

International Journal of Environmental Analytical Chemistry

Publication details, including instructions for authors and subscription information:

<http://www.tandfonline.com/loi/geac20>

Voltammetric determination of nitrate in water samples at copper modified bismuth bulk electrode

Dawei Pan ^a, Wenjing Lu ^{a b}, Haiyun Zhang ^{a b}, Li Zhang ^{a b} & Jianmei Zhuang ^c

^a Key Laboratory of Coastal Zone Environmental Processes, Yantai Institute of Coastal Zone Research(YIC), Chinese Academy of Sciences(CAS); Shandong Provincial Key Laboratory of Coastal Zone Environmental Processes, YICCAS, Yantai Shandong, 264003, P.R. China

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

^c 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

Published online: 14 Jun 2012.

To cite this article: Dawei Pan, Wenjing Lu, Haiyun Zhang, Li Zhang & Jianmei Zhuang (2013) Voltammetric determination of nitrate in water samples at copper modified bismuth bulk electrode, International Journal of Environmental Analytical Chemistry, 93:9, 935-945, DOI: [10.1080/03067319.2012.690149](https://doi.org/10.1080/03067319.2012.690149)

To link to this article: <http://dx.doi.org/10.1080/03067319.2012.690149>

PLEASE SCROLL DOWN FOR ARTICLE

Taylor & Francis makes every effort to ensure the accuracy of all the information (the "Content") contained in the publications on our platform. However, Taylor & Francis, our agents, and our licensors make no representations or warranties whatsoever as to the accuracy, completeness, or suitability for any purpose of the Content. Any opinions and views expressed in this publication are the opinions and views of the authors, and are not the views of or endorsed by Taylor & Francis. The accuracy of the Content should not be relied upon and should be independently verified with primary sources

of information. Taylor and Francis shall not be liable for any losses, actions, claims, proceedings, demands, costs, expenses, damages, and other liabilities whatsoever or howsoever caused arising directly or indirectly in connection with, in relation to or arising out of the use of the Content.

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing, systematic supply, or distribution in any form to anyone is expressly forbidden. Terms & Conditions of access and use can be found at <http://www.tandfonline.com/page/terms-and-conditions>

Voltammetric determination of nitrate in water samples at copper modified bismuth bulk electrode

Dawei Pan^{a*}, Wenjing Lu^{ab}, Haiyun Zhang^{ab}, Li Zhang^{ab} and Jianmei Zhuang^c

^aKey Laboratory of Coastal Zone Environmental Processes, Yantai Institute of Coastal Zone Research (YIC), Chinese Academy of Sciences (CAS); Shandong Provincial Key Laboratory of Coastal Zone Environmental Processes, YICCAS, Yantai Shandong, 264003, P.R. China;

^bGraduate School of the Chinese Academy of Sciences, Beijing, 100039, P.R. China;

^cThe 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

(Received 2 September 2011; final version received 11 April 2012)

Voltammetric determination of nitrate (NO_3^-) in 0.1 M Na_2SO_4 solution (pH 2.0) at copper modified bismuth bulk (BiB/Cu) electrode was presented in this article. Owing to the unique properties of bismuth bulk electrode, the proposed BiB/Cu electrode can be used for determination of NO_3^- without any deoxygenating pretreatment and shows low detection limit (6 μM), wide linear range (13 μM to 3 mM), high sensitivity (31.8 $\mu\text{A mM}^{-1} \text{cm}^{-2}$) and good anti-interference. The practical application of the proposed BiB/Cu electrode has been carried out for determination of NO_3^- in real environmental water samples.

Keywords: bismuth bulk electrode; copper; nitrate; voltammetric determination; water samples

1. Introduction

Nitrate (NO_3^-) has a widespread distribution within environmental, food, industrial and physiological systems. Lots of studies have proved that excessive NO_3^- can present both environmental and physiological problems [1,2]. Nitrate pollution in groundwater, rivers or lakes is now a common and increasing problem in numerous worldwide countries. Owing to the possible dangers associated with NO_3^- , the World Health Organization (WHO) recommends a maximum limit of 0.8 mM for NO_3^- concentration in drinking water [3]. The US Environmental Protection Agency (EPA) has also imposed a limit of 0.7 mM NO_3^- on drinking water. So it is clear that monitoring NO_3^- concentration in aqueous solutions is extremely important.

Different techniques such as UV/vis, chemiluminescence, fluorimetry, infrared, Raman and molecular cavity emission, chromatography, capillary electrophoresis and electrochemistry have been used for the quantification determination of NO_3^- . It should be pointed out that the majority of the procedures depend on a previous step involving the stoichiometric conversion of NO_3^- to nitrite (NO_2^-) by using convenient chemical reductors such as Cu/Cd [4].

