

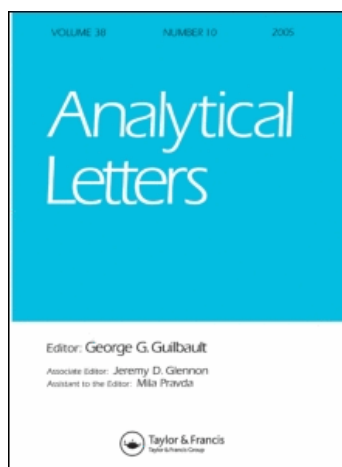
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### Ionophore Based Bismuth Film Electrode for Lead

Yuane Wang <sup>abc</sup>; Dawei Pan <sup>a</sup>; Wei Qin <sup>ad</sup>

<sup>a</sup> Laboratory of Environmental Chemistry, Yantai Institute of Coastal Zone Research for Sustainable Development, Chinese Academy of Sciences, Yantai, P.R. China <sup>b</sup> Institute of Oceanology, Chinese Academy of Sciences, Qingdao, P.R. China <sup>c</sup> Graduate University of Chinese Academy of Sciences, Beijing, P.R. China <sup>d</sup> School of Oceanology, Yantai University, Yantai, P.R. China

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## SENSORS

# Ionophore Based Bismuth Film Electrode for Lead

Yuane Wang,<sup>1,2,3</sup> Dawei Pan,<sup>1</sup> and Wei Qin<sup>1,4</sup>

<sup>1</sup>Laboratory of Environmental Chemistry, Yantai Institute of Coastal Zone  
Research for Sustainable Development, Chinese Academy  
of Sciences, Yantai, P.R. China

<sup>2</sup>Institute of Oceanology, Chinese Academy of Sciences,  
Qingdao, P.R. China

<sup>3</sup>Graduate University of Chinese Academy of Sciences, Beijing, P.R. China

<sup>4</sup>School of Oceanology, Yantai University, Yantai, P.R. China

**Abstract:** A Nafion/ionophore, 4-*tert*-butylcalix[4]arene-tetrakis(*N,N*-dimethylthioacetamide) composite coated and bismuth film modified glassy carbon electrode. (GC/NA-IONO/BiFE) was described to determine trace lead sensitively and selectively. The characteristics of such modified GC/NA-IONO/BiFE were studied by scanning electron microscopy and cyclic voltammetry. The influence of various experimental parameters upon the stripping lead signal at the GC/NA-IONO/BiFE was explored. Under the optimized conditions, the differential pulse voltammetric stripping response is highly linear over the 0.1–8.0 nM lead range examined (180 s preconcentration at –1.2 V), with a detection limit of

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Address correspondence to Yuane Wang, Laboratory of Environmental Chemistry, Yantai Institute of Coastal Zone Research for Sustainable Development, Chinese Academy of Sciences, Yantai 264003, P.R. China. E-mail: yewang@yic.ac.cn

0.044 nM and good precision ( $RSD = 5.4\%$  at 0.5 nM). Also applicability to seawater samples was demonstrated at such modified electrode. The high selectivity of ionophore coupled with the excellent electrochemical characteristics of bismuth endow the GC/NA-IONO/BiFE a promising and robust tool for monitoring of trace lead rapidly and precisely.

