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The Chronopotentiometric Stripping Analysis of Lead Based on Abrasively Immobilized Multi-walled Carbon Nanotubes Bismuth Film Electrode

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A novel mercury free carbon nanotubes-Bi film electrodes was fabricated based on abrasive immobilized MWCNTs and in-situ plated Bi film on graphite electrode. Scanning electron microscope (SEM) analysis indicated that the surface of graphite electrode was firmer and homogeneously coated by MWCNTs via abrasive immobilizing. The constant current chronopotentiometric stripping method for the determination of Pb was developed based on the abrasive immobilized MWCNTs Bi film graphite electrode. The factors that influence the stripping peak height (dt/dE) of Pb were investigated in detail. Well-defined peaks along with low background current were obtained in pH 4.6 acetate buffer with the stripping current of 5.0 µA and the Bi (III) concentration of 0.4 mg/L. Under the optimal conditions, the proposed method exhibited linear ranges from 10.0 µg/L to 100.0 µg/L with detection limit of 1.0 µg/L at the deposition time of 120 s. The assay results of Pb in soil examples with the proposed method were in acceptable agreement with ICP-AES with good accuracy and recovery when the interference caused by Cu (II) was alleviated by the addition of ferrocyanid.

Keywords: Bismuth film electrode; Multi-walled carbon nanotubes; Graphite electrode; Chronopotentiometric stripping analysis; Lead

1. INTRODUCTION

Pb is one of the most dangerous elements in environmental and biological systems [1-2], it is highly toxic to the liver, brain, kidneys, reproductive system and central nervous system of human. In particular, Pb can accumulate in environment and takes a very long time to be excreted [3-4]. Therefore, sensitive and practical analytical techniques are highly demanded because of lower content of Pb in environmental and biological samples [5-6]. Several analytical techniques including graphite furnace atomic absorption spectrometry (GFAAS) [7], inductive coupled plasma atomic emission spectrometry (ICP-AES) [8], inductively coupled plasma mass spectrometry (ICP-MS) [9] have been used for the determination of Pb in environmental, biological samples and medicinal herbs, but they are characterized by high costs and complex instrumentation, and the analysis must be performed in a specialized laboratory by skilled personnel.

One of the most potential methods for trace heavy metals analysis is chronopotentiometric stripping analysis (CPSA) [10-12] due to its sensitivity, low equipment cost and instrument compatibility. The remarkable sensitivity with stripping analysis is attributed to the deposition step in which the target analyte is preconcentrated onto the working electrode. In the second, the stripping step of CPSA, the accumulated metal is reoxidized by imposing a constant current and the quantification of the accumulated metal is based on the measurement of stripping time [12]. Reliable determination of stripping time can be achieved by measuring the area under the peak in the *dt/dE* versus E plots, where *dt/dE* denotes the inverse of the time derivative of the recorded potential [13]. The most notable advantages of CPSA are signal independence of the electrode surface, detection in the presence of some electroactive organic compounds, lower background contributions, and analysis in solutions with lower ionic strength [14].

Mercury-based electrode systems such as mercury film electrode and the hanging mercury drop electrode have traditionally been used to achieve high reproducibility and sensitivity based on their unique ability to preconcentrate heavy metal. However, mercury and the mercury salts are extremely toxic, hence it is highly desired to develop mercury free electrode [15] for stripping analysis. In 2000, Bi-based electrode [16-19] was proposed as an alternative to mercury-based electrodes. The attractive properties of Bi-based electrode, including high sensitivity, well-defined stripping signals, good resolution of neighbouring peaks (e.g. Cd, Cu, Pb, and Zn), large cathodic potential range, and insensitivity to dissolved oxygen were shown to compare favourably with that of mercury-based electrodes. In addition, Bi is a more environmentally friendly material and widely used in medicine and cosmetics with a low toxicity.

Nowadays, Bi-based electrode has already been accepted in many electroanalytical laboratories worldwide. Efforts have been made to improve the sensitivity and selectivity of Bi-based electrode. The carbon nanotubes (CNTs) modified Bi electrode (Bi-CNT electrode) was employed for the determination of trace heavy metals [20-25]. The presence of CNTs on the electrode surface significantly enhances the electrochemical activity of the electrode due to the unique electronic structures, high specific surface area, electrical conductivity, and excellent strength of CNTs [23].

