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Detection of lead ions in picomolar concentration range using underpotential deposition on silver nanoparticles-deposited glassy carbon electrodes

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ABSTRACT

The efficacy of silver-deposited glassy carbon electrode for the determination of lead ions at the sub-nanomolar concentration ranges is investigated. The silver nanoparticles are electrodeposited on glassy carbon electrode using chronoamperometry and the electrode surface is characterized using SEM. Lead ions are detected in the region of underpotential deposition. The analysis is performed in square wave mode in the stripping voltammetry without the removal of oxygen. The detection limit of 10 pM has been obtained with a constant potential of −0.7 V during the electrodeposition step for a period of 50 s. The interference of surfactants in the detection of lead ions is also studied.

1. Introduction

Anodic stripping voltammetry (ASV) is the most widely used form of stripping analysis in electroanalytical chemistry wherein electrodeposition leads to the pre-concentration of metal ions [1]. The deposition potential is made more anodic than the equilibrium potential of the depositing species. The metal ions are brought to the electrode by convection by either rotating the electrode or stirring the solution. However, the major drawbacks in ASV are the background correction and the need to eliminate the interference from oxygen. The SWASV is a more sensitive method of detection than the classical ASV since in SWASV there is a decrease in the effects of background currents [2]. Further, the SWASV can be used for the detection of metal ions even without the removal of oxygen. This feature makes SWASV a more convenient technique than ASV.

Among the detection of various metal ions in analytical chemistry that of lead ions is more crucial because of its detrimental effects on the environment. An earlier analysis for lead ions led to the detection limit of 2 pM with the help of mercury electrodes [3] and 8 pM using mercury-coated glassy carbon electrodes [4]. Since mercury is toxic, it is customary to extend the stripping voltammetry to solid electrodes such as glassy carbon [5], bismuth-coated glassy carbon [6,7], silver electrode [8], renovated silver ring electrode [9], platinum mesoporous microelectrode using the anodic alumina membrane [10], etc. Recently Kirowa-Eisner et al. [11–13] used the silver RDE electrode for the detection of lead ions wherein the low limit of detection of lead ions of 50 pM is achieved by using the subtractive anodic stripping voltammetry.

Nanomaterials have diverse applications in electrochemical supercapacitors [14], biosensors [15], electroanalysis [16], etc. Among various synthetic routes for nanomaterials, mention may be made of the following: (a) chemical method (gold nanoparticles using thiol [17]); (b) radiation using UV or electron beam (gold nanoparticles fabrication using two beam interference [18]) and (c) electrochemical methods (silver nanoparticles using PVP [19]). In recent times, electrodes modified using nanoparticles have been employed for quantitative estimation of (i) As(III) ions on Au-nanoparticle modified glassy carbon electrode [20]; (ii) copper(II) ions on Au-nanoparticle modified gold ultamicroelectrode [21]. Furthermore, Au/Ag bimetallic nanoparticles modified glassy carbon electrodes have been employed for the reduction of benzyl chloride [22]. The present study involves the use of nanoparticle modified electrode for the detection of lead ions exploiting the concept of the UPD of metals.

It is of interest to investigate whether the electrode surfaces wherein nanoparticles are deposited electrochemically can be employed for detection of metal ions in sub-nanomolar range. In this context, the UPD phenomena has not been sufficiently exploited in qualitative and quantitative analysis. The use of UPD in anodic stripping voltammetry was first suggested by Kirowa-Eisner et al. [8,11–13]. UPD [23] refers to the process of formation of a

Abbreviations: SEM, scanning electron microscope; SWASV, square wave anodic stripping voltammetry; UV, ultraviolet; UPD, underpotential deposition; PVP, polyvinyl pyrollidone.