*Corresponding author. Email: dwp@yic.ac.cn

Electrochemical techniques has great potential for on-site environmental monitoring due to its favourable portability, suitability for automation, short analysis time, low power consumption and inexpensive equipment. The studies in the electroanalytical field on the determination of NO_3^- are almost based on voltammetric/amperometric or potentiometric methods. The latter involves the use of ion-selective electrodes [5–8]. Comparatively, voltammetric/amperometric techniques depend on the electrochemical reduction of NO_3^- at electrode surfaces. Various substrate materials such as copper [9–14], nickel [15], copper–nickel alloys [16], copper–palladium alloys [17], platinum [18,19], lead [20], silver [21], rhodium [22], boron-doped diamond [23–25], gold [26,27] and integrated electronic tongue [28] have been used. But, owing to slow kinetics of charge transfer, direct reduction of NO_3^- on bare unmodified electrodes is usually difficult. The surface cumulative passivation effects of bare electrodes will also lead to low sensitivity and irreproducibility [13]. Additionally, oxygen reduction occurs at a more positive potential than nitrate reduction, the large current from the oxygen reduction interferes with the nitrate measurement. Direct reduction of NO_3^- on many electrodes is usually in deoxygenated solution [12,29–31]. Thus, new alternative electrode materials for voltammetric analysis are still highly desired to meet the growing demands for on-site environmental monitoring of NO_3^- .

Recently, metallic bismuth as an attractive new electrode material for either electrochemical or electroanalytical use has been reported [32–35]. Bismuth bulk (BiB) electrode possesses several advantages: besides being a non-toxic metal, it exhibits a relatively high hydrogen overvoltage resulting in wide pH dependent cathodic potential window approaching that of mercury. The anodic stripping voltammetry performance of the BiB electrode shows characteristics that are similar to those of the bismuth film electrode. Bi-based electrodes are less susceptible to oxygen interference according to studies, where measurements at Bi-based electrodes were performed in non-deaerated solutions, yielding a flat baseline [36].

In this article, BiB electrode has been used as a new substrate electrode for voltammetric determination of NO_3^- for the first time. To improve the selectivity and sensitivity in the process of quantifying nitrate, the electrodeposition of copper is pretreated on the surface of BiB electrode, because copper is an effective material for electroanalytical determination of NO_3^- and the deposition of copper is both inexpensive and simple. The proposed copper modified bismuth bulk (BiB/Cu) electrode can be used for voltammetric determination of NO_3^- without any deoxygenating pretreatment and shows wide linear range and high sensitivity to NO_3^- .

2. Experimental

2.1 Reagents

Bi rods (1.5 cm in length) were purchased from Sichuan University, China. The working BiB electrode was made from a Bi rod encapsulated in an insulating epoxy housing that was equipped with a copper wire to make the electrical contact. CuSO_4 , H_2SO_4 , Na_2SO_4 , NaNO_2 and NaNO_3 were obtained from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China). 0.1 M stock standard of NO_3^- was prepared by dissolving NaNO_3 into deionized water, and then diluted to various concentrations of working solutions. The supporting electrolyte (pH 2.0) in all experiments was a 0.1 M Na_2SO_4 solution containing 5 mM H_2SO_4 . All other chemicals were analytical reagents and used without

further purification. Deionized water (18.2 M Ω cm specific resistance) obtained with a Pall Cascada laboratory water system was used throughout.

2.2 Apparatus

All electrochemical experiments were carried out in a conventional three-electrode cell controlled by a CHI 660D Electrochemical Work Station (CH Instruments, Inc). A BiB (1 mm in diameter) electrode was used as working electrode. A Cu bulk disc electrode (3 mm in diameter) was also used as working electrode for comparison. A platinum foil was applied as the counter electrode, and a saturated calomel electrode (SCE) served as the reference electrode. All potential values given below refer to SCE. The pH measurements were performed at an E-201-C Model pH meter (Shanghai Leici Instrument Factory). All the electrochemical experiments were carried out at room temperature and non-deoxygenating condition.

The morphology and elemental composition of the modified electrodes were characterized by field emission scanning electron microscopy (SEM, Hitachi S-4800) and energy dispersive X-ray microanalyzer (EDS, HORIBA EX-350), respectively. The ion analysis was carried out by using a Dionex ICS3000 ion chromatography (USA).

2.3 Sample preparation

The laboratorial tap water was collected from the current authors' institute. The well water and underground water samples were obtained from Laishan district, Yantai city. The laboratorial tap water was used without any pretreatment. The well water and underground water samples were first filtered through a standard 0.45 μ m filter. All water samples were mixed with supporting electrolyte and acidified to pH 2. The water samples were stored at -4°C in acid-cleaned high-density polyethylene (HDPE) sample bottles.

2.4 Analytical procedure

The procedure for preparation of BiB/Cu electrode is based on several pieces of research [12,13,19] and optimized as follows: (1) the BiB electrode was polished with 0.3 and 0.05 μ m alumina slurries and washed with water and acetone, then activated in supporting electrolyte by cyclic sweeping from -0.5 V to 0.5 V at a scan rate of 50 mV s^{-1} . (2) Copper was electrodeposited on the BiB electrode by potentiostatic method from 0.1 M CuSO_4 aqueous solution at -0.5 V for 20 s.

