Electrochemical Determination of Lead Using Bismuth Modified Glassy Carbon Electrode[1]

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Abstract—Electrochemical application of bismuth film modified glassy carbon electrode was studied with the objective of lead detection. Bismuth film on glassy carbon substrate was formed in a plating solution of 2 mmol/L $Bi(NO_3)_3$, in 1 mol/L HCl at -1.1 V (vs. Ag/AgCl) for 300 s. Lead was detected by differential pulse anodic voltammetry in acetate buffer of pH 5.0 in the concentration range of 7.5 nmol/L to 12.5 μmol/L. Factors influencing the anodic stripping performance, including deposition time, solution pH, Bi(III) concentration, potential, pulse amplitude, pulse width, have been optimized. Three linear calibration plots in the range 7.5 nmol/L to 0.1 μmol/L, 0.25 to 1 μmol/L, 2.5 to 12.5 μmol/L with regression coefficients of 0.991, 0.986 and 0.978 respectively were obtained. The theoretical detection limit equivalent to three times standard deviation for 7.5 nmol/L lead ($n = 5$) was calculated to be 5.25 nmol/L utilizing a 5 min deposition time and sensitivity 83.97 A L/mol. The sensitivity and detection limit of the method was compared with reported voltammetric methods for detection of lead and the result obtained was found to be promising for determination of lead.

Keywords: lead, stripping voltammetry, bismuth electrode

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INTRODUCTION

Mercury electrodes, normally in the form of mercury films for flow systems, have been widely used for performing stripping voltammetry as a result of their high sensitivity and reproducibility, but, due to increasing concern and legislation regarding the toxicity of mercury, alternative working electrode (WE) materials have been investigated [1].

In 2000, bismuth-film electrodes [2] were mooted as a replacement for mercury-film electrodes, as bismuth exhibits negligible toxicity and are more environment friendly in comparison. Mercury use is increasingly regulated, motivating the search for mercury-free methods.

Many substrates have been used for bismuth films. While platinum [3—5] and gold [4] have both been investigated, the majority of films have been deposited on carbon substrates. Most studies have used glassy carbon [2, 4, 6—23], though wax-impregnated graphite [13, 15], pencil-lead graphite [24], carbon paste [4, 25—27], screenprinted carbon inks [12, 28, 29], carbon fibres [2, 4, 5] and boron-doped diamond [30] have all been employed as substrates. The uses of Bi_2O_3 containing pastes [25, 31] and a bismuth bulk electrode [32] have also been reported. The use of BiFE has recently been reviewed [33]. Bismuth film electrodes have mainly been applied to anodic stripping voltammetry (ASV) and adsorptive stripping voltammetry (AdSV) techniques for metal ion analysis, although cathodic detection of nitrophenols [8, 18, 32] and amperometric detection of glucose [3] have also been reported. Cd [19], Pb [9, 28], Zn [22, 23] and mixtures of all three ions [2, 11, 13, 14, 24, 27, 32] have been the most extensively studied by ASV. Tl, Cu [7], In [7, 34], Mn [30] and Sn [35] have also been analysed. Fewer reports have been made employing AdSV, though Ni [6] and Co [19—21] and Ni with Co [15, 17] have been examined using dimethylglyoxime (DMG). Inspire with the results of Bismuth film electrode this paper is an effort to detect lead in real sample through various voltammetric measurements.

EXPERIMENTAL

Apparatus

Voltammetry techniques were performed with a BAS CV-50W potentiostat in connection with a DELL computer (Model number MTC2) controlled using BAS CV-50W software version 2.3. Bismuth coated glassy carbon (GC) 3 mm in diameter served as working electrode, with the Ag/AgCl (BAS model 2052) and platinum wire (BAS model 1032) acting as reference electrode and counter electrode, respectively. All glasswares were carefully cleaned by soaking in 0.1 mol/L HNO_3 over 48 h, followed by thorough rinsing with distilled water. Stirring was carried out using a

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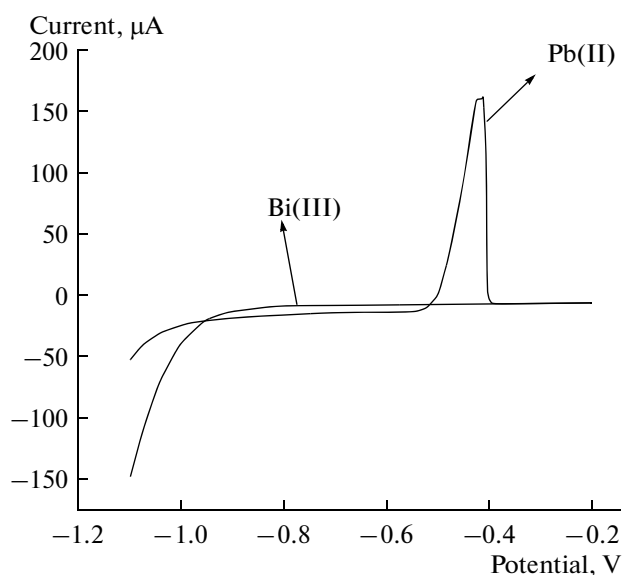[z] Corresponding author: chemdocprof@gmail.com (Khalid Siraj).