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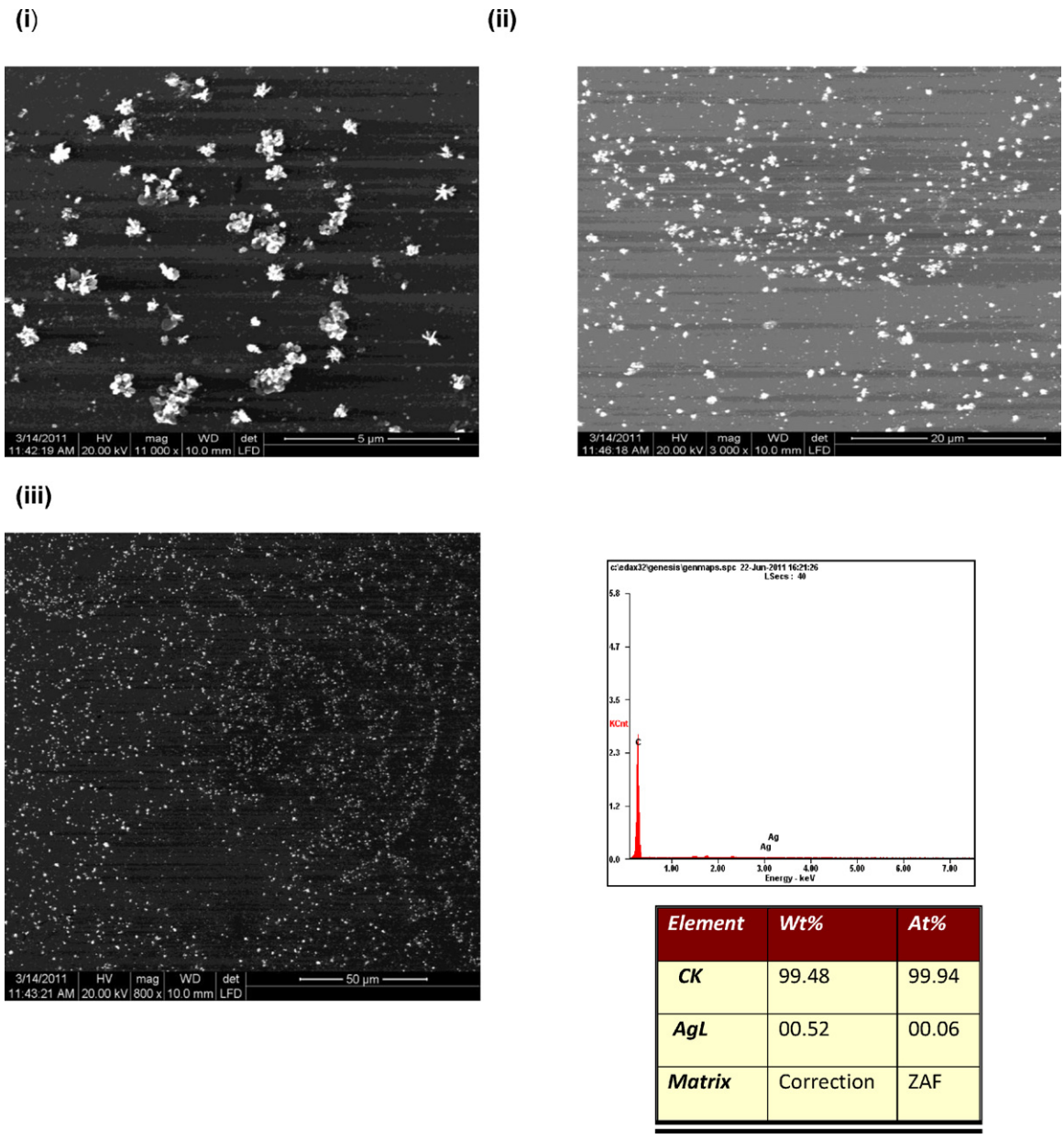

Fig. 1. SEM images of the Ag-deposited glassy carbon surface at different magnifications (i) 11,000 (ii) 3000 (iii) 800.

monolayer on foreign metal substrates at a potential more positive than Nernst equilibrium potential. The work function difference between the depositing species and the substrate should be ~0.5 eV for UPD to occur. The UPD of lead on gold and silver electrodes has been investigated extensively [24]. The thermodynamic analysis of UPD [25] yields new insights regarding various energetics involved in the process while quantum chemical studies delineate the role of electronic energy states in dictating the UPD shift. Since UPD refers to a controlled formation of (sub)monolayer coverages, it is anticipated that UPD will result in achieving extremely low detection levels of the analyte [26]. This significant feature is however absent if bulk deposition is resorted to.