The analysis of NO_3^- was performed in 20 mL beaker containing supporting electrolyte solution without removal of oxygen. Quantitative determinations of NO_3^- were performed with differential pulse cathodic voltammetry. The optimal conditions were as follows: increase of 0.01 V; amplitude of 0.05 V; pulse width of 0.2 s; pulse period of 0.5 s; quiet time of 15 s. After each measurement, the BiB/Cu electrode can be used continuously after cleaning with deionized water. Almost 20 times continuous measurement later, the BiB/Cu electrode was cut to obtain a renewable Bi surface and regenerated for the following experiment according to the above procedure.

3. Results and discussion

3.1 Characterization of the BiB and BiB/Cu electrodes

Figure 1 shows the morphology of the BiB and the BiB/Cu electrodes. From Figure 1(a), a porous mesh-like structure can be observed for the BiB electrode. After the electro-deposition of Cu, the different aspect can be obtained. The surface of BiB electrode was partially covered by the dendrimer-like structure of Cu (Figure 1b). At the same time, the presence of Cu on the surface of BiB electrode is also confirmed by EDS investigation. From Figure 1(c), C, O and Bi are the major elements. C and O may come from the treatment of Bi rod. The existence of Cu element on Figure 1(d) indicates that Cu exists actually on the BiB electrode surface. It is well known that Bi forms binary or multi-

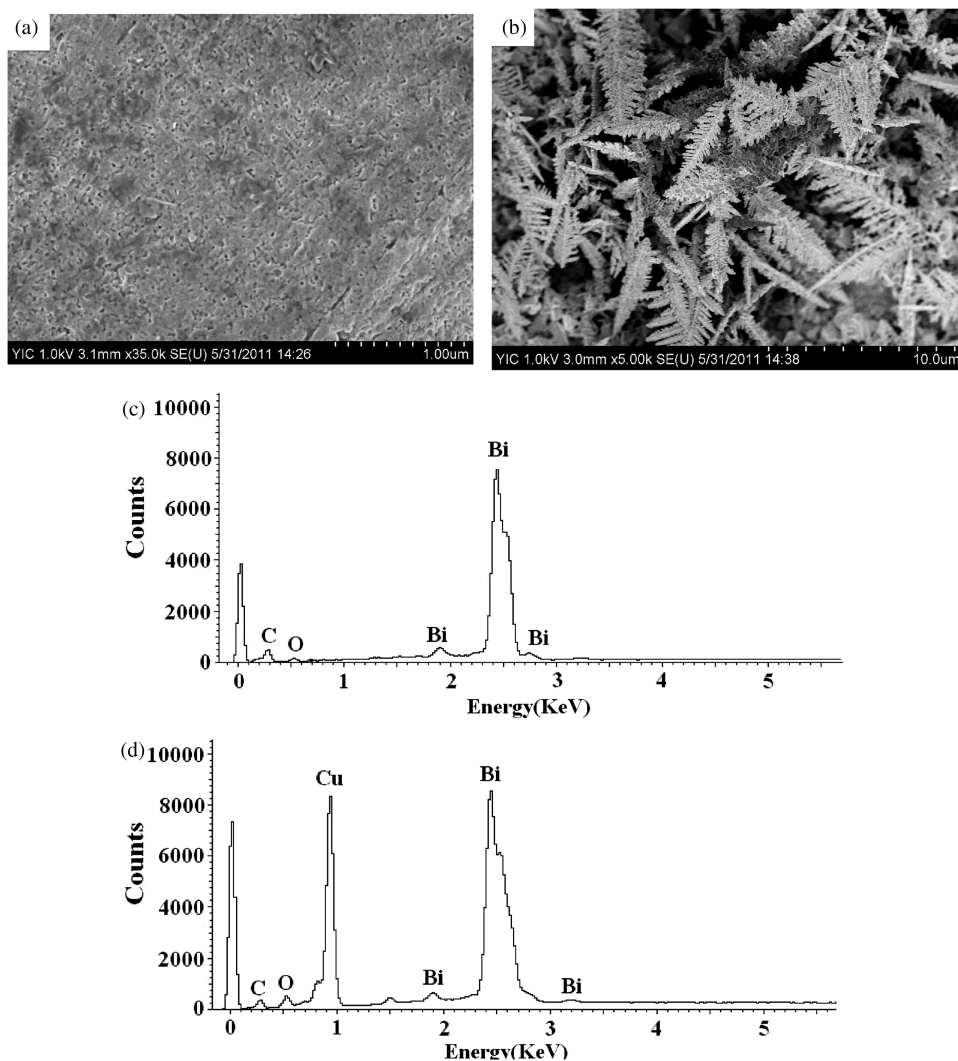


Figure 1. SEM images (a, b) and EDS pattern (c, d) of BiB (a, c) and BiB/Cu (b, d) electrodes.

component “fusing” alloy with any other metals [37]. Therefore, it can be inferred that the BiB electrode is essential to obtain Cu 3D electrodeposit and allows the strong accumulation of Cu at the electrode surface and results in better response to NO_3^- .