Fig. 1. Linear sweep stripping voltammogram at BiFE potential window from −1.2 to −0.2 V. Experimental conditions: 2 mmol/L Bi(III) deposition time for lead 300 s, pH 5, pulse amplitude (mV) = 50, sample width (ms) = 17, pulse width (ms) = 50 pulse period (ins) = 200.

magnetic stirrer. All potentials were given versus the Ag/AgCl reference electrode and pH/ion analyzer model 455.

Preparation of Reagents

All reagents were of analytical grade used in this research. Stock solution of 0.01 mol/L bismuth salt $(Bi(NO_3)_3 \cdot 5H_2O)$ was prepared by dissolving the salt in 1 mol/L HCl. Buffer preparation: acetate buffer was prepared by mixing 0.1 mol/L CH_3COOH and 0.1 mol/L CH_3COONa. The pH of the solution was adjusted to required pH (2.5−6) by mixing different volumes of 0.1 mol/L CH_3COOH and 0.1 mol/L CH_3COONa and pH values are controlled by pH-meter. Stock solution of lead salt was prepared by dissolving $Pb(NO_3)_3$ in acetate buffer (pH 5). Also stock solutions of all interfering ions solution were prepared in 0.1 mol/L acetate buffer pH 5.

Electrode Preparation

Glassy carbon electrode (GCE) surface was first polished with polishing paper (BAS model MF-32) and then polished thoroughly with 0.3 μm α-Al_2O_3 powder slurry on a polishing cloth mounted on glass plate and then soaking in ethanol and deionized water for 3 min each to remove alumina particles and other possible contaminants. After being dried, the GCE was immersed in a plating solution. Bismuth films were formed by deposition on the carbon film substrate at constant applied potential. The deposition was performed by ex-situ in a separate solution prior to

measurement of lead. The composition of the deposition solution was 1 mol/L HCl solution containing 2 mmol/L Bi(III). Bismuth was deposited at constant potential 1.1 V versus Ag/AgCl for 5 min for ex-situ deposition while the solution was stirred during deposition. Then the electrode was thoroughly rinsed with deionized water and dried, immediately transferred to the solution to be analyzed.

Anodic Stripping Voltammetry of Pb(II) at Bismuth Modified Glassy Carbon Electrode

For the differential pulse anodic stripping voltammetry measurement, firstly, the background response of 0.1 mol/L acetate solution of different pH (acidic pH) values was measured at BiFE. Then for measurement of Pb(II) the working electrode potential was held at −0.8 V for 300 s. With 10 s quiet times, the voltammograms was recorded between −0.8 and −0.3 V by applying a differential pulse waveform whose parameters are as follows: pulse amplitude of 100 mV, pulse width of 50 ms, pulse period = 200 ms.

RESULTS AND DISCUSSION

Linear scan stripping voltammetric technique was used to characterize bismuth film electrode. The scan rates, deposition time and peak position of lead were characterized using linear sweep stripping voltammetry. In potential window from −1.2 to −0.2 V there was no peak current for Bi(III) ion in 0.1 mol/L acetate buffer pH 5, but at −403 mV there was peak current for Pb(II) ion (Fig. 1). In potential window from −1.2 to 0.4 V there were two peaks current for Bi(III) ion and Pb(II) ion in 0.1 mol/L acetate buffer pH 4 in-situ deposited (Fig. 2).

Effect of Bi Film Thickness

The essential parameter which influences the quality of bismuth coating is the composition of plating electrolyte. The easily accessible sources of Bi(III) ions are their simple salts like $Bi(NO_3)_3 \cdot 5H_2O$ or $BiCl_3$ and their halogen complexes. Because of the risk of hydrolysis only acidic media (HCl, HNO_3, and acetic buffer) can be considered as the plating solutions for the bismuth film preparation [36]. After plating the GC support with the required amount of metallic bismuth, the electrode surface is no longer shiny and then covered with black deposit.

The amount and thickness of the electrodeposited Bi film on glassy carbon electrode was calculated using Faraday's equation for electrolysis. The mass deposited and thickness of the bismuth film layer is found to be 7 μg and 2.52×10^{-6} cm.