**Keywords:** Bismuth film electrode, ionophore, lead, nafion, stripping voltammetry

## INTRODUCTION

Anodic stripping analysis (ASV) has been proved an extremely sensitive electroanalytical technique which combines an effective preconcentration step with advanced electrochemical measurements of the accumulated analytes (Wang, 1985; Wang, 2006; Wang, 2005). Two electrode systems, mercury film electrode and hanging mercury drop electrode have been widely used as traditional electrode materials for ASV due to their high reproducibility and sensitivity (Economou, and Fielden, 2003). But the well-known toxicity of mercury and its compounds makes its use as an electrode material severely restricted or even banned. Therefore it is highly desired to develop new alternative electrodes, and so far lots of new materials have been investigated, such as gold, carbon, iridium, silver and bismuth (Wang, and Tian, 1993; Nolan, and Kounaves, 1999; Wang, et al. 2000). However, most of these materials have not approached the performances of mercury electrodes except for bismuth. Bismuth electrodes offer a well-defined, undistorted and highly reproducible stripping response, high hydrogen evolution, wide linear dynamic range, and insensitivity to dissolved oxygen in contrast to mercury electrodes (Wang 2006). The advantageous properties of bismuth are attributed to its ability to form "fused" or "low-temperature" alloys with heavy metals (Long, et al. 1978; Kruger, et al. 1985) that facilitates the nucleation process during accumulation of heavy metal ions thus leading to sensitivity similar to mercury film electrodes.

One of the most serious interferences in ASV arises from various surfactant compounds that adsorb on the electrode causing fouling of its surface (Economou, and Fielden, 1993; Wang, et al. 2001). The surfactant adsorption may affect both deposition and stripping steps, leading to lower or broader peaks, and peak potential shifts. Such problems can be alleviated by modifying the surface with a suitable permselective membrane (Economou, and Fielden, 2003). These polymeric coatings can improve resistance of the modified electrodes and minimize fouling by surface active compounds existing in samples (Gouveia-Caridade, et al. 2006; Hoyer, et al. 1987). Among several assessed polymers, Nafion

has been widely used (Kefala, and Ecpnomou, 2006; Xu, et al. 2008; Cao, et al. 2006; Kefala, et al. 2004). Nafion is a perfluorosulfonate cation-exchange polymer with many ideal properties, i.e. it is electroinactive, chemically inert, hydrophilic, and water insoluble. At present, Nafion has found a widespread application in conjunction with mercury film electrodes in ASV in order to increase the electrode's resistance against fouling by surface-active compounds (Hoyer, et al. 2001; Brett, et al. 1996; Murimboh, et al. 2000; Agra-Gutierrez, et al. 1999). An additional advantage associated with the use of Nafion coated mercury film electrodes is the improvement in terms of robustness towards mechanical damage (Matysik, et al. 1997). Kefala et al. (Kefala, et al. 2004) introduced of Nafion associated with a bismuth film electrodeposited on a glassy carbon (GC) substrate. However, the sensitivity of such modified BiFE is not satisfactory.

Recently, mixed polymeric coatings on GC electrodes were reported to improve the performances of Nafion coatings (Jia, et al. 2008; Monterroso, et al. 2006; Leelasattarakul, et al. 2007; Rocha, et al. 2006; Brett, et al. 1999; Brett, et al. 2001). A Nafion-coated GC electrode modified by neutral ionophore has been reported for simultaneously determine Pb(II), Cu(II), and Hg(II) (Chen, et al. 1999). However, both its selectivity and sensitivity are not favorable. 4-*tert*-butylcalix[4]arene-tetrakis(*N,N*-dimethylthioacetamide) is used as a Pb(II) ionophore in ion-selective electrodes (Ceresa, and Pretsch, 1999) because it offers a defined cavity for Pb ion complexation and hence enhances the sensitivity and selectivity. However, very few articles have been reported about the ionophore modified electrode in ASV determination of trace metals (Chen, et al. 1999; Ceresa, and Pretsch, 1999), and no one for BiFE. In this paper, a composite of Nafion and ionophore coated bismuth film electrode (GC/NA-IONO/BiFE) was developed for determination of trace Pb(II) in cadmium, copper and tin mixed solution combining the high selectivity of ionophore with outstanding sensitivity of BiFE. Compared with Nafion coated BiFE, the GC/NA-IONO/BiFE not only has a higher selectivity and lower detection limit, but also successfully excludes the suppression of stripping peak caused by Cu(II) and Cd(II), and the overlapping peaks problem from Sn(II).

