

On-Line Determination of Lead in Tap Waters at Two-Step Prepared Bismuth Electrode

Dawei Pan^{1,2,*}, Li Zhang^{1,3}, Jianmei Zhuang⁴, Tanji Yin¹, Wenjing Lu^{1,3}, Wei Qin¹

¹ CAS and Shandong Provincial Key Laboratory of Coastal Zone Environmental Processes, Yantai Institute of Coastal Zone Research, Chinese Academy of Sciences, Yantai 264003, P.R. China

² State Key Laboratory of Chemo/Biosensing and Chemometrics, Hunan University, Changsha 410082, P.R. China

³ Graduate School of the Chinese Academy of Sciences, Beijing 100039, P.R. China

⁴ The Key Lab in Molecular and Nano-materials Probes of the Ministry of Education of China, College of Chemistry, Chemical Engineering and Materials Science, Shandong Normal University, Jinan 250014, P.R. China

*E-mail: dwpan@yic.ac.cn

Received: 15 February 2011 / Accepted: 30 May 2011 / Published: 1 July 2011

An anodic stripping analysis system based on two-step prepared bismuth electrode for on-line determination of lead (Pb^{2+}) in tap water samples is presented here. Such two-step prepared electrode modified in-situ and ex-situ bismuth film shows remarkably improved sensitivity to Pb^{2+} in acidic solution ($\text{pH} \leq 2$). The designed electrode has been successfully used for determination of Pb^{2+} in acidic solution by anodic stripping voltammetry with a linear range of 1.3-20 μgL^{-1} . The sensitivity and detection limit are 19 $\text{nAL}\mu\text{g}^{-1}$ and 0.8 μgL^{-1} , respectively. The practical application of the proposed electrode has been carried out for the on-line determination of trace levels of Pb^{2+} in real tap water samples.

Keywords: On-line determination, lead, bismuth electrode, stripping voltammetry

1. INTRODUCTION

Among the highly toxic pollutants, heavy metals have been widely recognized and investigated [1-2]. Lead (Pb^{2+}) as a typical heavy metal is of great concern to the public since it has been widely applied in storage batteries, cable sheath, solders and petrol additives. Pb^{2+} in the environment is cycled through the biogeochemical cycle and has ended up in surface and ground water. Many techniques have been used to detect trace Pb^{2+} , including spectral methods [3-5] and electrochemical methods. Traditional spectral methods are somewhat cumbersome, time consuming and especially not

suitable for in situ measurement because of their complicated and ponderous instruments. In contrast, the electroanalytical methods have more attractive features, such as low cost, favorable portability and easy operation procedures. Anodic stripping voltammetry (ASV) is considered to be one of the most sensitive electroanalytical methods in trace analysis of heavy metals [6]. In the past years, mercury has been widely used as the working electrode, including hanging mercury, dropping mercury and mercury membrane modified electrodes, due to their advantages of easy formation of amalgam with reduced metals, excellent reproducibility and surface renewability. However, the toxicity of mercury restricts the continued use of mercury as an electrode material and intensive researches have been attempted to introduce mercury-free sensors [7-8].

Recently, bismuth (Bi) film electrode has become an attractive subject of electroanalytical investigations as a potential replacement for mercury film electrodes due to its environmentally friendly property and closest behavior to mercury [9-18]. Generally, Bi film electrode includes ex situ and in situ prepared electrode. However, ex situ Bi film electrode has relatively narrow potential window (below the oxidation potential of bismuth) and is easily oxidized in contact with air causing relatively low chemical stability [19]. For in situ Bi film electrode, Bi ions very easily hydrolyze forming insoluble compounds, so only acidic media can be considered as plating solutions [20], which limits the use of the electrode for the on-line determination of heavy metal in real environmental waters. Thus, new analysis methods and proper operation procedure are highly desired to meet the growing demands for on-line environmental monitoring of trace heavy metal.

In this study, the two-step modification method for working electrode through the ex-situ and in-situ bismuth film was first used for the on-line electrochemical stripping analysis of heavy metal. As a model, Pb^{2+} in tap waters was detected. The proposed electrode shows a wide linear range and high sensitivity.