The bismuth film plating time was used to control the thickness of the bismuth film. The effect of the bismuth plating time was studied in the range 60−360 s as shown in the Fig. 3. The lead peak increased with
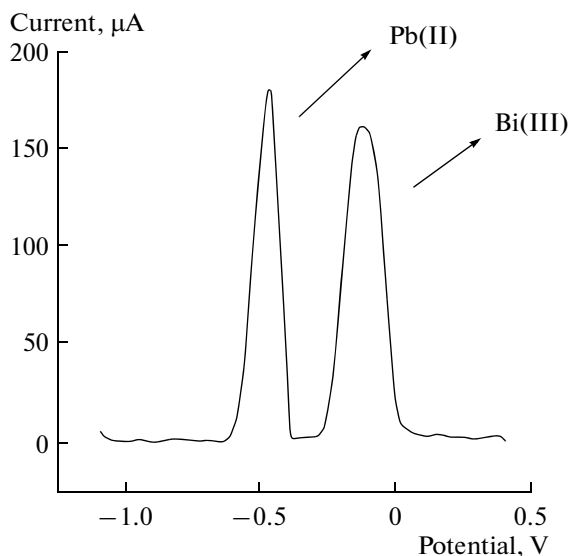
Fig. 2. Linear sweep stripping voltammogram at BiFE potential window from −1.2 to 0.4 V. Experimental conditions: 2 mmol/L Bi(III) deposition time for lead 300 s, pH 5, pulse amplitude (mV) = 50, sample width (ms) = 17, pulse width (ms) = 50 pulse period (ms) = 200.
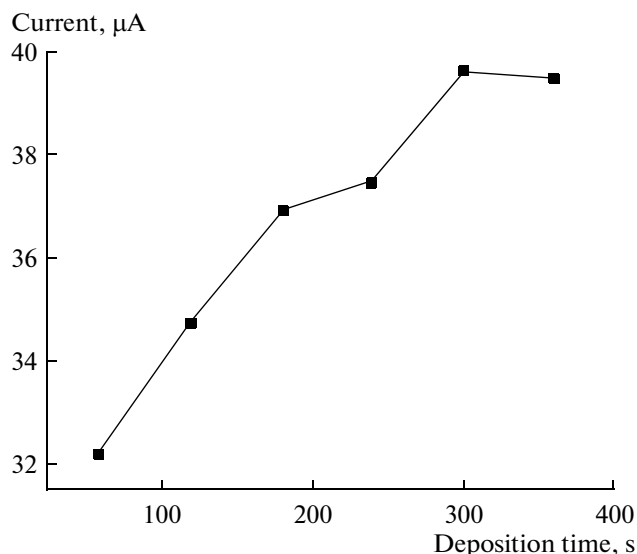

Fig. 3. Effect of deposition time of bismuth film formation upon the differential pulse stripping voltammetric response for 10 μmol/L Pb(II) and at BiFE. Experimental conditions: 2 mmol/L Bi(III) deposition time for lead 300 s, pH 5, pulse amplitude (mV) = 50, sample width (ms) = 17, pulse width (ms) = 50 pulse period (ms) = 200.

increasing bismuth deposition time up to 300 s and remained almost constant at higher deposition times and, additionally, the width of the peak increased at higher deposition times. So, a bismuth deposition time of 300 s was found to offer the best combination between sensitivity and peak sharpness of lead ions. The increase peak current with time was due to increase thickness with increase deposition time. But further increasing deposition time saturation of the film electrode was occurred.

The influence of the bismuth ion concentration on the peak currents of Pb(II) was studied in the range 0.5 mmol/L–2.5 mol/L for a solution containing 10 μmol/L Pb(II) in 0.1 M acetate buffer (pH 5) ex-situ plating as shown in the Fig. 4. The concentration of the Bi(III) ion influenced the thickness of the Bi film, whereas the thickness of the film did not affect the peak position of lead.

For Bi(III) concentrations lower than 2 mmol/L, the heights of the Pb peaks were affected by the Bi(III) concentrations. However, for Bi(III) concentrations higher than 2 mmol/L, the Pb, peaks decreased with increasing bismuth film thickness this is due to cracking of the film at higher concentration. The results revealed that the best combination of sensitivity, peak sharpness and background current was obtained for Bi(III) concentration of 2 mmol/L ex-situ deposited.