The CNT electrode is generally prepared by CNT paste (CNTP) [21] or surface coating of CNT (SCCNT) [26] dispersion solutions on an electrode and dried in N_2 flow or air. However, the prepared surface modified electrodes are time-consuming to prepare, considerable leaching of dispersing agent and always suffer from mechanical instability during measurement [27]. Hence, the simple and reliable methods to prepare CNT electrode are highly desired to overcome the above problems and to broaden the application of the CNT electroanalytical devices in Bi-based electrode. A. Salimi et al [28] reported that multi-walled carbon nanotubes (MWCNTs) could be abrasively immobilized on a electrode only by gently rubbing of a heated glassy carbon electrode (GCE) surface on a filter paper supporting the MWCNTs. This abrasively immobilized CNT (AICNT) electrode exhibited several advantages over CNTP and SCCNT, including long stability, good reproducibility, very simple and fast to prepare.

In the present work, we first report on the Bi film-modified graphite electrode (BiF/GE) incorporated with abrasively immobilized CNTs (AICNTs) for the derivative chronopotentiometric stripping analysis of Pb. The aim of our work was to demonstrate the advantageous properties of this abrasively immobilized MWCNTs Bi film-modified graphite electrode (AIMWCNTs/BiF/GE), which is attributed to the stabilization effect of the abrasive immobilization of MWCNTs on the electrode, the sensitizing effect of MWCNTs and the accumulation effect of Bi film. After the optimization of the chronopotentiometric stripping analysis parameters, the AIMWCNT/BiF/GE is adapted for the chronopotentiometric stripping analysis of traces Pb in soil.

2. EXPERIMENTAL

2.1. Apparatus

The potentiometric stripping analysis of Pb was performed by a MP-2 stripping analyzer with a MCP-2T polar graphic workbench (Shandong 7 Telecommunications Factory, China). Three-electrode system: a multi-walled carbon nanotubes modified graphite electrode (GE, 4 mm diameter) was used as the working electrode, a saturated calomel electrode (SCE) and a 223 platinum electrode were used as the reference electrode and auxiliary electrode, respectively. Scanning electron microscopy (SEM) image was performed with a SSX-550 SEM microscope (SHIMADZU, Japan). All the electrochemical experiments were carried out in a one-compartment electrochemical cell at room temperature (20±1 ^{o}C).

2.2. Reagents and solutions

All reagents were analytical pure or superpure grade. Pure water was redistilled in a quartz apparatus. Multi-walled carbon nanotubes (MWCNTs, purity $\geq$ 98%, 8–15 nm diameter and 1–5 μm in length) were obtained from Chengdu Organic Chemicals Co. Ltd., Chinese Academy of Sciences (China) . Stock aqueous solutions of Pb (II) were prepared weekly by dilution of Pb (II) AAS standard solution of 1000 mg/L (Alfa Aesar, U.S.A) in 0.06 M HNO_3. Bi (III) solution of 0.25 g/L (in 1.0 M HNO_3) . A 0.20 M acetate buffer was prepared by mixing appropriate amounts of acetate and sodium acetate, the pH value of the acetate buffer was adjusted by changing the composition of acetate and sodium acetate.

Pretreatment of MWCNTs was progressed according to the previous literature [30], 500.0 mg of the original MWCNTs was dispersed in 100 mL of 30% HNO_3 and then refluxed for 24 h at 140 ^oC to obtain carboxylic group-functionalized MWCNTs. The resulting suspension was centrifuged, the sediment was washed with pure water until the pH reached 7.0 and then dried in an oven at 80 ^oC for 12 h.

2.3. Preparation of abrasively immobilized MWCNTs graphite electrode

The graphite electrode (GE) was prepared for modification by renewing the electrode surface with cloth polish. Immediately after polishing, the electrodes were ultrasonically cleaned in 95% ethanol for 5 min, rinsed with triply distilled water and allowed to dry in air. The abrasively immobilized MWCNTs/GE was prepared by gently rubbing the electrode surface on a filter paper supporting two milligrams of functionalized MWCNTs for 2 min [28]. The prepared electrode was cleaned with distilled water before used.