2. EXPERIMENTAL

2.1. Reagents

Stock solution of 0.01 M Pb^{2+} was prepared by dissolving $\text{Pb}(\text{NO}_3)_2$ (Shanghai Reagent Corporation, China) into supporting electrolyte, and then diluted to various concentrations of working solutions.

A stock solution of Bi^{3+} (1000 mgL^{-1}) was prepared by dissolving 0.23 g of bismuth (III) nitrate 5-hydrate (Shanghai Reagent Corporation, China) in HNO_3 solution. A Bi^{3+} plating solution (1 mgL^{-1} , pH 2.0) was daily prepared by diluting the stock solution with supporting electrolyte. Unless otherwise stated, 0.01 M HNO_3 solution (pH 2.0) was used as the supporting electrolyte for Pb^{2+} determination and 0.1 M HNO_3 solution (pH 1.0) containing 10 mgL^{-1} Bi^{3+} was used as the test solution. Deionized water ($18.2 \text{ M}\Omega \text{ cm}$ specific resistance) obtained with a Pall Cascada laboratory water system was used throughout. All other chemicals were analytical reagents and used without further purification.

2.2. Apparatus

All electrochemical experiments were carried out in a conventional three-electrode cell controlled by CHI 660C Electrochemical Work Station (CH Instruments, Inc). A platinum foil served as the counter electrode, and a saturated calomel electrode (SCE) was used as the reference electrode. All potential values given below refer to SCE. All the electrochemical experiments were carried out at room temperature. The flow injection system was used for sample introduction, which comprised an flow injection analyzer (Ruimai Company, Xi'an, China) equipped with two three-channel peristaltic pump and an eight-port rotary injection valve, two three-way stopcocks and a home-made electrochemical flow cell. All the tubes and connectors were of PVC or PTFE. The ICP-MS analysis was carried out using a Perkin Elmer ELAN DRC II ICP-MS spectrometer (USA).

2.3. Analytical procedure

The on-line analysis of Pb^{2+} in real water samples has two main steps including accumulation and stripping. Firstly, the glassy carbon (GC) electrode (surface area 0.12 cm^2) was polished with 0.3 and $0.05 \mu\text{m}$ alumina slurries and washed with water and acetone fully, then activated in 0.5 M H_2SO_4 solution by cycling between -0.15 and 1.3 V until a stable profile was obtained.

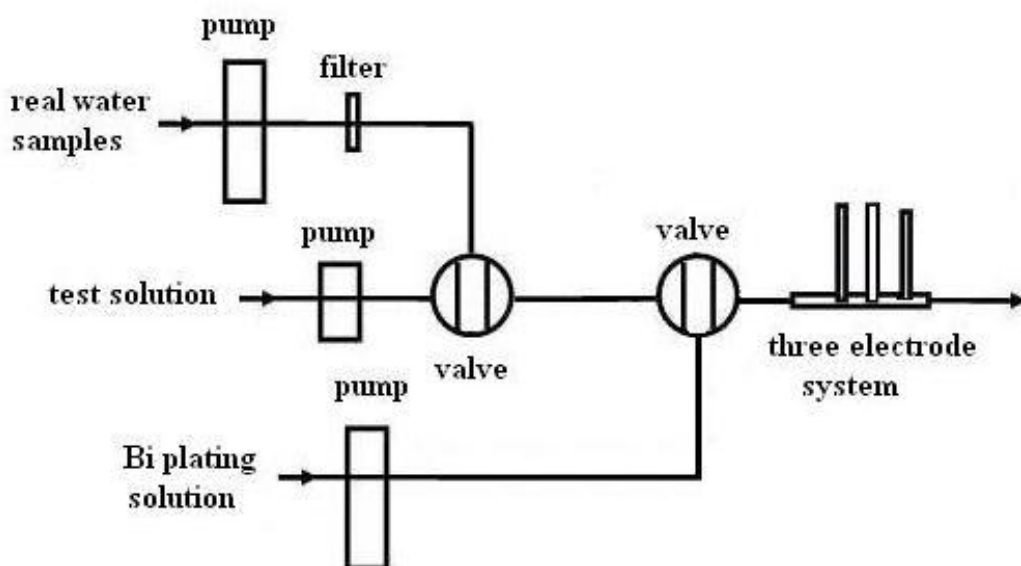


Figure 1. Manifold of the on-line determination system used.

