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Electroanalytical method for determination of mercury (II) by natural phosphate modified carbon paste electrode: analytical application in juice apple

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ABSTRACT

The electrochemical determination of Hg(II) at trace level using Natural Phosphate modified Carbon Paste Electrode (NP-CPE) is described. The NP-CPE electrodes were then applied to determine low Hg(II) concentrations using Cyclic Voltammetry (CV). The NP-CPE electrodes provided significantly improved performances in Hg(II) determination. The detection the mercury ion with high sensitivity and good values of relative standard deviation (RSD) in calibration curve. The developed method was applied for the detection of Hg(II) in juice apple.

KEYWORDS

Mercury;
Natural phosphate;
Modified carbon paste electrode;
CV.

INTRODUCTION

Heavy metal ions constitute a major problem with respect to environment and healthiness not only because they are widely distributed in natural systems such as atmosphere, water or soil, but also due to the great hazard they represent towards living organisms[1,2]. Amongst them, Hg and its speciation appear to be one of the highest priority targets since its strong affinity for biological compounds emphasizes its toxicity[3]. Hg(II) compounds, and particularly mono- and dimethylmercury, accumulate in vital organs and tissues and are responsible for chronic diseases, kidney injury, respiratory failure, central nervous system disorders, brain damages, and can even also induce death[4,5]. Thus, Hg(II) analysis, quantification and speciation in the environment is one of the most challenging research field for analytical chemists aiming at environmental survey, and there is an increasing need for systems that deliver rapid and reliable data. Moreover, bioaccumulation phenomena make Hg(II) dangerous even at very low concentration[6-10]. A particular effort has thus to be made in order to enhance the sensitivity and to reduce detection limits of such analytical devices. Many spectroscopic techniques are reported in the literature that offer selectivity and quite good sensitivity with respect to Hg(II) trace determination, such as Cold Vapor Atomic Absorption Spectroscopy (CVAAS), Cold Vapor Atomic Fluorescence Spectroscopy (CVAFS) and Inductively Coupled Plasma Mass Spectrometry (ICP-MS)[11]. Although these techniques allow very low concentrations to be determined, they all involve expensive material and require complicated procedures. Consequently they are not really suitable for in situ or on line and operando analysis. Comparatively, electrochemical sensors are cheap and portable devices with simple procedures and low energy requirement that can be used either in laboratory or for on-site measurements. Many electrochemical techniques are used for Hg(II) determination, such as potentiometry[12], chronopotentiometry[13] and pulsed amperometry[14], the most commonly used being Differential Pulse Voltammetry (DPV)[15,16] and Square Wave Voltammetry (SWV)[17-19]. Moreover, the combination of a preconcentration step like Anodic Stripping Voltammetry (ASV)[20] with those pulsed techniques allows detection limits in the picomolar range to be reached[15,18].

Many working electrode materials have also been tested, such as platinum[21], graphite[22], Glassy Carbon (GC)[16,23,24], carbon paste[25], multi-walled carbon nanotubes[26,27], cylindrical carbon fiber[28] and gold. Because of its strong affinity for Hg that enhances the preconcentration effect during the accumulation step, this latter is the most commonly used electrode material. A rapid glance to the literature offers a good insight of the wide range of such systems that have been reported: Au can be used as a bulk[15,17,29], film[30,31], microwire[18,32], microdisk[33], or microdisk array electrode[34]. Another strategy that is frequently encountered to improve the performances of the electrochemical sensor is to chemically modify electrode: the electroactive surface is then functionalized using either polymers[35,36], organic[37,50,51] or biological compounds[38,39] chosen for their complexing affinity towards Hg(II). During the last two decades, interests have focused on nanoscaled materials and their use in analytical chemistry because of their specific physico-chemical properties for a wide range of applications including electronics, optics, catalysis and biological sensors. Improvements resulting from metal nanoparticles for electroanalysis are numerous: sensing interface roughening, catalytic and conductive properties, and mass transport enhancement[40]. These attractive properties combined to the strong affinity of Au for Hg favoured the appearance of a new kind of electrode modification involving Au nanoparticles (AuNPs)[40,41]. AuNPs can be prepared by chemical synthesis[42,43] or by physical ways such as magneton sputtering, radiolytic and photolytic methods[44,45]. Electrodeposition provides a complementary easy, rapid and cheap alternative[46,47]. Most electrodeposited monometallic AuNPs-based electrodes have been used as gas sensors and for bioanalytical purposes. In comparison their application for ASV of metalloids and trace metals such as As(III) or Hg(II) is less explored[46,48]. To the best of our knowledge, Hg(II) trace determination on such monometallic AuNPs-based electrodes is limited to Gao et al.[49] and more recently to Abollino et al.[48] studies. In both cases AuNPs were electrodeposited by chronoamperometry on Au or GC electrode respectively.