2.4. Measurement procedure

Chronopotentiometric stripping analysis (CPSA) with constant current model was applied for the determination of Pb, an abrasively immobilized MWCNTs GE was employed as the substrate for in situ plated Bi film [31] in the solution containing a pH 4.6 acetate buffer with 0.4 mM Bi (III) and 0.1 mg/L Pb (II). The first step of this technique was the pre-concentration of Bi and Pb to the abrasively immobilized MWCNTs GE by applying the deposition potential of −1.1 V (vs SCE) for a deposition time of 90 s with solution stirring, followed by a rest period (without stirring) of 30 s. In this procedure, Bi and Pb were simultaneously deposited on the abrasively immobilized MWCNTs/GE. The second step was stripping during which the previously deposited Bi and Pb were re-oxidized by a stripping current of 5.0 μA and go into solution without stirring. Between each analysis, the stripping signal (dt/dE vs E) was recorded. An electrochemical cleaning method was adopted: after stripping, the working electrode was set to −0.1 V (vs SCE) for 20 s with stirring.

2.5. Sample preparation

The soil or lake sediment samples were air dried and grounded to pass through a 100-mesh sieve. 2.00 g prepared sample was placed in a teflon beaker and wetted. 10 mL HCl was added and heated at low temperature for 1 h, and then 20 mL HNO_3 was added as 5 mL solution left and heated to near dryness. After that 5mL HF was added and heated for 10 min. Finally, 5 mL $HClO_4$ was added, heated until no white smoke. The solution and beaker were rinsed with 3 mL pure water. 1 drop of 10 g/L methyl red solution was added into the solution, the pH of the solution was adjusted to about pH 4 by dripping ammonia until the solution changes from red to yellow. Then 5 mL 0.2 M acetate buffer (pH 4.6) and 20.0 μL of 0.20 g/L Bi (III) solution were added and diluted to 10.0 mL with water. The chronopotentiometric stripping analysis of Pb in the sample was performed according to the procedure of "*2.3.1*" section and the result was calculated by standard addition method. Elsewhere, a blank test was carried out by the same procedure.

3. RESULTS AND DISCUSSION

3.1. Surface morphologies of MWCNTs abrasively modified GC electrode

In the case of abrasively immobilized MWCNTs glassy carbon electrode (GCE) developed by A. Salimi *et al* [28], MWCNTs should be immediately immobilized onto a GCE electrode which was heated for 5 min at 50 ^{o}C in oven due to the high compact surface of GCE. In our work, graphite electrode (GE) was employed as the alternative of GCE for the preparation of abrasively immobilized MWCNTs electrode. Owing to the porous surface structure of GE [29], MWCNTs could be easily immobilized on the surface of GE at room temperature.

Scanning electron microscopy (SEM) was used to characterize the morphologies of the abrasively immobilized MWCNTs GE and the result is shown in Figure 1. The surface of bare GE exhibits a quite flat substrate with a very smooth and uniform morphology (as shown in Figure 1a). While, it can be clear seen that the surface of GE is completely and homogeneously coated by MWCNTs, the immobilization of MWCNTs on the surface of GE is firmer and evenly tangled distributing with special three-dimensional structure (Figure 1b), suggesting that MWCNTs were successfully immobilized on the surface of GE by abrasively modifying at room temperature. The spaghetti-like MWCNTs formed a porous structure on the surface of electrode, which increased the surface-to-volume ratio effectively and enhanced the electron-transfer reactions. Therefore, the stability and sensitivity of the modified electrode were improved effectively [33].

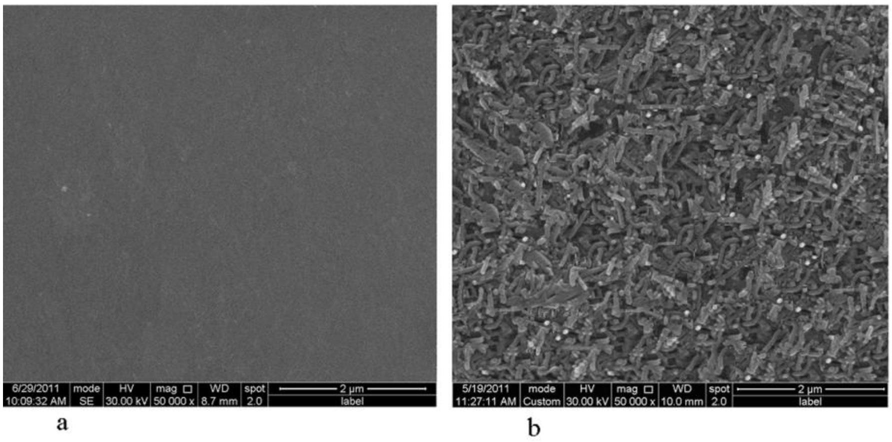

Figure 1. Scanning electron microscopy (SEM) images of bare GE (a) and abrasively immobilized MWCNTs/GE (b).