The ex situ bismuth film electrode was prepared by electro-depositing in Bi^{3+} plating solution at -0.8 V under stirring for 120 s. Secondly, tap water samples obtained from local were used without any pretreatment. Finally, tap water samples mixed with test solution for certain time until the pH value of the mixed solution was 2.0 and free metal ions were released. The mixed sample solution was

pumped by peristaltic pump in the electrochemical cell while the potential was held at -1.0 V for 3 min to allow deposition of in-situ bismuth film and lead. Quantitative determinations of Pb^{2+} were performed with differential pulse anodic stripping voltammetry. The other optimal conditions were as follows: quiet time of 15 s; quiet potential of -1.0 V; amplitude of 0.05 V; pulse width of 0.05 s; sampling width of 0.0167 s; pulse period of 0.2 s. In this step, the remaining sample solution was directed to waste. Prior to the next measurements, the modified electrode was activated at 0.6 V for 150s in the supporting electrolyte to remove the previous deposit completely. The operation sequence of on-line determination of heavy metal in real tap water samples was shown in Fig. 1.

3. RESULTS AND DISCUSSION

Most of works are based on the in situ electrochemical deposition of the bismuth film on the electrode, which seems more suitable for the analysis of very low metal concentrations. Nevertheless, it has to be considered that in those studies where the presence of Bi(III) ions can seriously disturb the medium (e.g., heavy metal speciation) [21]. However, the two-step prepared electrode modified ex-situ and in-situ bismuth film shows remarkably improved sensitivity to Pb^{2+} in acidic solution ($\text{pH} \leq 2$). The differential pulse voltammograms recorded from -0.85 to -0.30 V for stripping analysis of 50 and $5 \mu\text{gL}^{-1}$ Pb^{2+} with various electrodes are shown in Fig. 2.

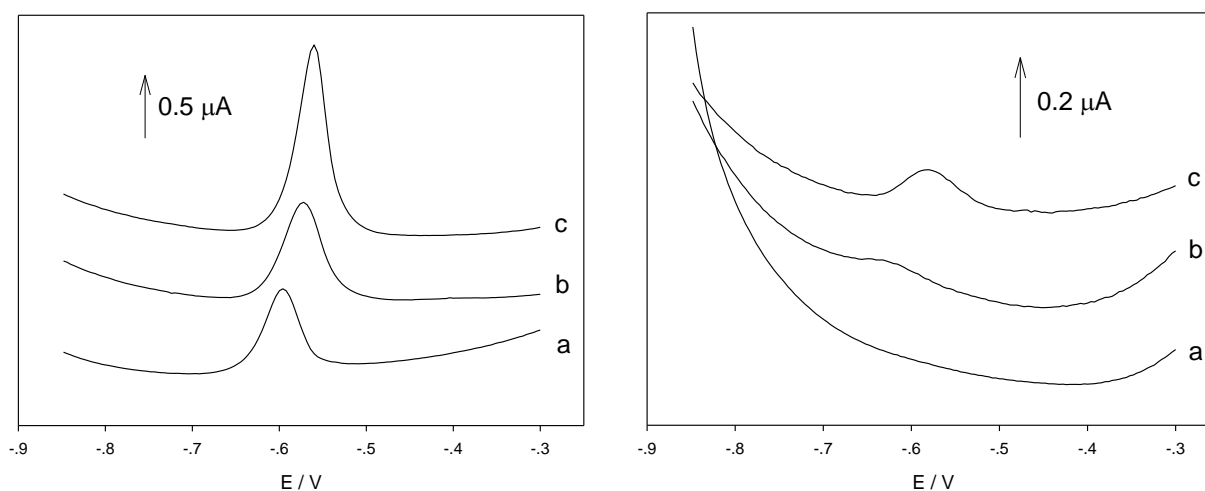


Figure 2. Anodic stripping differential pulse voltammograms of GC electrode modified (a) in-situ bismuth film, (b) ex-situ bismuth film, (c) ex-situ and in-situ bismuth film, in HNO_3 ($\text{pH} 2.0$) containing (left) $50 \mu\text{gL}^{-1}$ and (right) $5 \mu\text{gL}^{-1}$ Pb^{2+} .