The aim of the work reported here was to investigate the electrochemical properties of Hg(II) on phosphate modified carbon paste electrode as well as the electrochemical characterization of electrodes by cyclic and square wave voltammetric technique.

EXPERIMENTAL

Instrument

All electrochemical experiments were performed by a potentiostat (model PGSTAT 100, Eco Chemie B.V., The Netherlands) interfaced to a personal computer and controlled by voltalab Master 4 software. A three electrode design consisting of a platinum counter electrode, SCE reference electrode and a modified carbon paste working electrode. Prior to any electrochemical measurements the solutions was thoroughly de-gassed with nitrogen (BOC Gases), whilst a continuous flow of the gas was maintained through the electrochemical cell during the experiments. The pH meter (Radiometer Copenhagen, PHM210, Tacussel, French) was used for adjusting pH values.

Analytical procedure

The modified carbon paste electrode was immersed in a cell containing 20mL of c sample to get a chemical accumulation. Meanwhile, the solution was rotated about 600rpm at open circuit. After a desired preconcentration time, the electrode was removed from the preconcentration cell, rinsed with DW and placed in the measurement cell containing the supporting electrolyte (0.1mol L^{-1} Na_2SO_4). The solution was deaerated with nitrogen for 10min. The voltammetric curve was recorded. Potential window of -1 to 1V was for all the voltammetric measurements. The same procedure was carried out in sample analysis and all electrochemical experiments were carried out at room temperature. The cyclic voltammetry was recorded in the range from -1 V to 1 V.

Electrodes synthesis

The working carbon paste electrode was prepared by mixing appropriate weight of natural phosphate with a graphite powder to give an appropriate ratio NP-CP. The whole cell modified carbon paste was subsequently packed firmly into the electrode cavity (0.1256cm^2) and polished to a smooth shiny finish by gently rubbing over an ordinary weighing paper. Electrical contact was established with a bar of carbon. The resulting electrode is hereby denoted as NP-CPE. The carbon paste electrode (CPE) alone was prepared in a similar way.

RESULTS AND DISCUSSION

Cyclic Voltammetry behavior of Hg(II)

Figure 1 shows a cyclic voltammograms (CV) in the potential range -1 V to 1 V recorded for natural phosphate modified carbon paste electrode at 100mV.s $^{-1}$. No peak is observed in the case of NP-CPE for the absence at Hg(II) (Figure 1a), contrary to the Figure 2b shows as Hg(II) exhibits a pair of well-defined redox waves on the NP-CPE with Epa = 0.25V and Epc = -0.2 V.

Influence of accumulation time

The dependence of peak current on the preconcentration time for 0.18 mmol L^{-1} Hg(II) was also investigated (Figure 2). The peak current increases with the increasing in the preconcentration

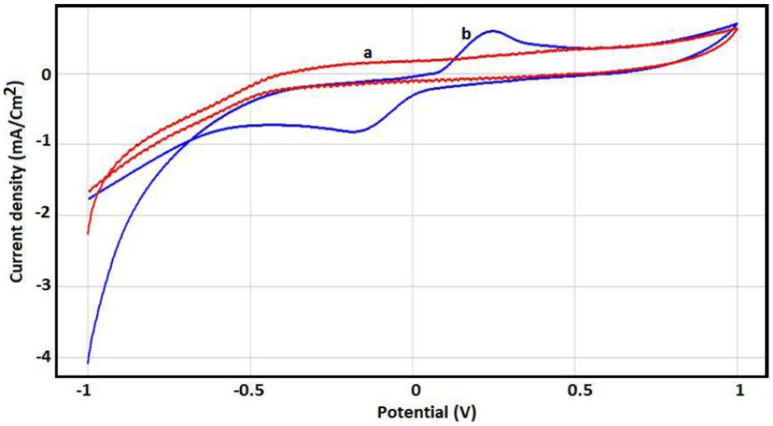

Figure 1 : CV recorded for 0.18 mM Hg(II) at pH=7 at bare NP-CPE (a) and NP-CPE/Hg(II) (b), scan rate 100 mV/s, preconcentration time (tp)= 7min