3.2. The effect of supporting electrolyte and pH

The stripping response for 0.10 mg/L Pb was examined in different supporting electrolyte solutions such as 0.04 M B-R buffer, 0.1 M PBS buffer, 0.1 M acetate buffer, 0.1 M disodium hydrogen phosphate-citric acid buffer and 0.1 M citric acid-citrate sodium buffer. High peak response and low background signal of Pb (II) were obtained with the addition of 0.1 M acetate buffer. The effect of concentration of acetate buffer on the stripping peak (*dt/dE*) of Pb (II) was then examined in the concentration range of 0.01 to 0.08 M. A rapid increase in the stripping peak height of Pb(II) was observed by increasing the acetate concentration from 0.01 to 0.08 M. The stripping peak height reached its maximum at 0.08 M, remained unchanged with the acetate concentration between 0.08 M to 0.2 M and decreased gradually thereafter, indicating that the electro-deposition of Bi and Pb is influenced by the ionic strength of supporting electrolyte. In the present work, 0.1 M was chosen as the optimal acetate buffer concentration.

The influence of pH was then investigated in 0.1 M acetate buffer, the pH was adjusted in the range of 3.0 to 6.0 by changing the composition of acetate buffer. The effect of pH on the stripping peak height (*dt/dE*) and the relative standard deviation (*RSD*, N=11) of Pb(II) at -1.1V (vs SCE) of deposition potential were showed in Figure 2 *dt/dE* increases and *RSD* decreases by increasing pH from 3.5 to 4.4, while *dt/dE* decreases and *RSD* increases with the increasing of pH in the range of 5.5 to 4.4. The decrease of *dt/dE* and the increase of *RSD* were more obvious at pH lower than 4.0 and higher than 5.0, indicating that the sensitivity and precision of Pb determination would become very poor at lower or higher pH. This phenomenon can be attributable to the prevailing effect of Bi (III) hydrolysis at higher pH [34], and the hydrogen evolution on the electrode surface at lower pH due to the lower hydrogen over potential of Bi [35]. Therefore, in all subsequent measurements, the pH of solution was controlled at 4.6.

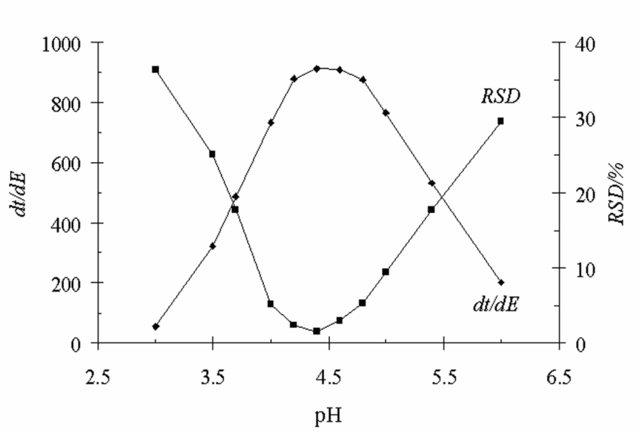

Figure 2. The effect of pH on the stripping peak height (*dt/dE*) and the relative standard deviation (*RSD*, N=11) of 0.1 mg/L Pb (II) at -1.1V (vs SCE) of deposition potential in 0.1 M acetate buffer.

3.3. Effect of the concentration of Bi (III)

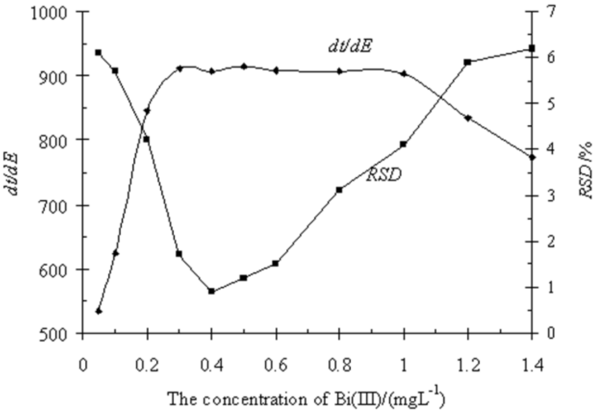

Figure 3. The effect of the concentration of Bi (III) on the stripping peak height (*dt/dE*) and the relative standard deviation (*RSD*, N=11) .