The objectives of this communication are (i) to employ SWASV on silver nanoparticle-modified glassy carbon electrode for the detection of lead ions; (ii) to demonstrate the feasibility of UPD phenomena in quantitative analysis of metal ions at ppb levels and (iii) to analyse the interference caused by the surfactants sodium dodecyl sulphate (SDS) and cetyltrimethylammoniumbromide (CTAB).

2. Experiment

2.1. Chemicals

Potassium nitrate (>98%), PVP, lead nitrate (>99%) and nitric acid suprapur from Merck (USA) were employed as received. Silver nitrate (>99%) from Finar reagents was employed without further purification. The triple distilled water was employed for preparing all the solutions. The temperature was maintained as 25 °C throughout.

2.2. Electrochemical measurements

Chronoamperometry, cyclic voltammery and square wave anodic stripping voltammetry were performed using a conventional three-electrode cell with IVIUM compact stat (the Netherlands) while the electrodes were procured from the CH Instruments, USA. The glassy carbon (GC) electrode (2 mm

diameter) is used as the working electrode while Ag/AgCl (1 M KCl) and platinum wire served as the reference and counter electrode respectively. For preparing the Ag-modified GC electrode, silver wire is used as reference electrode. The potential of the silver wire in 0.05 M $AgNO_3$ solution is measured as 0.286 V with respect to Ag/AgCl/(1 M KCl) reference electrode.

2.3. SEM imaging

SEM images and energy dispersive X-ray analysis (EDAX) were taken using FEI Quanta FEG 200 at an acceleration voltage of 10–20 kV in high vacuum mode.

2.4. Electrode preparation

The glassy carbon electrode was cleaned using alumina powders of various grades and sonicated for 15 min in triply distilled water. Initially, the deposition of silver onto the glassy carbon electrode is carried out in a solution containing 3 ml of PVP (5 g l^{-1}), 0.5 ml of 5 mM $AgNO_3$ and 1.5 ml of 0.1 M KNO_3. The silver particles were deposited at a constant potential of −0.2 V (vs. Ag wire calibrated with respect to Ag/AgCl reference electrode) for 10 s using chronoamperometry. The potential of the Ag wire electrode when dipped in a solution of 5 mM of $AgNO_3$ is measured as 0.286 V with respect to Ag/AgCl/(1 M KCl) reference electrode. The silver-deposited GC electrode is repeatedly washed with distilled water in order to remove any adsorbed species. This constitutes the working electrode for detection of sub-nanomolar quantities of lead.

2.5. SWASV procedure

The SWASV was performed in a 5 ml cell containing 10 mM of HNO_3. For the pre-concentration step carried out with constant stirring, the potential is kept at −0.7 V (vs. Ag/AgCl) while the deposition time ranged from 30 s to 150 s. The square wave voltammogram was obtained using the pulse amplitude as 25 mV, pulse width as 5 mV, the frequency being 15 Hz.

3. Results and discussion

While the detection of lead using SWASV is not in itself new, what demarcates the present analysis is in exploiting the concept of UPD in conjunction with the silver-nanoparticles coated GC. The deposition of nanosized silver atoms is expected to enhance the sensitivity; furthermore, since the UPD of lead does not occur on GC electrodes in contrast to its occurrence on bare Ag, the Ag-coated GC electrode is a suitable surface for estimating ppb levels of any species if the latter exhibits UPD.