For high concentration of Pb^{2+} ($50 \mu\text{gL}^{-1}$), obvious oxidation peak of Pb can be observed at all three kinds of electrode. The largest peak current can be obtained at GC electrode modified ex-situ and in-situ bismuth film. For low concentration of Pb^{2+} , almost no stripping peak was obtained at GC electrode modified in-situ bismuth film because the protons in acidic solution ($\text{pH} \leq 2$) are competing

with Pb^{2+} for these binding sites. Very small stripping peak was obtained at GC electrode modified ex-situ bismuth film. The largest stripping peak can be observed at GC electrode modified ex-situ and in-situ bismuth film.

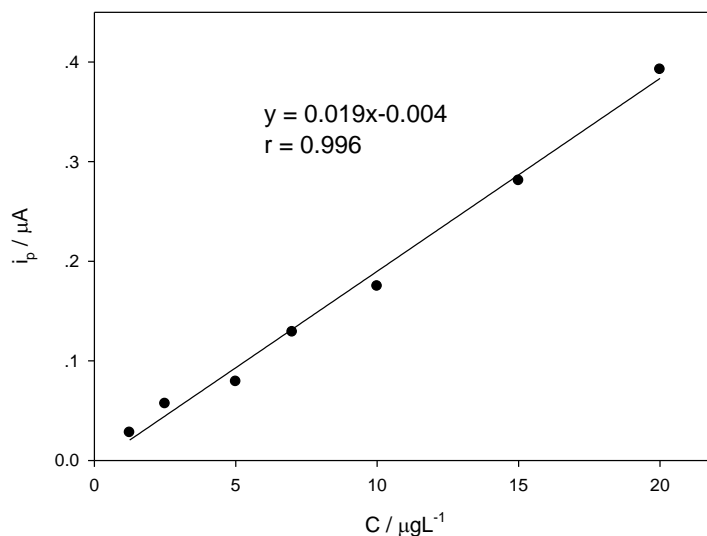


Figure 3. Calibration curves of Pb^{2+} at GC electrode modified ex-situ and in-situ bismuth film.