The modification of an electrode with Bi film for Pb detection essentially involves electroplating a film of Bi onto the surface of an electrode. This process can be carried out in two different ways (ex situ and in situ) [31]. In situ plating could produce better resolved and more stable response than that of ex situ plating [32], so, in situ plated Bi film was employed in this paper.

The concentration of Bi (III) is a crucial factor which controls the thickness of a Bi film [36], thereby affecting the electrochemical responses of the Bi based electrodes. Figure 3 demonstrates the effect of the concentration of Bi (III) on the stripping peak height (*dt/dE*) and the relative standard deviation (*RSD*, N=11). It was observed that the stripping peak of Pb(II) was markedly increasing with the concentration of Bi (III) increasing from 0.05 mg/L to 0.25 mg/L, which may be the results of the increase of the nucleation sites and the alloy formation with the increasing of Bi (III) concentration [32]. The stripping peak of Pb (II) reached a plateau when the concentration of Bi (III) increased from 0.3 mg/L to 1.0 mg/L, this phenomenon can be explained by the saturation effect of Bi film on the electrode surface [37]. A decrease of the stripping peak was observed at the concentration of Bi (III) more than 1.0 mg/L, meanwhile, the stripping peak also became wider, this effect could be attributed to the mass transfer resistance of Pb (II) in thick Bi film on the electrode surface at high concentration of Bi (III) [38]. In this work, 0.4 mg/L was chosen as the optimal Bi (III) concentration.

3.4. Effect of deposition potential and time

The effect of deposition potential on the stripping peak of Pb (II) was investigated at Bi (III) concentration of 0.4 mg/L and pH 4.6. No stripping peak was observed at a potential more positive than -0.5 V (vs SCE) , which means that the deposition potential was not sufficiently negative to initiate the reduction of Pb (II). As seen in Figure 4, *dt/dE* increased when the deposition potential increased from -0.60 V to -1.20 V (vs SCE) , and then decreased when the deposition potential was more negative than -1.3 V (vs SCE) , this decrease effect can be attributed to the hydrogen evolution on the electrode surface at more negative deposition potential [39]. Hence, a deposition potential of -1.10 V (vs SCE) was chosen in the subsequent work.

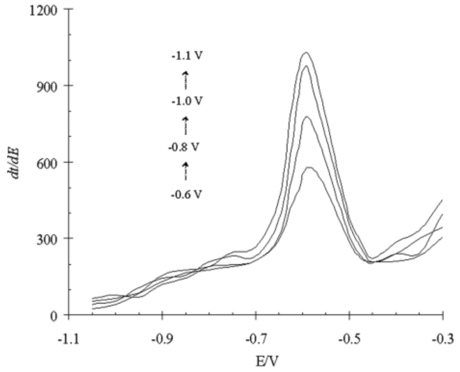

Figure 4. The stripping peak of 0.1 mg/L Pb (II) at different deposition potential at Bi (III) concentration of 0.4 mg/L and pH 4.6.

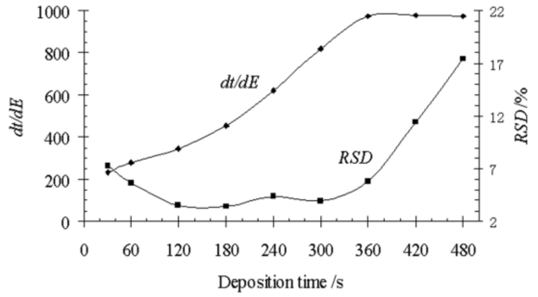

Figure 5. The effect of the deposition time on *dt/dE* and *RSD* (N=11) of 0.1 mg/L Pb (II) at -1.10 V (vs SCE) deposition potential.

The effect of the deposition time on *dt/dE* and *RSD* (N=11) of Pb (Ⅱ) was also investigated for 0.1 mg/L Pb (II) at -1.10 V (vs SCE) deposition potential. As can be seen from Figure 5, *dt/dE* of Pb(II) increased linearly when the deposition time increased from 30 s to 300 s. While the curve of peak current versus time began to leave off and the repeatability of *dt/dE* became very poor when the deposition time was longer than 360 s, this phenomenon can be explained by the fact that the increase of Bi film thickness could affect the electron transfer rate of metal stripping [32]. For this reason, the deposition time should be in the range of 30 s to 300 s and considers the satisfactory compromise between high sensitivity and short analysis time. For this reason, a deposition time of 120 s was chosen for subsequent experiments.