The voltammetric behaviors of BiB (solid line) and BiB/Cu (dotted line) electrode in 0.1 M Na_2SO_4 solution (pH 2.0) were shown in Figure 2. From the inset of Figure 2, two oxidation peaks at -0.02 V and 0.09 V and one reduction peak at -0.26 V can be obviously observed for BiB electrode, which correspond to the redox procedure of Bi. Comparatively, a huge sharp peak at 0.22 V can be obtained after electro-deposition of Cu on BiB electrode (dotted line in Figure 2), which is in accordance with the oxidation of Cu. Only one oxidation peak at 0.0 V and one reduction peak at -0.25 V of Bi were also seen. The another oxidation peak of Bi was suppressed in the huge oxidation peak of Cu. These indicate the Cu particles were easily electro-deposited on BiB electrode surface, but not covered the whole BiB electrode surface. This interesting Bi–Cu coexisting situation on electrode surface will keep the good anti-interference to dissolved oxygen of Bi and excellent electrocatalysis property of Cu, resulting in better voltammetric determination of NO_3^- .

The electrochemical behaviour of the BiB and BiB/Cu electrode in 0.1 M Na_2SO_4 solution (pH 2.0) with or without $100\text{ }\mu\text{M}$ NO_3^- was shown in Figure 3. From Figure 3, no reduction peak of NO_3^- can be found at BiB electrode in 0.1 M Na_2SO_4 solution (pH 2.0), which shows that the direct reduction of NO_3^- at Bi electrode is difficult. But at the BiB/Cu electrode, an obvious reduction peak at -0.4 V can be observed. These phenomena were coincidence with the reported literature [13,29]. Additionally, the electrochemical behaviour of NO_3^- at the unpretreated Cu bulk electrode was also shown (the inset in Figure 3). Compared with the BiB/Cu electrode, no reduction peak of NO_3^- can be observed at unpretreated Cu bulk electrode, which is in accordance with the report [10]. This is may be the reason that the reduction of dissolved oxygen at unpretreated Cu bulk

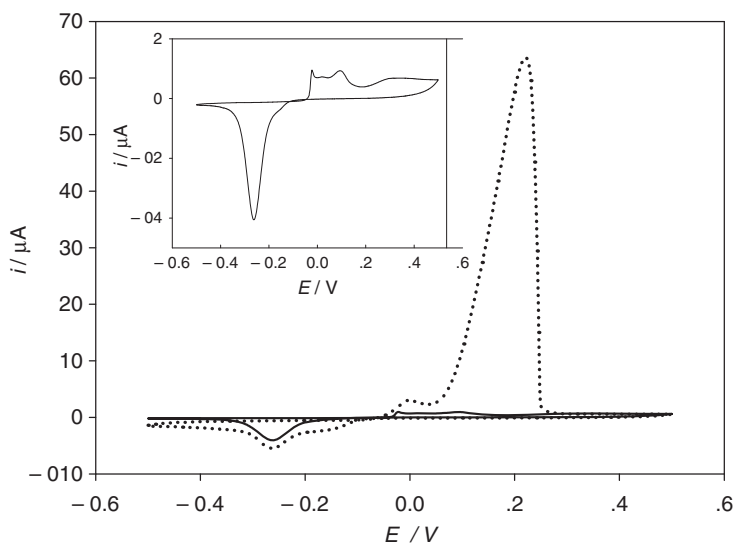


Figure 2. Cyclic voltammograms recorded at the BiB (solid line) and BiB/Cu (dotted line) electrodes in 0.1 M Na_2SO_4 solution (pH 2.0). Scan rate, 50 mV s^{-1} .

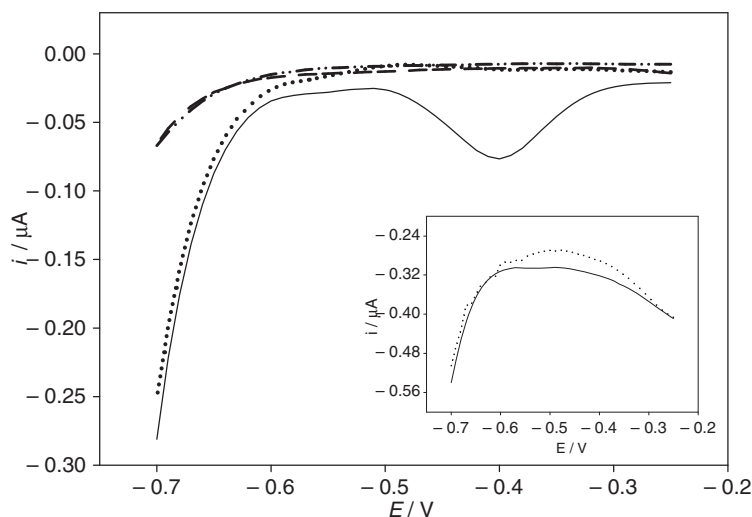


Figure 3. Differential pulse voltammograms recorded at BiB (dashed line, dashed and dotted line), BiB/Cu electrode (dotted line, solid line) and Cu bulk electrode (dotted line and solid line in Inset) in 0.1 M Na₂SO₄ solution (pH 2.0) with (dashed line, solid line) and without (dashed and dotted line, dotted line) 100 μM NO₃⁻. Amplitude, 0.05 V; Pulse width, 0.2 s; Sampling width, 0.0167 s; Pulse period, 0.5 s; Quiet time, 15 s.

electrode caused the large background current and resulted in the disappearance of the reduction peak of low concentration of NO₃⁻. The BiB electrode is essential to obtain active Cu electrodeposits and the resulting BiB/Cu electrode is contributed to nitrate reduction.