3.1. SEM analysis

The SEM images of Ag-deposited glassy carbon electrode are depicted in Fig. 1; these reveal silver nanoparticles of size ~100 nm with uniform coverage. The presence of silver on glassy carbon has been confirmed by energy dispersive X-ray analysis (EDAX) wherein the peak corresponding to Ag is noticed. The percentage of silver is very low due to the charging of the electrode during the SEM analysis which inhibits a quantitative measurement of the EDAX analysis. The electrode prepared in this method is stable and is found to be suitable for a large number of quantitative measurements. The silver nanoparticle formed on the electrode is stabilized by PVP which prevents the aggregation of silver particles consequently yielding nanostructures. The lone pair of electrons present in oxygen and nitrogen of PVP are donated to the two sp orbitals of silver ions to form a complex [27]. The next step is the reduction of silver ions followed by deposition on the electrode.

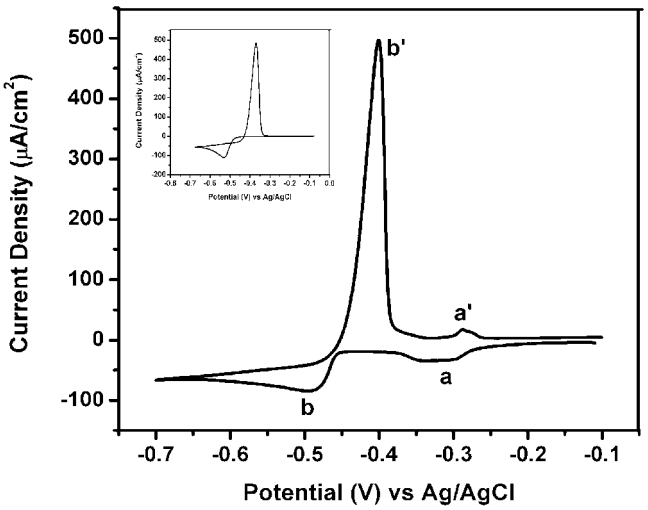

Fig. 2. Cyclic voltammogram of the silver-deposited glassy carbon electrode in the solution consisting of 2 mM $PbNO_3$ and 10 mM of HNO_3 at a scan rate of 50 mV/s. The Inset depicts the Cyclic voltammogram of deposition of lead in a solution of 10 mM HNO_3 and 2 mM of $PbNO_3$ on the *bare glassy carbon electrode* at scan rate of 50 mV/s.

The large polyvinyl group causes steric hindrance and the chemical bond between PVP and silver prevents aggregation of the particles.

3.2. Cyclic voltammetry

Fig. 2 depicts the cyclic voltammogram of the underpotential deposition of lead on silver modified glassy carbon electrode. The peaks appearing at −0.33 V and −0.30 V (labeled respectively as a and a′) indicate the UPD and the corresponding stripping peak of lead. The peaks appearing at −0.48 V and at −0.42 V (denoted respectively as b and b′) correspond to the bulk deposition and stripping peak of lead. The UPD shift obtained here on Ag-nanoparticle modified electrode is 0.16 V which is identical with UPD shift for Pb on Ag [23] thus implying that the presence of nanoparticles does not significantly alter the UPD shift of the bulk substrate. As seen from the inset of Fig. 2 pertaining to the cyclic voltammogram of lead ions on GC, UPD does not occur on bare GC surface. On the other hand, the UPD is observed if the GC surface is modified by the presence of silver nanoparticles.

The adsorbed amount of lead deposited on the electrode per unit area (calculated from the charge of the stripping peak) can be evaluated using [21]:

$$\Gamma = \frac{Q}{nFA}$$

where Q denotes the charge corresponding the stripping peak, A being the area of the electrode (0.2826 cm^2), n is the number of electrons involved equal to 2. The charge corresponding to the UPD stripping peak is calculated from Fig. 2 as 83.2 μC cm^{-2}. The amount of adsorbed atoms per unit area is 0.234×10^{-9} mol cm^{-2}. Assuming a square lattice of sites with nearest neighbour distance of ~3 Å, the total amount of sites available for Pb^{2+} ions is 1.84×10^{-9} mol cm^{-2}, thus yielding an approximate surface coverage of ~0.13.