3.5. Effect of stripping current

The applied stripping current has significant influence on the sensitivity and reproducibility of response obtained using chronopotentiometric stripping analysis.

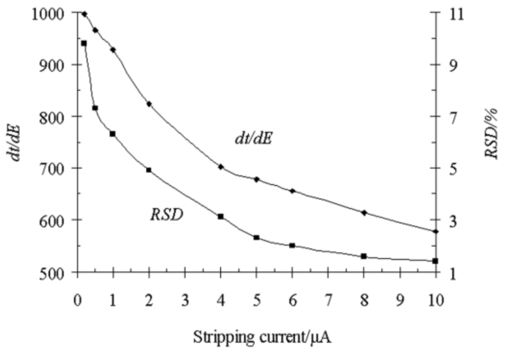

Figure 6. The influence of stripping current upon *dt/dE* and *RSD* (N=20).

Figure 6 shows the influence of stripping current upon *dt/dE* and the reproducibility, expressed as relative standard deviation (*RSD*, N=20). As expected, *dt/dE* of Pb (II) decreased significantly when the stripping current increased from 0.2 μA to 5.0 μA due to shorter stripping time, indicating that lower stripping current is beneficial to enhance analytical sensitivity, but the reproducibility would become poor when much lower currents were applied as Fig. 6 shown, meanwhile, the stripping period of Pb was prolonged obviously along with a stronger background baseline. For this reason, a stripping current of 5.0 μA was considered to ensure the reproducibility of the determination.

3.6. The chronopotentiometric stripping behaviors of Pb at the electrodes

Figure 7 displays a comparison among the stripping peak of 0.1 mg/L Pb at bare GE (a), in situ plated Bi/GE (b) and in situ plated Bi/MWCNTs/GE (c) electrodes. A stripping peak near 0.60 V (vs SCE) can be observed at the three electrodes. The bare GE electrode displays a poorly defined response for Pb, with a strong background contribution and ill-defined stripping peak, In contrast, in situ plated Bi/GE electrode yielded much higher response signal with well-defined stripping peak. Furthermore, the stripping response of Pb at in situ plated Bi/MWCNTs/GE electrode was almost two times higher than that at in situ plated Bi/GE along with practically flat background, implying that the sensitivity of the Bi film electrode towards Pb has been significantly enhanced by MWCNTs. Overall, the data of Fig.7 indicates that coating Bi layer on MWCNTs/GE electrode dramatically improves the ability of electrode to detect trace Pb as compared with coating Bi layer on bare GE electrode [40].

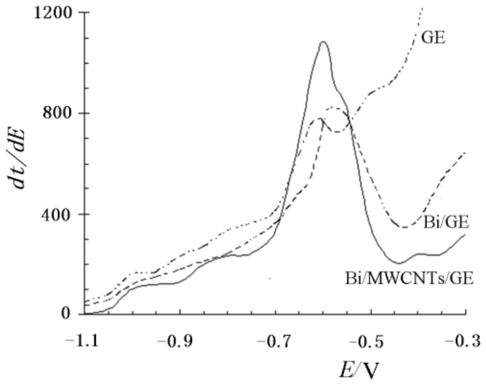

Figure 7. The stripping peak of 0.1 mg/L Pb at bare GE (a), in situ plated Bi/GE (b) and in situ plated Bi/MWCNTs/GE (c) electrodes in 0.4 mg/L Bi (III), 0.1 M acetate buffer (pH 4.6) and at -1.10 V (vs SCE) deposition potential and 120 s deposition time.

The stability and reproducibility of in situ plated Bi/MWCNTs/GE were investigated by duplicate tests. *dt/dE* of Pb at in situ plated Bi/MWCNTs/GE remained nearly unchanged and was almost 98% of its initial value for 200 duplicate measurements. Additionally the storage stability of in situ plated Bi/MWCNTs/GE stored in air at room temperature was also investigated by measuring the stripping peak of response Pb every day, in situ plated Bi/MWCNTs/GE was found to have reserved 94.3% of its initial stripping peak value after 10 d.

The results clearly indicate that MWCNTs abrasive immobilization on GE significantly improves the sensitivity of Pb determination with high stability and reproducibility. The reasons for the excellent analytical response of Bi/MWCNTs/GE may be summarized as follows: (1) MWCNTs immobilized on GE has large specific surface area, excellent adsorptive ability and catalytic effect to Pb. (2) MWCNTs immobilized on GE facilitates the nucleation processes of Bi/Pb fused alloy. (3) The chemical and mechanical stability of MWCNTs modified GE prepared by abrasive immobilization, so Bi can be deposited with Pb on MWCNTs to form Bi/Pb layer time after time with high repeatability.