Effect of pH of the Supporting Electrolyte

The effect of pH of deposition/measurement solution upon the ex-situ bismuth film formation and

anodic stripping voltammetric performance of the BiFE, examined in buffered solutions containing 10 μmol/L Pb(II) is shown in Fig. 5. As clearly evident, the optimum performance (highest stripping peak currents) was achieved in the pH range of 4 to 5, while it was only slightly decreased at pH below 4. On
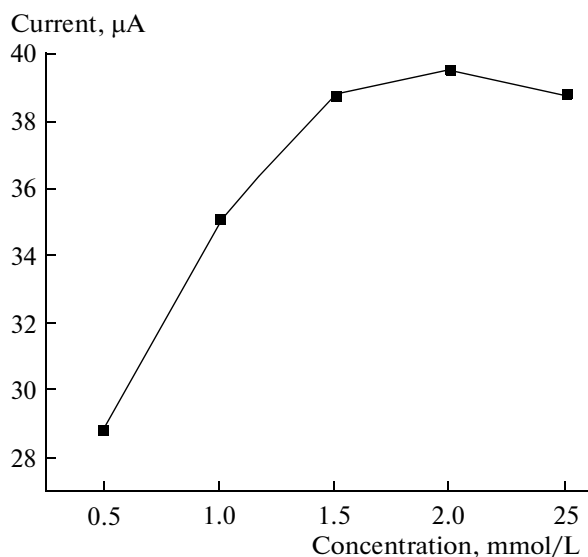

Fig. 4. Effect of concentration of Bi(III) upon the differential pulse stripping voltammetric response 10 μmol/L Pb(II) and at BiFE. Experimental conditions: deposition time(s) = 300 s, pH 5, pulse amplitude (mV) = 50, sample width (ms) = 17, pulse width (ms) = 50 pulse period (ms) = 200, quiet lime (s) = 10.

Current, µA

Fig. 5. Effect of pH upon the differential pulse stripping voltammetric response to 100 µmol/L Pb(II) and at BiFE. Experimental conditions: 2 mmol/L Bi(III) deposition time(s) 300 s, pulse amplitude (mV) = 50, sample width (ms) = 17, pulse width (ms) = 50 pulse period (ms) = 200, quiet time (s) = 10.
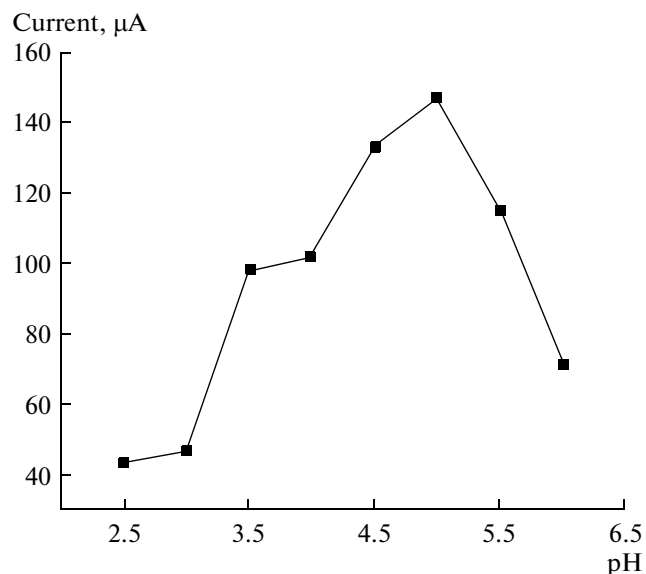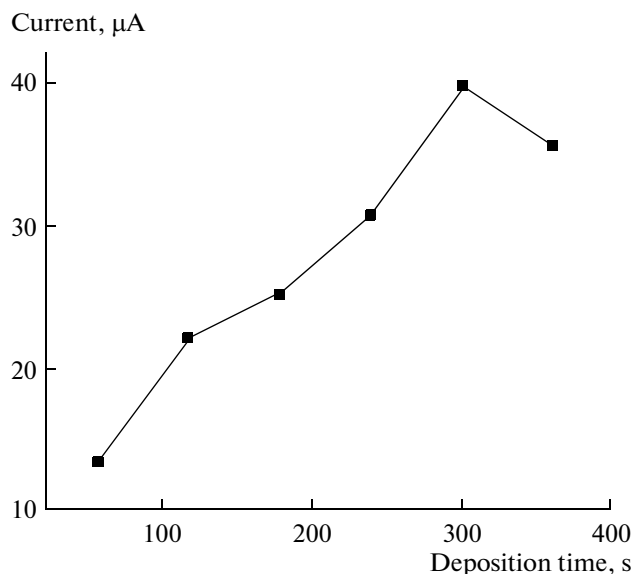
Current, µA

Fig. 6. Effect of disposition time upon the differential pulse stripping voltammetric response to 10 µmol/L Pb(II) and at BiFE. Experimental conditions: 2 mmol/L Bi(III), pH 5, pulse amplitude (mV) = 50, sample width (ms) = 17, pulse width (ms) = 50 pulse period (ms) = 200, quiet time(s) = 10.

the other hand, at higher pHs, a fast decrease of stripping voltammelric signals for lead ion was observed indicating that the use of ex-situ prepared BiFE at pH's above 5 is unfavorable, most probably due to a prevailing effect of Bi(III) hydrolysis in acetate medium.