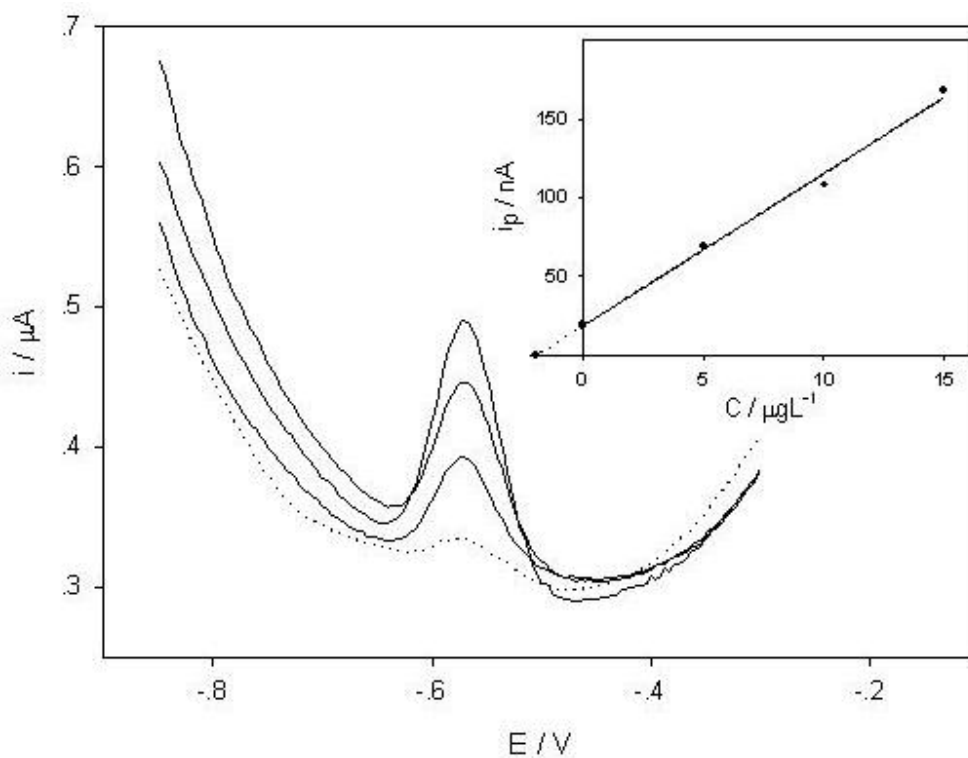


Figure 4. Anodic stripping differential pulse voltammograms for Pb^{2+} in tap water (Sample 1) by using standard addition method at GC electrode modified ex-situ and in-situ bismuth film. The addition concentrations of Pb^{2+} from bottom to top are 0, 5, 10, 15 $\mu\text{g L}^{-1}$. The inset is the fitted curve of Pb^{2+} measurement obtained from standard addition.

The response current obtained at GC electrode modified ex-situ bismuth film is increased by nearly 10-20 fold as compared to that one-step prepared GC electrode. This indicates the ex-situ and in-situ bismuth film modified GC electrode has lower background current and better anti-interference for dissolved oxygen and H^+ , which result in the lower detection limit and larger sensitivity for Pb^{2+} determination in acid solution.

The calibration curve of Pb^{2+} was derived from the differential pulse stripping voltammetry curves obtained at the two-step prepared bismuth electrode. From Fig. 3, the stripping peak current (i_p) is proportional to the concentration of Pb^{2+} from 1.3 to 20 μgL^{-1} ($i_p = 0.019C - 0.004$, $r = 0.996$, i_p in μA , C in μgL^{-1}). The sensitivity of the electrode to Pb^{2+} is 19 $nAL\mu g^{-1}$. The detection limit was given by the equation $C_L = 3s_{bl}/S$, where s_{bl} is the standard deviation of the blank measurements and S is the sensitivity of the calibration graph. The detection limit of Pb^{2+} was calculated to be 0.8 μgL^{-1} . The relative standard deviations for 5 μgL^{-1} Pb^{2+} were found to be 5.8% for one electrode with five measurements. The two-step prepared electrode has a wider linear dynamic range, lower detection limit and larger sensitivity than most of other methods for voltammetric stripping determination of Pb^{2+} [22-26].

Table 1. Comparison of two-step prepared electrode modified ex-situ and in-situ bismuth film and ICP-MS for determination of Pb^{2+} in tap water samples

Sample	Detected by ICP-MS	Detected by proposed electrode
sample 1	4.0 ppb	3.8 ppb
sample 2	3.4 ppb	3.3 ppb
sample 3	3.0 ppb	3.1 ppb

Fig. 4 shows the stripping responses for tap water (sample 1) at GC electrode modified ex-situ and in-situ bismuth film. The voltammetric peak current of Pb^{2+} in tap water can be detected at proposed electrode, indicating the possibility of successful determination of Pb^{2+} in real samples by using standard addition method. The concentration of Pb^{2+} in real sample can be calculated from fitted curve (inset of Fig. 4). Experiments show that the proposed electrode exhibit high sensitivity and good selectivity for the determination of Pb^{2+} under the optimum experimental conditions. In order to illustrate its accuracy in practical analysis, the comparison between such two-step prepared electrode modified ex-situ and in-situ bismuth film and Inductively Coupled Plasma Mass Spectrometry (ICP-MS) for detection of Pb^{2+} in real tap water samples was carried out and the corresponding results are shown in Table 1. Tap water samples were directly mixed with test solution and analyzed by the standard addition method. The values of Pb^{2+} in tap waters obtained by proposed electrode were in very good agreement with those found from ICP-MS measurements. It can be seen that the two-step prepared electrode modified ex-situ and in-situ bismuth film indeed has a great potential for real sample analysis with a high accuracy and good reliability.

4. CONCLUSIONS

In summary, an on-line analysis system based on two-step prepared bismuth electrode was established for the determination of Pb^{2+} by anodic stripping analysis. Such electrode modified ex-situ and in-situ bismuth film shows remarkably improved sensitivity to Pb^{2+} in acidic solution ($pH \leq 2$). The practical application of the proposed electrode was assessed. This new analysis method and proper operation procedure can be used as a potential platform for on-line electroanalysis of heavy metals in environmental water samples. Our future work is seeking for determination of heavy metals by our proposed electrode in lake waters and sea waters, which indeed need UV-digestion in acidic solution.