## EXPERIMENTAL

### Reagents

Bismuth, lead, copper, cadmium, tin, alcohol and DMF were purchased from Sinopharm Chemical Reagent and of analytical grade purity or

better. Sodium hydroxide (99.998%), acetic acid (99.99 + %), ionophore 4-*tert*-butylcalix[4]arene-tetrakis(*N,N*-dimethylthioacetamide) and Nafion. (5 wt.% mixture of lower aliphatic alcohols and water) were supplied by Sigma Aldrich. The ionophore and Nafion solutions were prepared in THF and alcohol, respectively, and mixed in appropriate ratio to give the modifying solution. The supporting electrolyte was 0.1 M acetate buffer (pH 4.5) prepared with sodium hydroxide and acetic acid. Deionized water with specific resistance of 18.2 M $\Omega$  cm was used throughout.

### Apparatus

All the electrochemical measurements were performed on a CHI 660 C electrochemical workstation (Chenhua Instruments, Shanghai, China) with a conventional three electrode configuration. The modified glassy carbon (3 mm diameter, Chenhua Instruments) electrode was employed as the working electrode. An Ag/AgCl (3 M KCl) electrode and a platinum electrode were used as reference and counter electrodes, respectively. Experiments were performed in a 50 mL polytetrafluoroethylene beaker at room temperature. Scanning electron microscopy (SEM) images were obtained from a JSM-6700F with an accelerating voltage of 5.0 kV. For ICP-MS determination of lead, an Elan DRC II inductive coupling plasma-mass spectrometer (Perkin Elmer Sciex) was used.

### Preparation of Electrode

The GC electrode was hand-polished with 0.3 and 0.05  $\mu$ m alumina slurry on a polishing pad, then rinsed with deionized water and sonicated for 2 min, and then air-dried prior to being coated with the modifying solution. The GC/NA-IONO electrode was fabricated by placing 3  $\mu$ L mixed solution (1wt. % Nafion was mixed with equal volume of 2 mM ionophore) on the GC surface and left to dry in air. Then, the polymer membrane was cured with a hot air stream from a heat-gun for 1 min and left to cool to room temperature before being used.

### Measurement Procedure

The in-situ prepared GC/NA-IONO/BiFE was obtained by immersing the three electrodes into 0.1 M acetate buffer (pH 4.5) containing 1000  $\mu$ g L<sup>-1</sup> Bi(III) and the target metals. The deposition potential (-1.2 V) was applied to GC/NA-IONO or GC electrode for 180 s, while

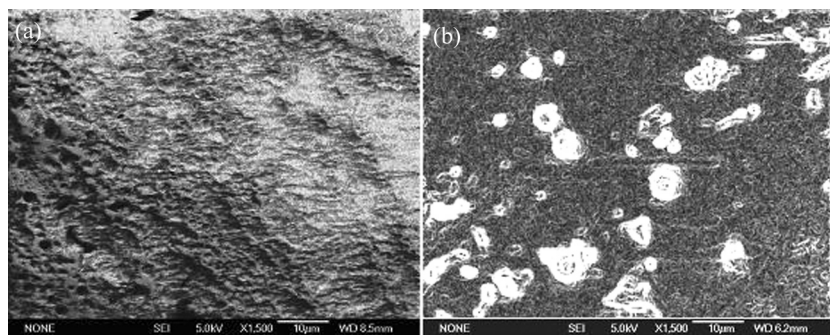
the solution was stirred. Following the preconcentration step, the stirring was stopped and after 15 s, the voltammogram was recorded by applying a positive-going differential pulse voltammetric potential scan (with a modulation amplitude of 50 mV, pulse duration time of 50 ms, interval time of 0.2 s and potential step of 4 mV) which was terminated at  $-0.3$  V. The target metals and bismuth were removed at 0.5 V for 60 s under stirring prior to the next cycle. All measurements were carried out without deoxygenation in advance.