$$Bi^{3+} + 3H_2O \rightarrow Bi(OH)_3\downarrow + 3H^+.$$

Effect of Deposition Time of Pb

During the deposition step, the potential applied to the BiFE electrode is held at a constant deposition potential at which the lead ions are reduced to lead metal for a pre-determined time period (deposition time). The initial potential of the stripping step is used as the deposition potential. The metallic lead within Bi film (Bi (Pb^0)) like amalgamates on mercury electrode was formed as a result of the reduction of Pb(II) on Bi film modified electrode [37]. The efficiency of the deposition can be increased by stirring the solution. After the deposition step, the stirring was stopped, and the system is allowed to reach equilibrium. This is the quiet time, which was typically 10 s.

During the stripping step, the applied potential was scanned in a positive direction, and the lead in the BiFE electrode is oxidized back to lead ions in solution; that is, the lead is "stripped" from the electrode. The potential at which the stripping occurs is related to the redox potential of the analyte, and the magnitude of the current of the stripping peak is proportional to the concentration of the analyte in the BiFE elec-

trode. Since the concentration of the analyte in the electrode is related to its concentration in solution, the stripping peak current is therefore proportional to the solution concentration.

The effect of deposition time on the lead peak current was studied within the range 60−360 s in solutions containing 10 µmol/L Pb(II) as illustrated in Fig. 6. It is seen that the peak current of Pb(II) increases linearly as deposition time increases, up to 300 s. At longer times the peak current became almost constant, probably due to saturation of the film electrode. For succeeding studies, deposition time of 300 s was chosen.

Effect of Instrumental Parameters

Potential window. BiFE exhibit a wider negative potential window than carbon film electrodes in the negative range, but cannot be used in the positive potential region due to re-oxidation of Bi itself [36]. In order to efficiently coat the glassy carbon support with metallic bismuth, a plating potential more negative than −0.24 V should be applied. Already after 5 s the bismuth coating achieves 30% of the total mass. However, the value of the plating potential influences not only the duration of the film deposition process but also the deposit microstructure: i.e., size and distribution of crystallites [36]. The effect of the pre-concentration potential on the lead peak height was studied in the range −0.6 to −1.1 V. But there was no significant change in peak current in this range (Fig. 7). Due to sharpness of the peak current at −0.8 V it was used throughout the experiment.
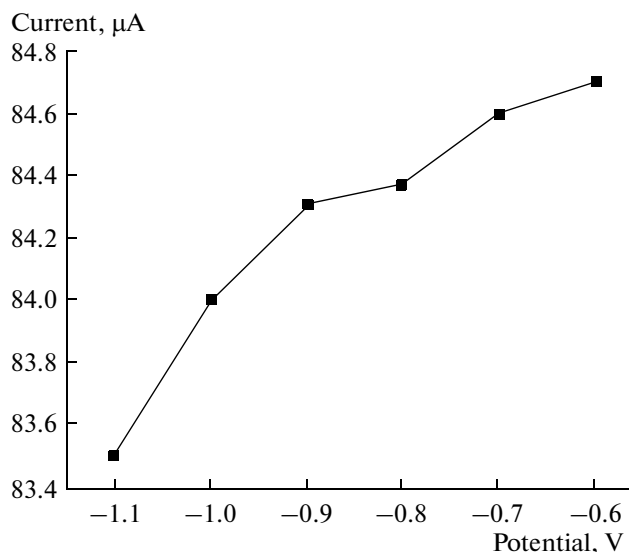
Fig. 7. Effect deposition potential of lead upon the differential pulse stripping voltammetric response to 10 μmol/L Pb(II) and at BiFE. Experimental conditions: 2 mmol/L Bi(III) deposition time(s) 300 s, pH 5, pulse amplitude of 100 mV, sample width (ms) = 17, pulse width (ms) = 50 pulse period (ms) = 200, quiet time(s) = 10.
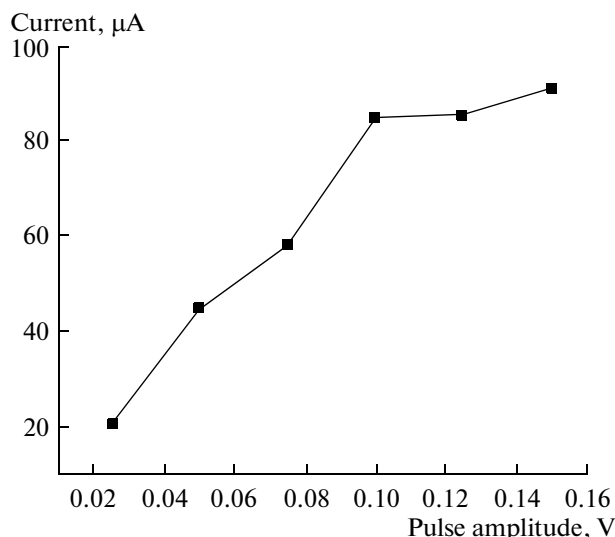

