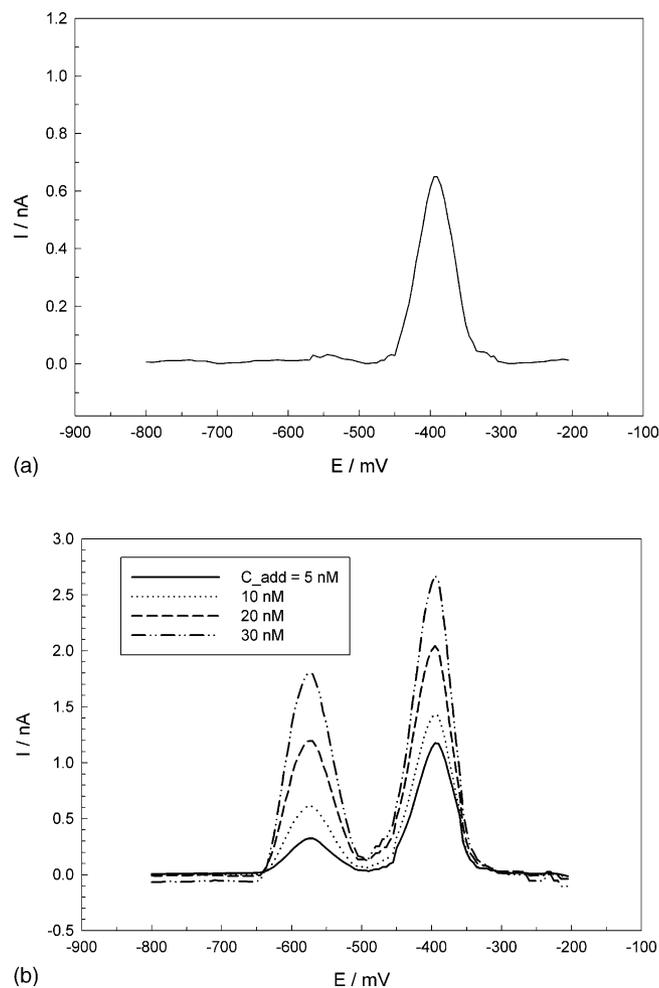

Fig. 5. SWASV for untreated pond water with Nafion-coated electrode: (a) direct analysis and; (b) result of standard addition of Cd^{2+} and Pb^{2+}.

ative methods to enhance the analytical performance. Among those techniques, ICP–MS shows best sensitivity and is capable of analyzing trace ions as little as sub-micrograms per liter, namely sub-ppb [21]. The detection limit of electrochemical method described in this article (0.3 ppb) is a bit higher than ICP–MS, yet the merit of this method remains in simple procedure and fast analysis within 10 min.

All samples were analyzed by ICP–MS and compared with result of SWASV to validate the capability of this electrochemical method. Result of each sample by different analyzing technique is in Table 1. It is clear that two methods show similar results and hence the SWASV with Nafion-coated

Table 1
Comparison of results from SWASV and ICP–MS

	ICP–MS		SWASV	
	Cd^{2+}	Pb^{2+}	Cd^{2+}	Pb^{2+}
Distilled water	0.00	0.00	0.0	0.0
Tab water	0.00	2.70	0.0	2.5 ± 0.3
Pond water	0.00	3.38	0.0	3.5 ± 0.3
River water	0.00	1.41	0.0	1.5 ± 0.2
Mine water	6.83	10.97	6.6 ± 0.5	11.2 ± 0.9

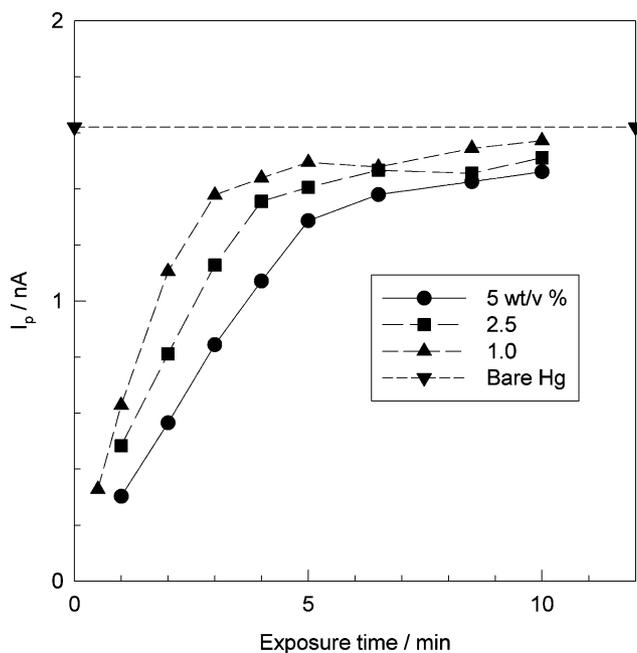The unit of metal ion concentration is mass ppb (part per billion)

Fig. 6. Peak current variation of Nafion-coated electrode with respect to exposure time to sample solution containing 20 nM Pb^{2+}.

mercury microelectrode can afford the direct sensing of metal ions in environmental water samples.

3.4. Reproducibility of Nafion-coated electrodes

As mentioned in previous section, the Nafion-coated electrodes showed peak current decrease by continued exposure to samples [13]. Fig. 7 shows the result of successive analysis of pond water containing 20 nM of added Cd^{2+} and Pb^{2+} with same electrode. The voltammograms are slowly distorted as the number of experiment increases, as well as the peak current itself has decreased. The peak of cadmium seems to be more severely influenced by adsorption of interfering materials than that of lead.