3.3. Detection of lead using SWASV

The SWASV is a convenient technique for detection of lead without the necessity for removing oxygen [2]. The presence of acids is a pre-requisite in the analysis of Pb^{2+} ions and among various acids investigated here, HNO_3 with a concentration of 10 mM exhibited a large magnitude of the peak height with the occurrence of sharp

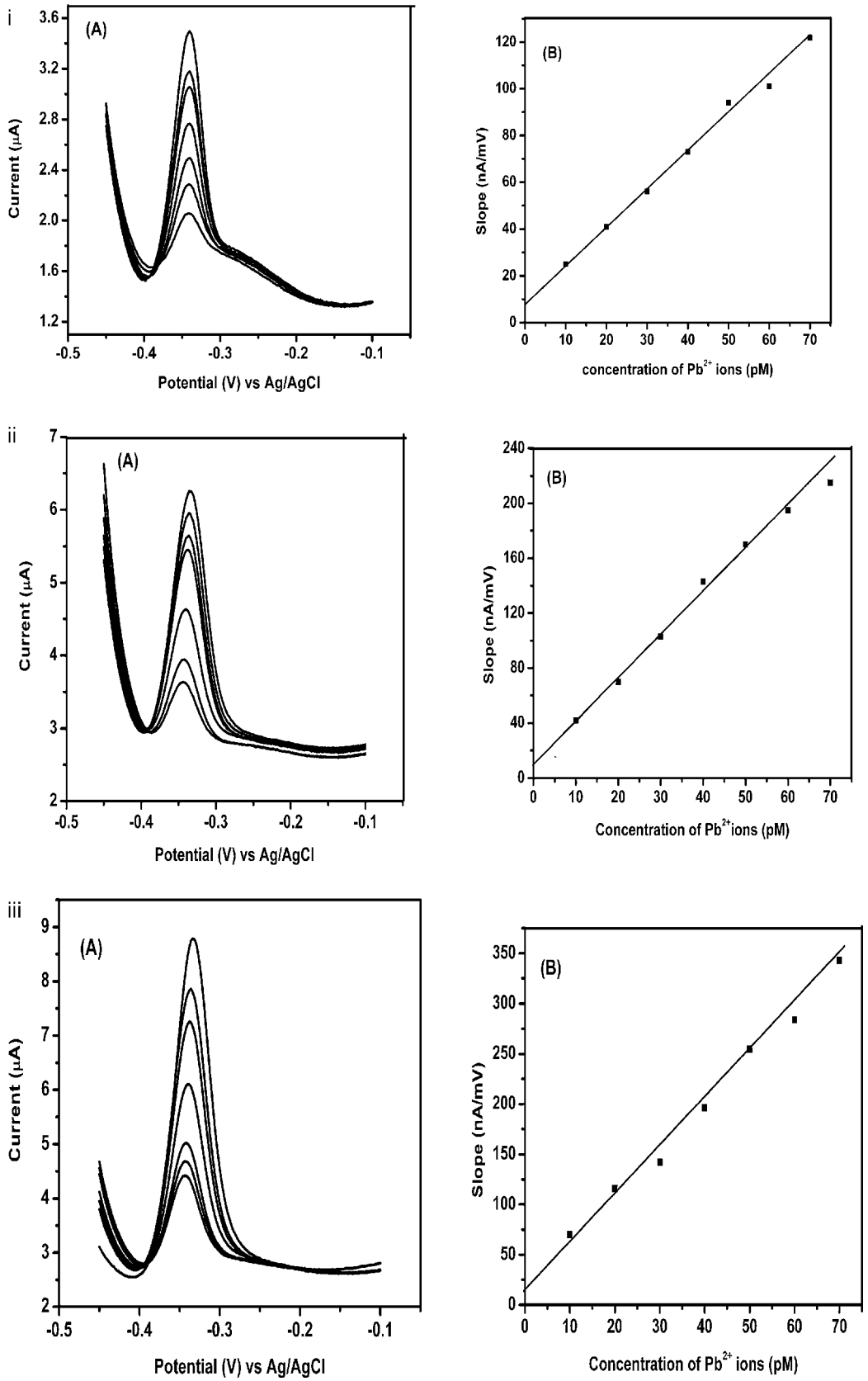

Fig. 3. (A) Square wave anodic stripping voltammetry of the silver modified glassy carbon electrode at various concentrations of Pb^{2+} ions (0, 10, 20, 30, 40, 50, 60, 70 pM) at different deposition times and (B) the corresponding calibration plots. (i) 50 s; (ii) 100 s; (iii) 150 s.