Fig. 8. Effect of pulse amplitude upon the differential pulse stripping voltammetric response to 10 μmol/L Pb(II) and at BiFE. Experimental conditions: 2 mmol/L Bi(III) deposition time(s) 300 s, pH 5, sample width (ms) = 17, pulse width (ms) = 50 pulse period (ms) = 200, quiet time (s) = 10.

Effect of Pulse Amplitude

The effect of pulse amplitude on current response was studied by varying the pulse amplitude from 25–100 mV at scan rate of 50 mV/s. The result shows as the amplitude increased from 25–150 mV the peak current was also increased. But peak currents above 150 mV were not reproducible and sharp as a result 100 mV was taken throughout the experiment (Fig. 8).

Effect of Pulse Width

The effect of pulse width on current response was also studied by varying the pulse width from 50–100 mV at scan rate of 50 mV/s. The result showed (Fig. 9) that, as the pulse width increased from 50–100 ms the peak current was decreased. Pulse width of 50 ms was taken throughout the experiment. In pulse voltammetry, as the pulse width increases, the peak or limiting current decreases. This agrees with the theoretical equations. For normal pulse and different pulse, square wave techniques, the limiting or peak current decreases linearly as square root of pulse time increases.

OPTIMAL EXPERIMENTAL CONDITIONS

Interferences

Some ions were tested to evaluate the possible interference with the determination of Pb(II) ion at bismuth modified glassy carbon electrode. The results suggest that 1000-fold Mn^{2+}, Mg^{2+}, Ba^{2+} and Ag^+ (concentration ratios) had no significant influence on the signal of 10^{-5} mol L^{-1} Pb(II) ion. It was also found that 10-fold Ni^{2+}, Zn^{2+}, Sn^{2+}, and Fe^{3+}, 100-fold Co^{2+} and 1000-fold Cd^{2+} produced negligible contributions to the signal of Pb(II) ion but 1 : 1 ratio of Hg^{2+}, Cu^{2+} and Cr^{3+} affect the peak current by 6.9, 21.7 and 4.6% respectively (Table 2).
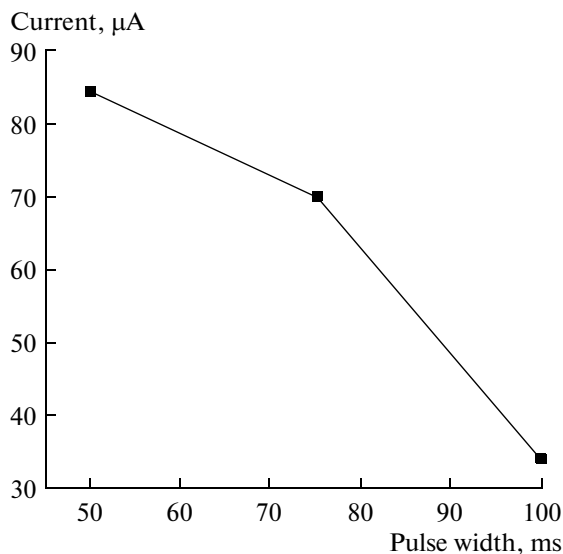

Fig. 9. Effect of pulse width of upon the differential pulse stripping voltammetric response to 10 μmol/L Pb(II) and at BiFE. Experimental conditions: 2 mmol/L Bi(III) deposition time(s) 300 s, pH 5, pulse amplitude of 100 mV, sample width (ms) = 17, pulse period (ms) = 200, quiet time(s) = 10.

Table 1. Summary of optimized condition for detection of lead(II) ion

Optimized Parameter	Optimum value	Studied Range
Deposition time for lead detection	300 s	60–360 s
Deposition time for BiFE formation	300 s	60–360 s
pH	5	2.5–6
Pulse width	50 ms	50–100 ms
Bi ion concentration	2 mol/L	0.5–2.5 mol/L
Potential window	−800−(−300 mV)	−800−(−300 mV)
Pulse amplitude	100 mV	25–150 mV

Table 2. Change in DPASV peak current of 1×10^{-5} mol/L Pb(II) ion in presence of other ions