An electrochemical cleaning method was adopted to reduce the interference from adsorption. After stripping, the working electrode was set to −200 mV, the final potential of stripping step, for 30 s. This step was followed by a potential sweep from −800 mV to 0 V with the rate of 200 mV/s. Four sweep cycles were performed to clean electrode surface, and it also took about 30 s. Results of the electrochemical cleaning are shown in Fig. 8. The symbols represent peak current ratio (i_{pn}/i_{p1}) for cadmium where i_{pn} is peak current from Nafion-coated electrode at given time and i_{p1} is that from first analysis. The dots, circles, and triangles are the results obtained from no treatment (same result as Fig. 7(b)), electrochemical cleaning in same sample, and electrochemical cleaning in distilled water, respectively. In third case, the electrode was moved to distilled water, cleaned in distilled water, and put into sample solution again. Electrodes were also tested with media change without electrochemical cleaning (i.e. working electrode was moved to distilled water and stayed for
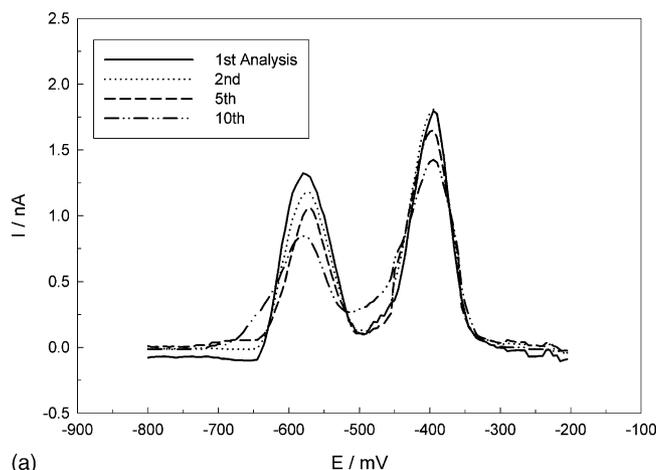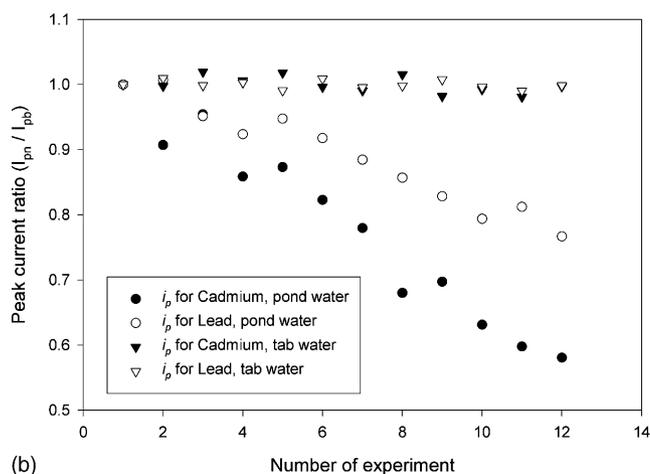
Fig. 7. SWASV for untreated water with Nafion-coated electrode: (a) deactivation of electrode by repeated experiment in pond water and; (b) change of peak current ratio in the sample.

1 min), but there was not any significant difference between this method and no treatment.

As the Fig. 8, the electrochemical cleaning reduced interference from adsorption. Reproducible data can be obtained
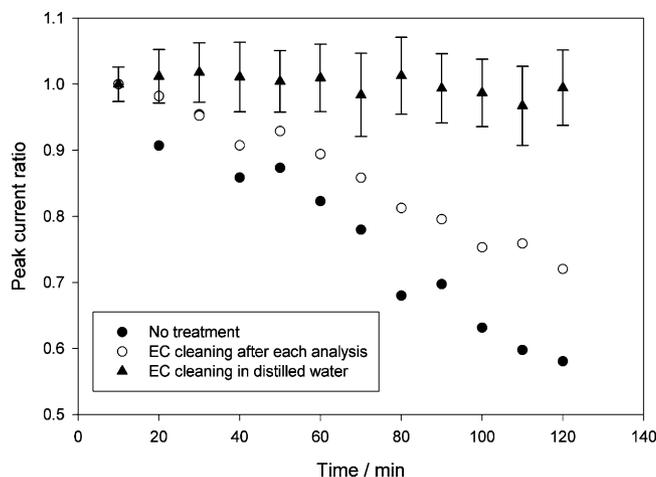

Fig. 8. Peak current change for Cd: effect of electrochemical cleaning.

with the electrochemically cleaned Nafion-coated electrode for at least 2 h, namely a dozen of analyses. All previously mentioned analyses were done with electrochemical cleaning in distilled water as this cleaning method showed best property.

4. Conclusions

We observed excellent performance for analyzing metal ions in aqueous solution by combining square wave anodic stripping voltammetry with microfabricated microelectrodes. To solve problems occurring in real environmental samples, Nafion was used to form a protective layer on the electrode surface. The Nafion-coated microelectrode was free from disturbing impurities and was capable of analyzing natural water samples directly. Results from the direct water analysis showed similar performance to those from pre-treated samples in both sensitivity and analysis time. They were compared with ICP–MS data and proven to be an efficient analyzing method. With the comparison to environmental standard for drinking water, 10 ppb (91 nM) for cadmium and 50 ppb (250 nM) for lead in case of Korea, the sensitivity of several nM is enough for the practical application.

The Nafion-coated microelectrodes are sufficiently reproducible in short-term basis, and the long-term stability is under evaluation.

Acknowledgments

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