On the other hand, the reduction of NO₃⁻ at BiB/Cu electrode in 0.1 M Na₂SO₄ solution (pH 2.0) with or without deoxygenating pretreatment was investigated and the corresponding results are shown in Figure 4. Two distinct reduction peaks of NO₃⁻ and NO₂⁻ can be observed at BiB/Cu electrode in no deoxygenating solution, which is similar to those at the copper electrode pretreated by dissolution/redeposition [10]. However, only the reduction peak of NO₃⁻ can be found at BiB/Cu electrode in deoxygenating solution. As far as the electrode reactions are concerned, the thermodynamically preferred product of NO₂⁻ reduction is N₂, but other products such as NO, N₂O, hydroxylamine and ammonium are also formed [38]. The transformation of product in deoxygenating solution may cause the shift of the reduction peak of NO₂⁻. More interesting, the peak currents of NO₃⁻ are 0.272 μA in deoxygenating solution and 0.279 μA in ambient solution. Almost same peak currents indicate that the BiB/Cu electrode can be used for the determination of nitrate without deoxygenating sample solutions because the existence of Bi might slow the reduction of dissolved oxygen.

3.2 Calibration curve

The mechanism of nitrate reduction at solid electrodes is to be resolved gradually and would appear to be dependent upon the experimental conditions employed. However, in most cases the final product of the electroreduction reaction at copper is ammonium in

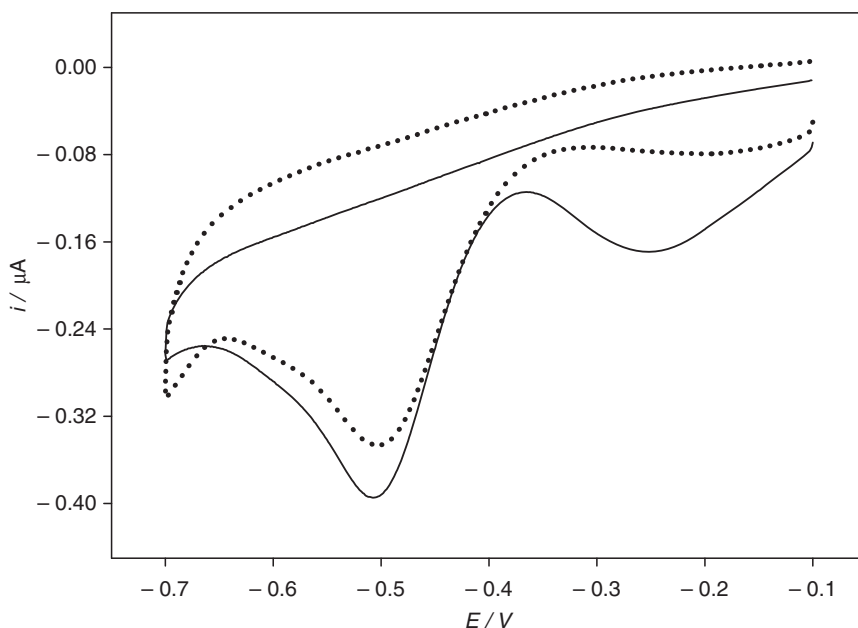
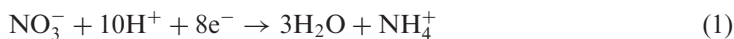


Figure 4. Cyclic voltammograms of the BiB/Cu electrode in 0.1 M Na₂SO₄ solution (pH 2.0) containing 0.5 mM NO₃⁻ without (solid line) and with (dotted line) deoxygenating pretreatment. Scan rate, 50 mV s⁻¹.

acidic solution [39–40] and nitrite in alkaline solution [21]. NO₃⁻ reduction in sufficient acidic conditions can occur as an eight-electron process according to the following equation [13]:



As shown in Equation 1, an acidic medium is required for the cathodic process. However, at very low pH values the onset of hydrogen evolution may interfere with the NO₃⁻ electroreduction as both processes occur at similar potentials. The optimized experiments were performed at pH 2.0. The calibration curve for NO₃⁻ at the BiB/Cu electrode was derived from the differential pulse voltammetric curves (Figure 5). The peak current (i_p) is proportional to the concentration of NO₃⁻ from 13 μM to 3 mM ($i_p = 0.012 + 0.25 C$, $r = 0.9994$, i_p in μA, C in mM). The sensitivity of the BiB/Cu electrode to NO₃⁻ is 31.8 μA mM⁻¹ cm⁻². The detection limit of NO₃⁻ calculated at $S/N = 3$ is 6 μM. It is found that the BiB/Cu electrode shows higher sensitivity, wider linear range and lower detection limit than many other works [9–13,41]. The BiB/Cu electrode has also good reproducibility and repeatability. The relative standard deviations for 100 μM NO₃⁻ were found to be 5.6% for one electrode with five measurements and 8.2% for five electrodes prepared with identical procedures. The long-time stability of proposed electrode in deionized water was performed in supporting solution containing 200 μM NO₃⁻ for three determinations in each day and the corresponding result shows that almost 10% decrease of the original current response to NO₃⁻ is observed in the first continuous 7 days.