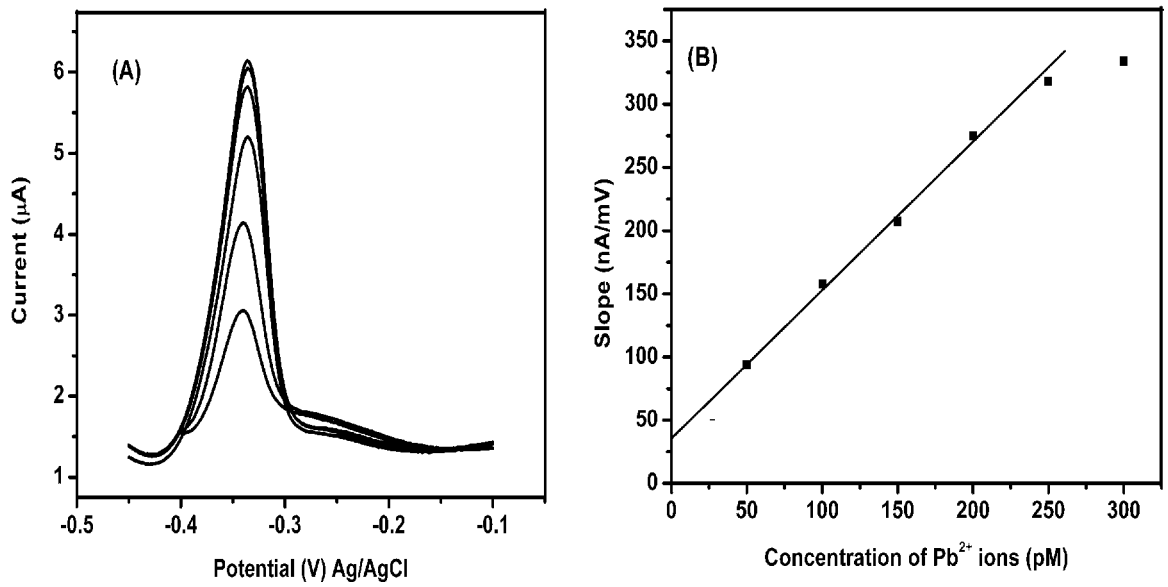

Fig. 4. (A) Square wave anodic stripping voltammetry of Pb^{2+} ions at different concentrations (50, 100, 150, 200, 250, 300 pM) at the silver modified glassy carbon electrode at a deposition time of 50 s and (B) the corresponding calibration plots.

peaks. As mentioned earlier, the detection of trace amount of lead is due to the UPD occurring on silver-nanoparticles coated GC. Since the dissolution of Ag starts at ~0.1 V vs. Ag/AgCl/(1 M KCl), negative potential ranges need to be chosen. An optimum value of −0.7 V ensures that the concentration of oxygen becomes low at the vicinity of the electrode during the pre-concentration step so that interference from oxygen is avoided.