## RESULTS AND DISCUSSION

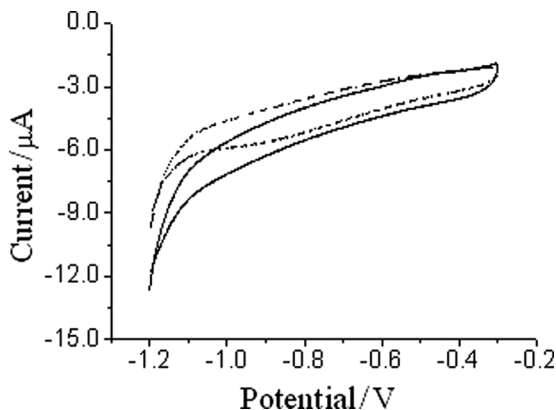
### Characterization of GC/NA-IONO/BiFE

SEM can take useful insights into the growth patterns of bismuth. (Wang, et al. 2000) mentioned that the SEM image of the bismuth coated GC electrode exhibited a highly porous, three-dimensional fibril-like network. Figure 1 shows scanning electron micrographs of GC/NA-IONO before (a) and after (b) bismuth deposition, respectively. The GC/NA-IONO film presents a non-homogeneous and dense polymer membrane covering on GC electrode surface. While for GC/NA-IONO/BiFE, Bi deposits can be seen as white droplets scattered randomly on the GC/NA-IONO electrode surface.

Electrochemical behaviors of BiFE and GC/NA-IONO/BiFE were studied in 0.1 M acetate buffer solution (pH 4.5) by cyclic voltammetry in negative potential range from  $-1.2$  V to  $-0.3$  V. As shown in Fig. 2, the GC/NA-IONO/BiFE gives almost identical voltammograms for



**Figure 1.** SEM images of GC/NA-IONO before (a) and after (b) Bi deposition. Deposition, 180 s, from a 0.1 M acetate buffer solution (pH 4.5) containing  $1000 \mu\text{g L}^{-1}$  bismuth.



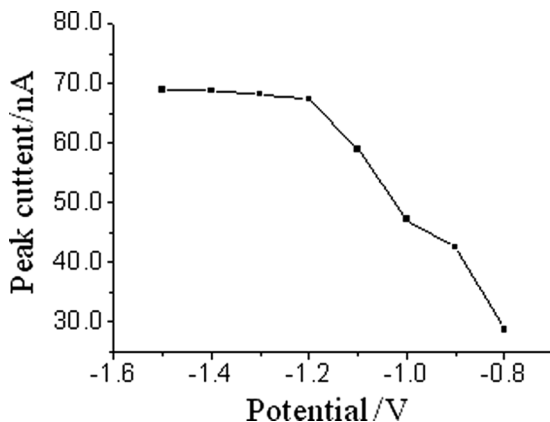
**Figure 2.** Cyclic voltammograms at BiFE (dotted line) and GC/NA-IONO/BiFE (solid line), conditions, as in Fig. 1.

BiFE, however, a larger background current was obtained. The change may be attributed to addition of nonconductive ionophore, which increases the capacitive thickness at the electrode/electrolyte interface and hence leads to an increase of capacitive current and a less efficient electrodeposition of Bi film since the reduction of bismuth ions and the growth of bismuth phase take place at the GC/NA-IONO interface (Hoyer, et al. 1987).

### Optimization of Experimental Parameter

Both NA and ionophore concentrations in coating solution have profound effects on the stripping response of Pb(II). As NA content increased to 0.1, 0.5, 1, 2 and 3% at constant concentration of ionophore, the peak current reached a climax at 1%, and reduced at higher or lower concentrations. Similar phenomenon has been found at the ionophore concentration of 2 mM. The reason is that thinner coating brings on small ion-exchange capacity, while thicker coating blocks the electron transfer on the electrode surface. Furthermore, very thick coating can cause the complexations more difficult which largely occur at the electrode/electrolyte interface.