3.7. Analytical performance characteristics of the method

The linear range of Bi/MWCNTs/GE for detection of Pb was determined under the optimal conditions mentioned above, using a deposition time of 120 s. A good linear relationship was obtained between *dt/dE* and the concentration of Pb^{2+} within the range of 10.0 μg/L to 100.0 μg/L, with the linear regression equation dt/dE=1.31 c - 6.17 ($r^2 = 0.997$), where, *dt/dE* is the peak height, c is the concentration of Pb^{2+} (μg/L). According to the method recommended by IUPAC, detection limit (CL)=$3S_b/S_x$, where, 3 is confidence factor, S_b is background noise standard deviation, S_x is the measurement sensitivity (The slope of the standard curve). It was found that the detection limit was related to deposition time, *dt/dE* of Pb^{2+} increased by one time for every doubling of the deposition time. S_b and the average *dt/dE* for 12 repetitive determinations were calculated, as the result, the detection limit was 1.0 μg/L at the deposition time of 120 s. By increasing the deposition time this value can be further improved. The repeatability of the method was evaluated by analyzing seven replicates of 20.0 μg/L Pb^{2+}, *RSD* was found to be 2.72% at the deposition time of 120 s.

Table 1. Comparison of the detection limit and *RSD* for Pb^{2+} with other previously reported methods

Methods	LOD/ (μg/L)	*RSD* (N)	References
GFAAS[a]	0.08	2.8%(10)	[41]
ICP-AES[b]	10	0.9%(10)	[42]
ICP-MS[c]	11	6%(6)	[43]
AAS[d]	1.1	3.5%(20)	[44]
NCBFE's[e]	0.1	3.7%(10)	[45]
CNTs-coated GCE[f]	0.83	4.6%(8)	[46]
Electrochemical method using a AIMWCNTs/BiF/GE [g]	1.0	2.72%(7)	This work

[a] graphite furnace atomic absorption spectrometry; [b] inductively coupled plasma atomic emission spectrometry; [c] inductively coupled plasma mass spectrometry; [d] atomic absorption spectrometry; [e] Nafion-coated bismuth-film electrodes; [f] carbon nanotubes - coated glassy carbon electrode; [g] abrasively immobilized MWCNTs Bi film-modified graphite electrode.

The detection limit and *RSD* of the proposed method has been compared with that of the other previously reported methods for Pb^{2+} shown in Table 1. It is evident that the proposed electrochemical method shows highly sensitive and reproducibility with the lower detection limit and *RSD*, indicating that Bi/MWCNTs/GE can be used as a sensor for the sensitive electrochemical detection of Pb^{2+} in various samples.

3.8. Interference studies

Table 2. Interferences of inorganic species on the stripping peak height of 20.0 μg/L Pb^{2+}

Interferences	Concentration /(mg/L)	Signal charge/%	Interferences	Concentration /(mg/L)	Signal charge/%
Na^+	4.0	+3.0	Zn^{2+}	0.2	+3.0
K^+	4.0	+2.2	Zn^{2+}	1.0	+9.2
Mg^{2+}	4.0	+1.4	Cd^{2+}	0.2	-3.7
Ca^{2+}	4.0	-1.7	Cd^{2+}	1.0	-8.4
Fe^{3+}	4.0	+5.1	Cu^{2+}	0.1	-27. 2
NH_4^+	4.0	-2.9	Cu^{2+}	0.4	-51.7
Mn^{2+}	4.0	-4.5	$Cu^{2+\,*}$	0.1	-4.4
Al^{3+}	4.0	+1.1	$Cu^{2+\,*}$	0.4	-6.7

* Addition of 0.1mM potassium ferricyanide

The possible interferences of some inorganic species in soil sample were investigated by addition of different inorganic ions in the extract of soil to a solution containing 20.0 μg/L of Pb^{2+}. The result is shown in Table 2, 200-fold concentration of K^+, Na^+, Ca^{2+}, Mg^{2+}, Mn^{2+}, Fe^{3+}, Al^{3+}, NH^{4+}, Cl^-, SO_4^{2-}, $NO_3^{2-}$and 10-fold concentration of Cd^{2+} and Zn^{2+} did not cause significant interference. The response signal for 20.0 μg/L of Pb^{2+} was found to decrease by 8.4% upon addition of 50-fold concentration of Cd^{2+}. Where, addition of 50-fold concentration of Zn^{2+} caused the response signal to increase by +9.2%.