The mass transport of ions in SWASV customarily arises from convection since the deposition current is related to the flux of the metal ions at the surface. The convection of ions in the solution towards the electrode is brought about either by rotating the electrode or by stirring the solution. Here, the stirring of the solution is carried out using a magnetic stirrer at a chosen rate for each addition as well as for different deposition time. A rest time of 10 s is provided in order to obtain a uniform diffusion layer.

The quantitative detection of any species in stripping voltammetry can be accomplished by employing the following strategies viz. using (i) the peak current; (ii) the charge corresponding to the stripping peak and (iii) the sum of slope of the two inflection points of the curve. Since the base line is asymmetric, the peak current method can yield inaccuracies while the method involving the charge corresponding to the stripping suffers from background interferences. Hence the method (iii) using two inflection points is especially convenient for constructing the calibration curve.

Fig. 3 shows the stripping voltammogram pertaining to different concentrations of Pb^{2+} ions. As anticipated, the peak current increases with concentration of the analyte for a given deposition time. The peak width is narrow due to employing low frequencies in the square wave mode, while the peak potential is independent of concentration. The latter behavior is attributed to the detection at UPD potential. The linearity between concentration and the SWASV analytical signal is obeyed from 10 pM to 0.3 nM. Fig. 4 depicts SWASV for concentrations of lead ions ranging from 50 pM to 300 pM. The lowest detection limit of 10 pM of lead is achieved which corresponds to 16.6 ppb. The experiments are performed at different deposition times and their corresponding calibration plot is determined. A linear relationship between the analytical signal and deposition time has been obtained for the tested range of 50–150 s. As the deposition time increases from 50 s to 100 s, the value of the analytical signal also doubles. An analogous increase is observed when the deposition time is increased from 50 s to 150 s. The correlation coefficient of the relationship at different deposition times are 0.9970 (50 s), 0.9956 (100 s), 0.9962 (150 s). However, for the deposition time of 50 s, the slope of the analytical signal increases six times despite the increase in concentration by seven times. This may be due to the surface coverage of silver nanoparticles on the glassy carbon electrode which is not commensurate with the deposition time.

It should be emphasized that a small background current is noticed despite the absence of lead ions in the solution. This arises due to the trace level of impurities present in the electrolyte and was confirmed by carrying out the analysis with progressive increase in purity of the electrolyte. In fact, the purity of the electrolyte may even be inferred by such studies. The short deposition time of 50 s is found to be the optimum condition in view of the well-defined peak. The linear regime gets altered if the deposition time is increased significantly. Unlike customary silver electrodes, these nanoparticle modified electrodes require only a short deposition time for detection of lead ions.

3.4. Interference of surfactants

The electrochemical reactions are in general influenced by the presence of surfactants; in particular, their presence leads to the vanishing of the stripping peak [9] in stripping voltammetry while in polarographic techniques, they suppress the polarographic maxima [28]. Hence it is imperative to investigate whether the detection of lead ions will be influenced by the presence of surfactants. For this purpose, two commonly known surfactants viz. sodium dodecyl sulphate (SDS) and cetyltrimethylammonium-bromide (CTAB) are considered. Different concentrations of each surfactant are added to the analyte solution containing lead ions. The SWASV is carried out by keeping the concentration of lead ions constant while increasing that of the surfactants. Fig. 5 depicts the influence of surfactants on the peak current wherein it can be seen that surfactants have no significant effect until 20 μM concentration of each addition of the surfactant when the concentration of Pb^{2+} is 10 nM. Upon further addition of the surfactant, the peak current decreases and finally the stripping peak vanishes. The inset of Fig. 5 indicates the increase in the peak current with increase in the concentration of lead ions in the absence of surfactant. However, this increase is not observed in the presence of surfactant