The effect of bismuth was investigated by varying Bi(III) concentration from  $200 \mu\text{g L}^{-1}$  to  $2000 \mu\text{g L}^{-1}$  in samples, each containing 1.0 nM of target metals with deposition time of 180 s. Even the lowest concentration of Bi(III) produced well-defined and sharp peak of Pb(II). As Bi(III) concentration increased, the bismuth stripping peak became more predominant, whilst Pb(II) peak kept constant at  $\text{Bi(III)} \geq 500 \mu\text{g L}^{-1}$  and



**Figure 3.** Effect of deposition potential in the plating solution upon the current signal of Pb(II) at the GC/NA-IONO/BiFE. Measurement solution:  $1.0 \times 10^{-9}$  M Pb(II), Cd(II), Cu(II) and Sn(II) in 0.1 M acetate buffer (pH 4.5), adsorption time: 180 s.

decreased in height with Bi(III) higher than  $1000 \mu\text{g L}^{-1}$ . Consequently,  $1000 \mu\text{g L}^{-1}$  was selected considering sensitivity and stability.

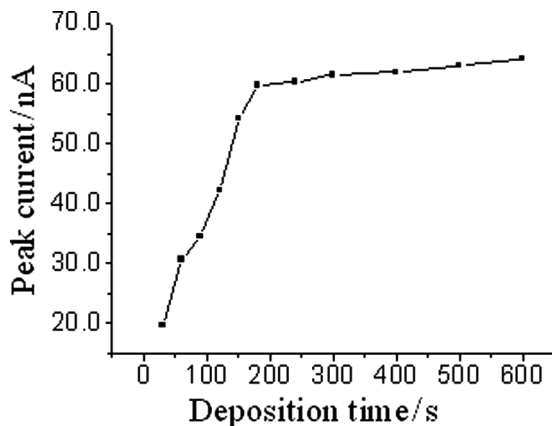
The influence of deposition potential was examined in the range from  $-0.8$  V to  $-1.5$  V in the solution containing 1.0 nM of target metals as illustrated in Fig. 3. It can be seen that the peak current for Pb(II) oxidation increased rapidly when potential changed from  $-0.8$  V to  $-1.2$  V, then kept almost constant. Additionally, hydrogen revolution starts to become more significant in acetate buffer at  $-1.4$  V. Thereby,  $-1.2$  V was selected for the optimal deposition potential.

Experiments to optimize the adsorption time were conducted in the time range from 30 to 600 s, the results are shown in Fig. 4. The peak current for Pb(II) oxidation increased rapidly with the increment of adsorption time until 180 s, thereafter increased gradually. In addition, the oxidation peak of cadmium appears with deposition time longer than 300 s. Considering a compromise between sensitivity and analysis time, 180 s was selected.

### Interferences Study

Cd(II) has influence on the stripping response of Pb(II) at BiFE due to the competition between lead and cadmium ions at the limited active sites of the electrode surface. In this work, it was studied by increasing Cd(II) from 10 nM to 1  $\mu\text{M}$  in 0.1 M acetate buffer (pH 4.5) while keeping Pb(II)

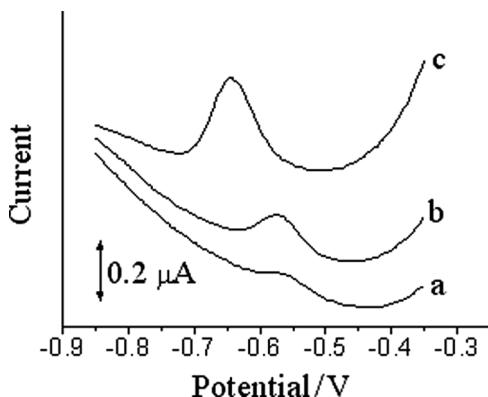




**Figure 4.** Effect of deposition time in the plating solution upon the current signal of Pb(II) at the GC/NA-IONO/BiFE. Experimental conditions as in Fig. 3

at 10 nM. With Cd(II) increasing, the peak currents of Pb(II) held constant all through even far beyond 50 nM where the oxidation peak of Cd(II) appeared. It was found that 100-fold excess of Cd(II) showed no effect on Pb(II) stripping response.