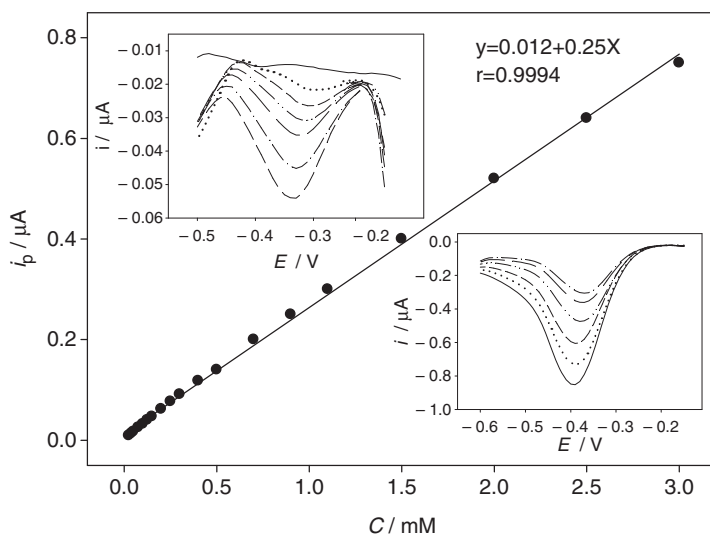


Figure 5. Calibration curves of NO_3^- at BiB/Cu electrode. The values from bottom to top are 0, 13, 25, 38, 50, 75, 100 μM for the left inset curves and 0.9, 1.1, 1.5, 2.0, 2.5, 3.0 mM for the right inset curves respectively, which are in the linear range. The conditions are the same as in Figure 3.

3.3 Study of interferences

The interference of common anions (Cl^- and NO_2^-) to the detection of NO_3^- was investigated and the results are shown in Figure 6. In this case, the scan was initiated at -0.15 V which may induces the partial stripping of copper from the electrode surface. The presence of Cl^- in the electrolyte solution serves to scavenge some of the stripped copper and the reduction of NO_3^- at copper electrodes is known to be dependent upon Cl^- concentration [12]. The differential pulse voltammetric curves obtained at the BiB/Cu electrode before and after the addition of Cl^- were compared (Figure 6a). It can be seen that although Cl^- serves to enhance the NO_3^- reduction peak, it also shifts the peak towards more negative potentials. The presence of chloride serves to stabilize the Cu^+ state and the reduction of chloro-copper species occurs at more negative potentials. This behaviour is consistent with previous report [12]. On the other hand, the reduction of NO_2^- was also investigated at the BiB/Cu electrode in order to evaluate the possibility of simultaneous detection of NO_3^- and NO_2^- . Accordingly, Figure 6(b) shows voltammetric curves recorded with the BiB/Cu electrode in solution containing NO_3^- in the presence and absence of NO_2^- . The peak at -0.1 V attributed to the reduction of NO_2^- can be observed at the BiB/Cu electrode in solution without NO_2^- , which imply the reduction of NO_3^- accompanies with the reduction of NO_2^- [12]. At the same time, the peak of reduction of NO_2^- does not interfere with the peak of NO_3^- . The potential difference between NO_3^- and NO_2^- is almost 250 mV. With the increase of the concentration of NO_2^- , the peak currents of NO_3^- do not change significantly, while the peak currents of NO_2^- increase obviously. The good resolution between both cathodic peaks makes it possible further studies involving speciation between NO_3^- and NO_2^- at some particular samples.