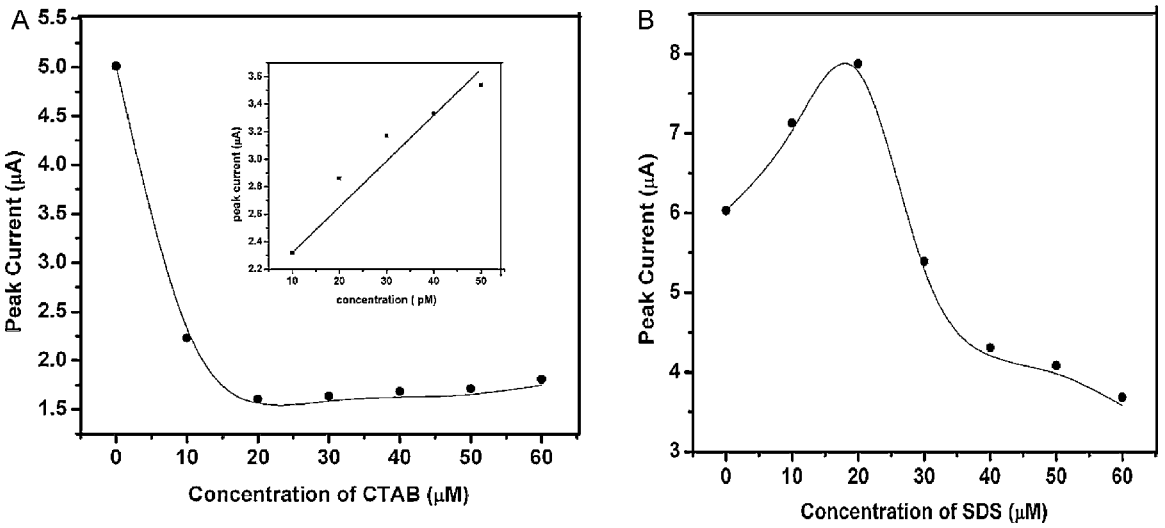

Fig. 5. Effect of concentration of (A) cetyltrimethylammonium bromide and (B) sodium dodecyl sulphate on the stripping peak current in a solution containing 10 mM of HNO_3 and 10 nM of Pb^{2+} ions. Inset shows the increase of peak current for different concentrations of Pb^{2+} ions (10–50 pM) without the presence of the surfactants. The points denote the experimental data while lines are drawn as guides to the eye.

Table 1
Prediction of concentration of Pb^{2+} using the present method in a given sample.

Amount of Pb^{2+} present (ppb)	Amount of Pb^{2+} predicted using SWASV (ppb)
82.082	80.259 ± 1.33
165.60	165.64 ± 5.62
414.012	410.147 ± 6.32

on account of its interference. The surfactants tend to block the active sites on the electrode thereby hindering the analysis. Among the above two surfactants, CTAB has a more pronounced interfering effect than SDS for detection of lead. This may be due to its slower rate of adsorption of SDS in comparison with that of CTAB [29].

3.5. Prediction of concentrations of lead ions

The proposed method is subjected to tests for unknown concentrations of lead ions. The amount of lead present is found from the calibration plot performed earlier. The amount of lead actually present and experimentally predicted is provided in Table 1

In order to confirm the reliability and reproducibility, three different concentrations (ranging from low to high) are considered. The amount present is predicted experimentally using SWASV and subsequently calculating the slope at the inflection point and determining the concentration corresponding to the slope from the calibration plot. Each experiment has been performed repeatedly and the results were reproducible with standard deviations being not significant.

4. Summary

The concept of UPD is exploited for detection of lead ions in picomolar to nanomolar range using silver-modified glassy carbon electrode with the help of square wave anodic stripping voltammetry. The calibration of the SWASV curve is constructed from the derivative of the inflection point at both the ascending and descending part of the stripping peak. The lowest limit of detection of 10 pM is obtained and the surfactants CTAB and SDS do not interfere in the detection when present in a concentration range of 1–10 μM.

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