Cu(II) can form intermetallic compound with Pb(II) at BiFE, and therefore may affect the stripping peak of Pb(II). As illustrated in Fig. 5, curves (a) and (b) were stripping peaks of Pb(II) at BiFE after



**Figure 5.** Effect of Cu(II) upon the differential pulse voltammograms of Pb(II) at BiFE and GC/NA-IONO/BiFE. (a): With addition of Cu(II) at BiFE; (b): without addition of Cu(II) at BiFE; (c) with addition of Cu(II) at GC/NA-IONO/BiFE; measurement solution:  $1.0 \times 10^{-9}$  M of target metal ions in 0.1 M acetate buffer (pH 4.5); deposition 180 s at  $-1.2$  V.

**Table 1.** Comparisons of Pb(II) stripping response at BiFE and GC/NA-IONO/BiFE

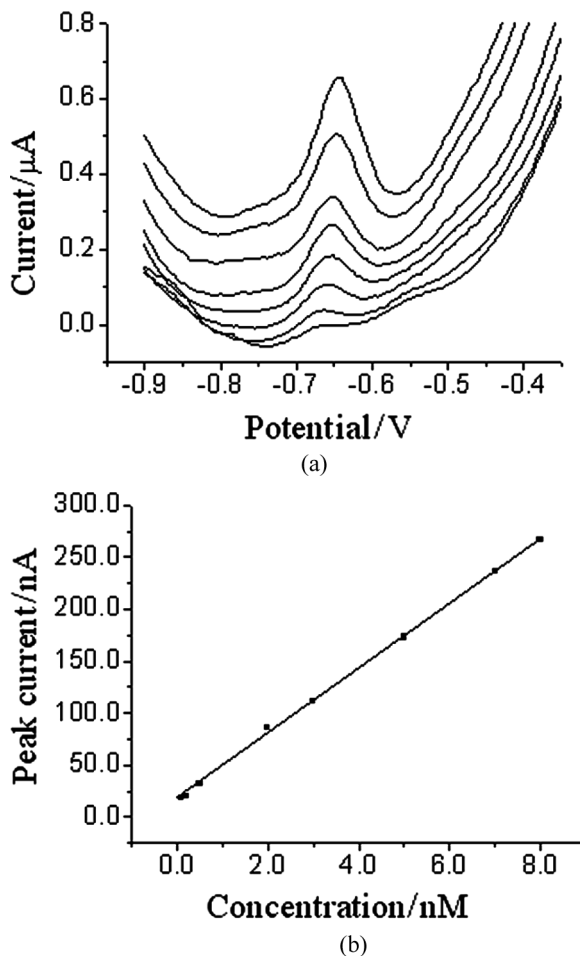
Electrode	Sample solution	Peak potential/V	Peak current/nA
BiFE	Pb	−0.558	33.06
	Pb&Sn	−0.556	11.04
GC/NA-IONO/BiFE	Pb	−0.646	186.2
	Pb&Sn	−0.646	181.1

and before addition of Cu(II), and (c) was Pb(II) stripping signal at the GC/NA-IONO/BiFE in the presence of Cu(II). At the BiFE, before addition of Cu(II), Pb(II) yielded an undistorted and excellent stripping signal, but after addition of Cu(II), the peak signal was suppressed by about 50%. At the GC/NA-IONO/BiFE it was even much larger than that obtained at BiFE before addition of Cu(II), although peak potential shifted to more negative value. This can be explained by assuming that, in the presence of the polymer film, stripping of metals is thermodynamically more reversible as the oxidized metal species are retained close to the electrode surface by the negatively charged sulfonic groups of Nafion, so that the effects of diffusion are reduced (Kefala, and Ecpnomou, 2006). The peak current of Pb(II) was not suppressed by 50-fold excess of Cu(II) but was suppressed by 20% with 100-fold.