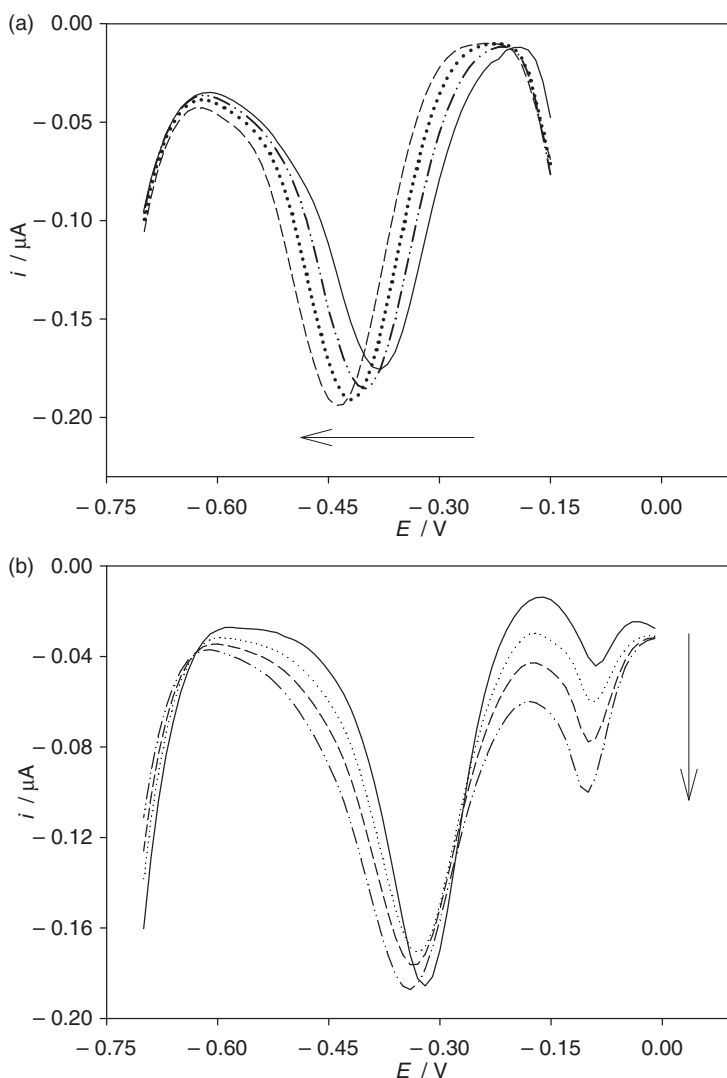


Figure 6. Differential pulse voltammograms recorded at BiB/Cu electrode in 0.1 M $\text{Na}_2\text{SO}_4 + 0.5 \text{ mM NO}_3^-$ solution (pH 2.0) before and after addition of Cl^- (a) and NO_2^- (b). The concentration of Cl^- (from left to right) and NO_2^- (from bottom to top) are both 1.5, 3 and 5 mM. The conditions are the same as in Figure 3.

3.4 Practical application of BiB/Cu electrode

The BiB/Cu electrode exhibits high sensitivity, wide linear range and good interference for the determination of NO_3^- under the optimum experimental conditions. In order to illustrate its accuracy in practical analysis, the comparison between the proposed BiB/Cu electrode and ion chromatography for detection of NO_3^- in real samples was carried out. Several different types of environmental water samples including laboratorial tap water, underground waters and well water were filtered through a standard $0.45 \mu\text{m}$ filter and analyzed by the standard addition method. The results are shown in Table 1. It can be seen

Table 1. Comparison of the BiB/Cu electrode and ion chromatography for determination of NO_3^- in real water samples.

Sample	Detected by BiB/Cu electrode ^a (mM)	Detected by ion chromatography (mM)
Laboratorial tap water	1.06 ± 0.08	1.10
Underground water 1	0.18 ± 0.02	0.16
Underground water 2	0.52 ± 0.09	0.58
Underground water 3	0.19 ± 0.03	0.19
Well water	2.30 ± 0.14	2.39

Note: ^aAverage value of three determinations \pm standard deviation.

that the BiB/Cu electrode indeed has a great potential for real sample analysis with a high accuracy and good reliability.

4. Conclusions

A simple, inexpensive method for direct determination of NO_3^- based on the Cu modified solid BiB electrode has been demonstrated. BiB electrode is less susceptible to oxygen interference and the proposed BiB/Cu electrode is tolerant of a range of potential interferences (Cl^- and NO_2^-) that can significantly influence rival the determination of NO_3^- . The BiB/Cu electrode has lower detection limit, higher sensitivity and wide linear range, which is suitable for a number of analytically relevant applications and particularly those requiring water quality measurements. BiB can be used as a new alternative electrode material to provide an excellent platform for electroanalysis of anions.

Acknowledgements

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

References

- [1] D. Reyter, D. Bélanger, and L. Roué, *Electrochim. Acta* **53**, 5977 (2008).
- [2] R. Desai, M.M. Villalba, N.S. Lawrence, and J. Davis, *Electroanalysis* **21**, 789 (2009).
- [3] World Health Organization, Rolling Revision of the WHO Guidelines for Drinking-Waters Quality, Nitrates and Nitrites in Drinking-Waters. World Health Organization (2004).
- [4] M.J. Moorcroft, J. Davis, and R.G. Compton, *Talanta* **54**, 785 (2001).
- [5] A.R. Asghari, M.K. Amini, H.R. Mansour, and M. Salavati-Niasari, *Talanta* **61**, 557 (2003).
- [6] J. Gallardo, S. Alegret, and M. Del Valle, *Sens. Actuators B* **101**, 72 (2004).
- [7] T.A. Bendikov, J. Kim, and T.C. Harmon, *Sens. Actuators B* **106**, 512 (2005).
- [8] S.S.M. Hassan, S.A.M. Marzouk, and H.E.M. Sayour, *Talanta* **59**, 1237 (2003).