Interfering ion	Compound	Concentration, mol/L	Change in peak current, %
Cu^{2+}	$Cu(NO_3)_2 \cdot 3H_2O$	1.0×10^{-5}	−21.7
Hg^{2+}	$Hg(NO_3)_2 \cdot H_2O$	1.0×10^{-5}	−6.9
Cr^{3+}	$Cr(NO_3)_3$	1.0×10^{-5}	−4.6
Co^{2+}	$CoCl_2 \cdot 6H_2O$	1.0×10^{-3}	−5.4
Cd^{2+}	$CdCl_2 \cdot H_2O$	1.0×10^{-2}	−6.9
Mn^{2+}	$MnCl_2$	1.0×10^{-2}	0
Fe^{3+}	$Fe_2(SO_4)_3$	1×10^{-4}	−9
Sn^{2+}	$SnCl_2 \cdot 2H_2O$	1×10^{-4}	1
Ba^{2+}	$BaCl_2 \cdot 2H_2O$	1.0×10^{-2}	0
Ag^+	$AgNO_3$	1.0×10^{-2}	0
Mg^{2+}	$MgHPO_4 \cdot 3H_2O$	1.0×10^{-2}	0
Zn^{2+}	$ZnCl_2$	1×10^{-4}	−6.1
Ni^{2+}	$Ni(NO_3)_2 \cdot 6H_2O$	1×10^{-4}	−9.2

Calibration Curve, Detection Limit and Precision

Using the optimum differential pulse anodic stripping voltammetery parameter described the calibration curve for the determination of lead concentration was established. Three linear calibration plots in the range 7.5 nmol/L to 0.1 µmol/L, 0.25 to 1 µmol/L, 2.5 to 12.5 µmol/L with regression coefficients of 0.991, 0.986 and 0.978 respectively were obtained as shown in Figs. 10a, 10b and 10c. The calibration curves exhibits good linearity with the concentration in the given ranges. As it is indicated using the numerical value regression coefficient (R) for this study the data set show good linear fit because the value of (R) approaching to positive one, since R can take value in the range of $-1 \leq R \leq +1$. The theoretical detection limit for lead was calculated to be 5.25 nmol/L utilizing a 5 minutes deposition time and sensitivity 83.97 A L/mol from equation $Y = 83.967X + 0.371$.

Figures 11a, 11b depicting bismuth film glassy carbon electrode sensitivity is higher than bare glass carbon electrode.

Detection of Lead in Real Sample and Reproducibility

The usefulness of the present method evaluated by examining the analysis of Pb(II) ion in potassium hydrogen phosphate (certified reference material containing 0.001% lead). The concentration of lead(II) ion in 1 g potassium hydrogen phosphate in 100 mL was 4.83×10^{-8} mol/L. The concentration of lead(II) ion potassium hydrogen phosphate was determined from the equation of calibration curve $Y = 83.967X + 0.371$ (Fig. 10a) and hence the concentration of lead ion is equal to 4.38×10^{-8} mol/L.