ACKNOWLEDGEMENTS

This work was financially supported by the Science and Technology Development Project of Yantai City (2009164), the Natural Science Foundation of Shandong Province (2008ZRA06004, BS2010HZ030), the National Natural Science Foundation of China (21007087) and the Chinese Academy of Sciences (KZCX2-YW-JS208).

References

1. S. Wang, E.S. Forzani, N. Tao, *Anal. Chem.*, 79 (2007) 4427.
2. J. Li, S. Guo, Y. Zhai, E. Wang, *Electrochem. Commun.*, 11 (2009) 1085.
3. G. A. Zachariadis, E. Sahanidou, *J. Pharm. Biomed. Anal.*, 50 (2009) 342.
4. K. Yoosaf, B. I. Ipe, C. H. Suresh, K. G. Thomas. *J. Phys. Chem. C*, 111 (2007) 12839.
5. Y. Chen, H. Chang, Y. Shiang, Y. Hung, C. Chiang, and C. Huang, *Anal. Chem.*, 81 (2009) 9433.
6. J. Wang, *Stripping analysis*, VCH, Deerfield Beach, Florida, 1985.
7. S.B. Hocevar, I. Švancara, B. Ogorevc, K. Vytřas, *Anal. Chem.*, 79 (2007) 8639.
8. V. Urbanová, K. Vytřas, A. Kuhn, *Electrochem. Commun.*, 12 (2010) 114.
9. J. Wang, J.M. Lu, S.B. Hocevar, P.A.M. Farias, B. Ogorevc, *Anal. Chem.*, 72 (2000) 3218.
10. A. Alberich, N. Serrano, C. Arino, J.M. Diaz-Cruz, M. Esteban, *Talanta*, 78 (2009) 1017.
11. N.S.A. Alberich, J.M. Diaz-Cruz, C. Arino, M. Esteban, *Electrochim. Acta*, 53 (2008) 6616.
12. M. Slavec, S.B. Hocevar, B. Ogorevc, *Electroanalysis*, 20 (2008) 1309.
13. C. Prior, G.S. Walker, *Electroanalysis*, 18 (2006) 823.
14. J. Wang, *Electroanalysis*, 17 (2005) 1341.
15. R. Pauliukaite, C.M.A. Brett, *Electroanalysis*, 17 (2005) 1354.
16. C. Gouveia-Caridade, R. Pauliukaite, C.M.A. Brett, *Electroanalysis*, 18 (2006) 854.
17. G. Kefala, A. Economou, *Anal. Chim. Acta*, 576 (2006) 283.
18. C. Kokkinos, A. Economou, I. Raptis, C.E. Efstathiou, T. Speliotis, *Electrochem. Commun.*, 9 (2007) 2795.
19. M. Korolczuk, A. Moroziewicz, and M. Grabarczyk, *Anal. Bioanal. Chem.*, 382 (2005) 1678.
20. M. Buckova, P. Grundler, and G.U. Flehsig, *Electroanalysis*, 17 (2004) 440.
21. N. Serrana, J.M. Díaz-Cruz, C. Ariño, M. Esteban, *Anal. Bioanal. Chem.*, 396 (2010) 1365.
22. L. Zhu, C. Tian, R. Yang, J. Zhai, *Electroanalysis*, 20 (2008) 527.
23. W. Yantasee, L. A. Deibler, G. E. Fryxell, C. Timchalk, Y. H. Lin, *Electrochem. Commun.*, 7 (2005) 1170.

24. D. Dragoie, N. Spataru, R. Kawasaki, A. Manlivannan, T. Spataru, D. A. Tryk, A. Fujishima, *Electrochim. Acta*, 51 (2006) 2437.
25. M. Ghiaci, B. Rezaei, R. J. Kalbasi, *Talanta*, 73 (2007) 37.
26. G. Li, Z. M. Ji, K. B. Wu, *Anal. Chim. Acta*, 577 (2006) 178.