Tin is another interfering metal since its stripping peak overlaps with that of lead. Table 1 illustrates lead stripping response obtained at BiFE and GC/NA-IONO/BiFE before and after addition of equivalent Sn(II), respectively. Lead stripping peak potential makes no difference before and after addition of Sn(II) at BiFE and GC/NA-IONO/BiFE. In the presence of tin, the peak current at BiFE was suppressed by nearly 60% and 3% at the GC/NA-IONO/BiFE. The peak current at GC/NA-IONO/BiFE was nearly 6 and 16 times higher than that at the BiFE before and after addition of Sn(II) ions, respectively.

### Calibration Plot

The newly developed GC/NA-IONO/BiFE offers a well-defined concentration dependence. Figure 6 displays stripping voltammograms recorded following increments of lead concentration over the 0–8 nM range. Well-defined peaks can be observed following 180 s deposition period at −1.2 V. The peak current increases proportionally with the metal concentration to yield a highly linear calibration plot, as shown in Fig. 6(b) with a slope of 31.38 nA/nM, correlation coefficient higher than 0.999 and



**Figure 6.** (a) Stripping voltammograms of Pb(II) along with Cu(II), Sn(II) and Cd(II) at concentrations from 0 to  $8 \times 10^{-9}$  M; (b) the resulting calibration plot. Other conditions in Fig. 1.

detection limit of  $4.4 \times 10^{-11}$  M. The relative standard deviation of GC/NA-IONO/BiFE is 5.4% obtained for a series of 10 repetitive measurements of 0.5 nM lead with the deposition time of 180 s.

### Application

The developed electrode was applied for measuring lead in seawater samples. With 180 s deposition, the electrode yielded a defined stripping

**Table 2.** Results of Pb(II) determination in water samples obtained at the GC/NA-IONO/BiFE

Sample	Pb(II) concentration (nM)	
	Proposed method <sup>a</sup>	Reference value <sup>b</sup> (ICP-MS)
Seawater 1	5.4 ( $\pm 0.29$ )	7.7 ( $\pm 0.38$ )
Seawater 2	1.2 ( $\pm 0.09$ )	2.3 ( $\pm 0.12$ )
Seawater 3	3.1 ( $\pm 0.16$ )	2.8 ( $\pm 0.15$ )
Seawater 4	2.9 ( $\pm 0.15$ )	2.4 ( $\pm 0.12$ )

<sup>a</sup>Average value of 3 determinations  $\pm$  standard deviation<sup>b</sup>Average value of 5 determinations  $\pm$  standard deviation

peak of lead, which allowed convenient quantitation by 0.4  $\mu$ M successive standard additions. As shown in Table 2, the data obtained by the present method were compared with that of ICP-MS, and the two methods provided consistent results. Thus, the proposed method can be used for determination of traces of Pb(II) in real water samples.

## CONCLUSIONS

We have demonstrated that bismuth film electrodes modified with Nafion and lead ionophore can be used for the stripping voltammetry of lead in cadmium, copper and tin mixed solution. The Nafion acts as both a suitable conducting medium and matrix for the ionophore, and an ion exchanger. The stability of the ionophore and the ability of the Nafion to extract cations into the membrane, along with the excellence of bismuth film endow an electrode that possesses high precision and accuracy. The GC/NA-IONO/BiFE achieved a very low detection limit ( $4.4 \times 10^{-11}$  M) which is much lower than those reported (Jia, et al. 2008; Legeai, and Vittori, 2006; Jia, et al. 2007). Research in our laboratory is in progress for further utility of GC/NA-IONO/BiFE as a flow-through sensor for online determination of lead.

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