The reproducibility of DPASV at a particular carbon film electrode was determined by forming a bismuth film and applying it to the anodic stripping analysis of the lead, repealing the process six times. The
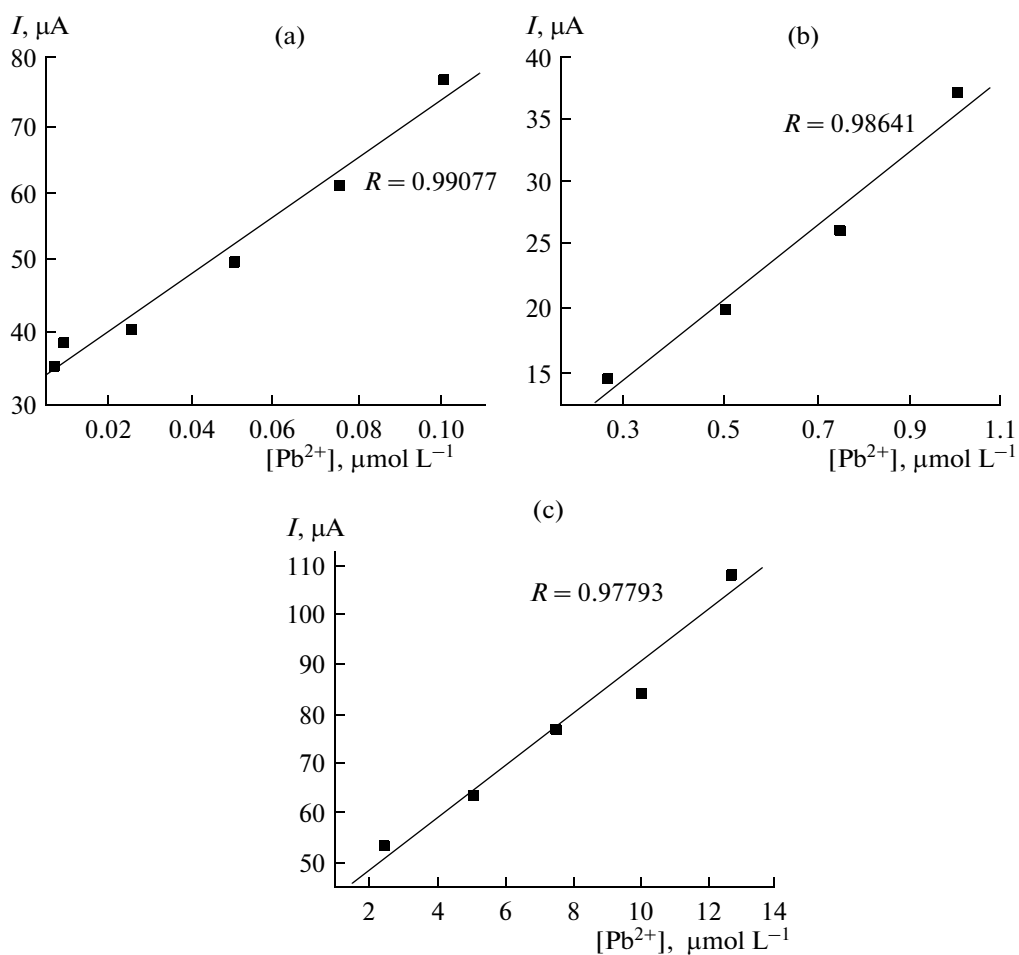
Fig. 10. Calibration graph concentration of lead (II) ion (a): 7.5 nmol/L to 0.1 µmol/L; (b): 0.25 to 1 µmol/L; (c): 2.5 to 12.5 µmol/L.
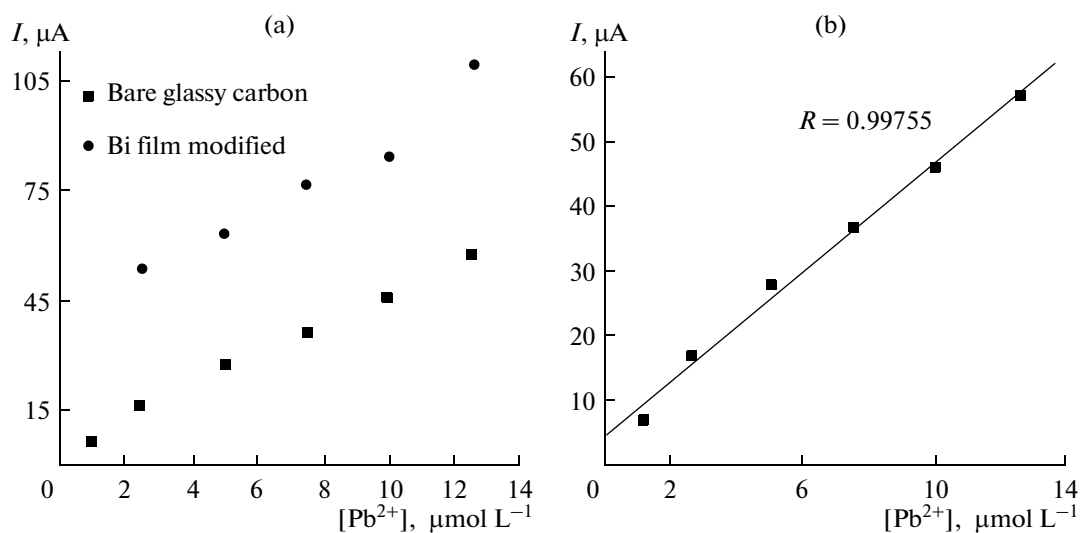

Fig. 11. (a) Comparison for bare and Bismuth modified glassy carbon electrode. (b) Calibration graph concentration of lead(II) ion at bare glassy carbon electrode from 2.5 to 12.5 µmol/L.

results mean peak current obtained was 2.26 μA with a range of 2.18−2.34 μA at 2.5×10^{-8} mol/L and relative standard deviation 2.5%. The 95% confidence level was 2.26 ± 0.056.

CONCLUSIONS

The results described above demonstrate the suitability of bismuth film electrodes for differential pulse anodic stripping voltammetric detection of lead(II) ion. The proposed method is inexpensive and fast relative to spectroscopic method. The theoretical detection limit for lead was calculated to be 5.25 mmol/L utilizing a 5 min deposition time and sensitivity 83.97 L A/mol. The present method offered a promising characteristic of good sensitivity and relatively free from coexisting ions in excess amounts. But there were interferences like Cu^{2+}, Hg^{2+} and Cr^{3+} which can inhibit to lower the detection limit. Acceptable agreement was found between the results obtained and the values of certified reference material. This is promising for future application of this method for real sample analysis.

ACKNOWLEDGMENTS

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