The stripping response for Pb^{2+} was significantly affected by additions of Cu^{2+}, the addition of 0.1 mg/L Cu^{2+} caused *dt/dE* of 20.0 μg/L Pb to decrease by 27.2%, 0.2 mg/L Cu^{2+} by 51.7%. Wang et al [47] have explained that this is due to the competition between electrodeposited Bi and Cu for surface sites on the electrode as well as the formation of intermetallic compound between Cu and Pb. In addition, Hg^{2+} could increase the stripping peak current of Pb^{2+} due to the formation of amalgam on the electrode surface at −1.2V (vs SCE). 0.1 mM potassium ferricyanide was found to be appropriate for the selective masking of Cu interference with the analysis of Pb in aqua-regia extracted soil samples [15]. Table 2 shows that *dt/dE* of Pb is suppressed in the presence of Cu(II), while, it is restored when 0.1 mM potassium ferricyanide was added.

3.9. Real soil samples analysis

The lake sediment was from Dianchi Lake dredging of sediment, the mining area soil from a mine tailing dam in Yunnan, the farmland soil taken from a periphery of Kunming vegetable farm and the city garbage was from a municipal landfill in Kunming. All the samples were digested according to 1.2.4 section, the content of Pb was determined by the proposed method and the quantitative analysis was accomplished by the standard addition method, with 5 repetitive determinations. The sensitivity suitable for the detection of different content of Pb in the samples was adjusted by the deposition time. The results of Pb^{2+} in the soil samples obtained by the proposed method were compared with those obtained by ICP-AES. Meanwhile, Cu content in the samples was also determined by ICP-AES.

Table 3. The analytical results of Pb in soil samples (n=5)

Sample	By this method		Added /(mg/kg)	Found /(mg/kg)	Recovery /%	By ICP-AES /(mg/kg)	Cu /(mg/kg)
	Average /(mg/kg)	RSD/%					
Caohai slduge	1.47	11.1	2.00	3.14	77.6		7.31
Mining soil	13.14	12.4	20.00	29.21	70.1		31.66
Garden Soils	0.512	7.2	0.500	0.98	93.8		0.077
Municipal soil waste	0.923	6.2	1.000	1.96	104.0		1.09
0.1mM ferricyanide							
Caohai slduge	1.61	6.3	2.00	3.54	96.5	1.52	

Mining soil	17.31	4.8	20.00	36.41	95.5	18.16
Garden Soils	0.517	5.4	0.500	1.01	98.6	0.506
Municipal soil waste	0.917	3.3	1.000	1.97	105.3	0.94

The analysis results were showed in Table 3. For lower Cu content samples, such as farmland soil and city garbage, high accuracy and good recovery were obtained and the results obtained by the proposed method are consistent well with the results obtained by ICP- AES [48]. While, the accuracy and recovery were poor for the higher Cu content samples, such as lake sediment and mining area soil, and the analysis presented some relatively high deviations in the concentration levels of Pb (II) between the proposed method and the reference method, which could be attributed to the interference effect of Cu [49]. To suppress the interference effect from Cu, 0.1 mM potassium ferricyanide was adopted as the masking agent in this paper. Good accuracy and recovery was obtained for higher Cu content samples when 0.1 mM potassium ferricyanide was added, and the results showed a good agreement with that of ICP-AES. From these results, we can conclude that the as-prepared electrode could provide a satisfactory method for the determination of Pb in soil.

4. CONCLUSIONS

A novel method for the fabrication of Bi-CNTs electrode was developed by abrasive immobilized MWCNTs and in-situ plated Bi film on graphite electrode. The results obtained within this investigation have shown the good prospect of the proposed method in mercury free stripping analysis. The abrasive immobilized MWCNTs graphite electrode exhibit significant advantages compared to other Bi-CNTs electrodes: The electrode is stability and very easy to prepare, the dispersion solution of CNTs is not necessary, which is favorable to improve the electrical conductivity of electrode. The application of abrasive immobilized MWCNTs graphite electrode in the constant current chronopotentiometric stripping analysis of Pb was exhibited to have many desirable properties including high stability, good reproducibility and high sensitivity. Good accuracy and recovery was obtained in the measurements of Pb in soil when the interference caused by Cu(II) was alleviated by the addition of 0.1mM ferrocyanid.

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