- [9] J.C.M. Gamboa, R.C. Peña, T.R.L.C. Paixão, and M. Bertotti, *Talanta* **80**, 581 (2009).
- [10] S.M. Shariar and T. Hinoue, *Anal. Sci.* **26**, 1173 (2010).
- [11] N. Aouina, H. Cachet, C. Debiemme-chouvy, and T.T.M. Tran, *Electrochim. Acta* **55**, 7341 (2010).
- [12] J. Davis, M.J. Moorcroft, S.J. Wilkins, R.G. Compton, and M.F. Cardosi, *Analyst* **125**, 737 (2000).
- [13] T.R.L.C. Paixão, J.L. Cardoso, and M. Bertotti, *Talanta* **71**, 186 (2007).
- [14] J. Davis, M.J. Moorcroft, S.J. Wilkins, R.G. Compton, and M.F. Cardosi, *Electroanalysis* **12**, 1363 (2000).
- [15] J.O. Bockris and J. Kim, *J. Electrochem. Soc.* **143**, 3801 (1996).
- [16] M.J. Moorcroft, L. Nei, J. Davis, and R.G. Compton, *Anal. Lett.* **33**, 3127 (2000).
- [17] K. Soropogui, M. Sigaud, and O. Vittori, *Electroanalysis* **18**, 2354 (2006).
- [18] V. Mori and M. Bertotti, *Anal. Lett.* **32**, 25 (1999).
- [19] Y. Li, J. Sun, C. Bian, J. Tong, and S. Xia, *Key Engineer. Mater.* **483**, 595 (2011).
- [20] J.D. Genders, D. Hartsough, and D.T. Hobbs, *J. Appl. Electrochem.* **26**, 1 (1996).
- [21] D. Kim, I.B. Goldberg, and J.W. Judy, *Analyst* **132**, 350 (2007).
- [22] J.W. Peel, K.J. Reddy, B.P. Sullivan, and J.M. Bowen, *Water Res.* **37**, 2512 (2003).
- [23] P. Bouamrane, A. Tadjeddine, J.E. Butler, R. Tenne, and C. LevyClement, *J. Electroanal. Chem.* **405**, 95 (1996).
- [24] C.M. Welch, M.E. Hyde, C.E. Banks, and R.G. Compton, *Anal. Sci.* **21**, 1421 (2005).
- [25] S. Ward-Jones, C.E. Banks, A.O. Simm, L. Jiang, and R.G. Compton, *Electroanalysis* **17**, 1806 (2005).
- [26] Y.P. Chen, S.Y. Liu, F. Fang, S.H. Li, G. Liu, Y.C. Tian, Y. Xiong, and H.Q. Yu, *Environ. Sci. Technol.* **42**, 8465 (2008).
- [27] K. Fajerwerg, V. Ynam, B. Chaudret, V. Garçon, D. Thouron, and M. Comtat, *Electrochem. Commun.* **12**, 1439 (2010).
- [28] I. Campos, R. Masot, M. Alcañiz, L. Gil, J. Soto, J.L. Vivancos, E. García-Breijo, R.H. Labrador, J.M. Barat, and R. Martnez-Mañez, *Sens. Actuator. B* **149**, 71 (2010).
- [29] A.O. Solak, P. Gülser, E. Gökmeşe, and F. Gökmeşe, *Microchim. Acta* **134**, 77 (2000).
- [30] A.O. Solak and P. Çekirdek, *Anal. Lett.* **38**, 271 (2005).
- [31] X.L. Zhang, J.X. Wang, Z. Wang, and S.C. Wang, *Sensors* **5**, 580 (2005).
- [32] R. Pauliukaite, S.B. Hočevár, B. Ogorevc, and J. Wang, *Electroanalysis* **16**, 719 (2004).
- [33] M. Bučková, P. Gründler, and G. Flechsig, *Electroanalysis* **17**, 440 (2005).
- [34] K.C. Armstrong, C.E. Tatum, R.N. Dansby-Sparks, J.Q. Chambers, and Z.L. Xue, *Talanta* **82**, 675 (2010).
- [35] W. Pimrote, R. Ratana-Ohpas, and L. Renman, *Electroanalysis* **23**, 1607 (2011).
- [36] J. Wang, J. Lu, S.B. Hočevár, and P.A.M. Farias, *Anal. Chem.* **72**, 3218 (2000).
- [37] J. Wang, J. Lu, Ü.A. Kirgöz, S.B. Hočevár, and B. Ogorevc, *Anal. Chim. Acta* **434**, 29 (2001).
- [38] V. Rosca, M. Duca, M.T. de Groot, and M.T.M. Koper, *Chem. Rev.* **109**, 2209 (2009).
- [39] D. Pletcher and Z. Poorabedi, *Electrochim. Acta* **24**, 1253 (1979).
- [40] N.G. Carpenter and D. Pletcher, *Anal. Chim. Acta* **317**, 287 (1995).
- [41] A.G. Fogg, S.P. Scullion, and T.E. Edmonds, *Analyst* **116**, 573 (1991).