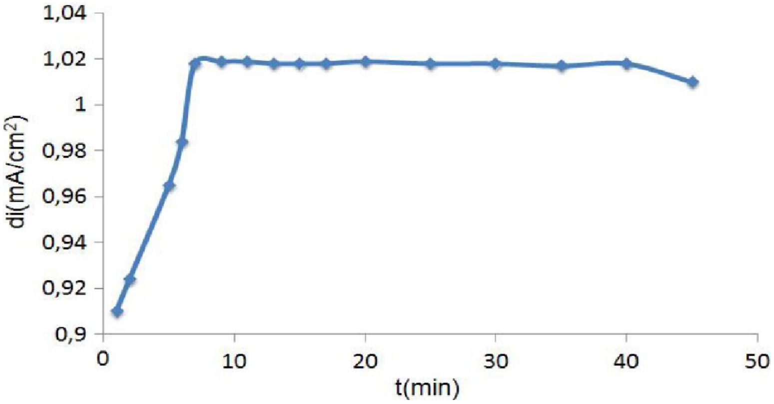

Figure 2 : Effects of accumulation time on Hg(II) oxidation peak currents

time between 0 and 45 min above which it became nearly constant due to the surface saturation. Hence, a 7 min preconcentration time was used in all subsequent experiments.

Effect of scan rate

The effect of scan rate on the redox of Hg(II) was examined in 0.1 M Na_2SO_4 buffer solution of pH=7 as a supporting electrode. The Figure 3 shows both the anodic and the cathodic peak currents linearly increase with the scan rate over the range of 40 to 120 mVs^{-1}, suggesting that the electron transfers for Hg(II) at the phosphate modified CPE is adsorption controlled reaction. The Figure 4 shows the linear relationship between the scan rate anodic peak and cathodic peak currents of Hg(II) at NP-CPE.

Effect of concentration of Hg(II)

Figure 5 shows the CV curves of different con-

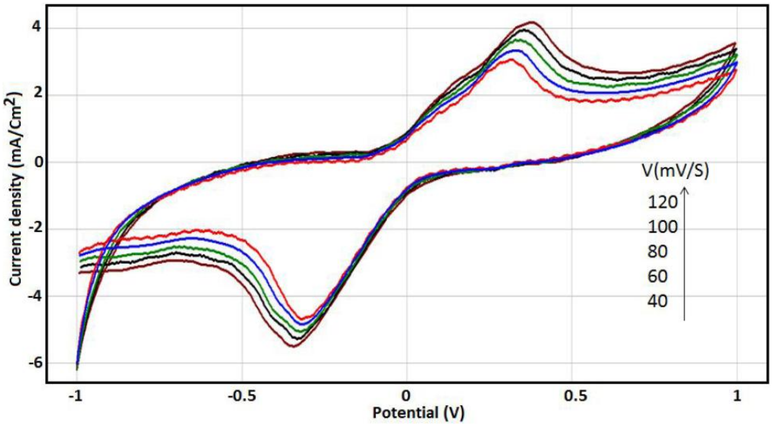

Figure 3 : CV acquired on NP-CPE with 3.81 mM Hg(II) in the buffer solution at different scan rates

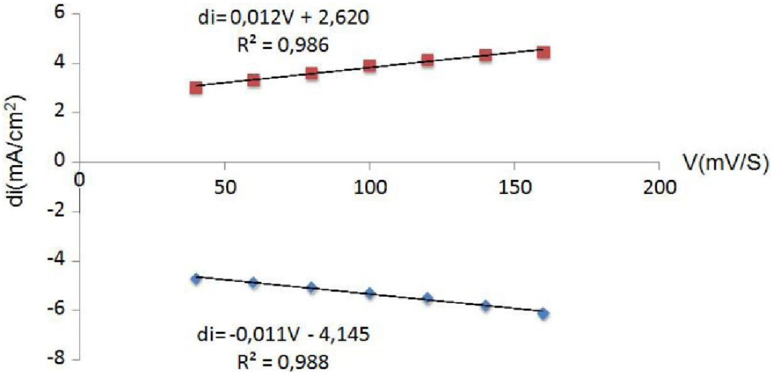

Figure 4 : Plot of peaks area versus scan rate

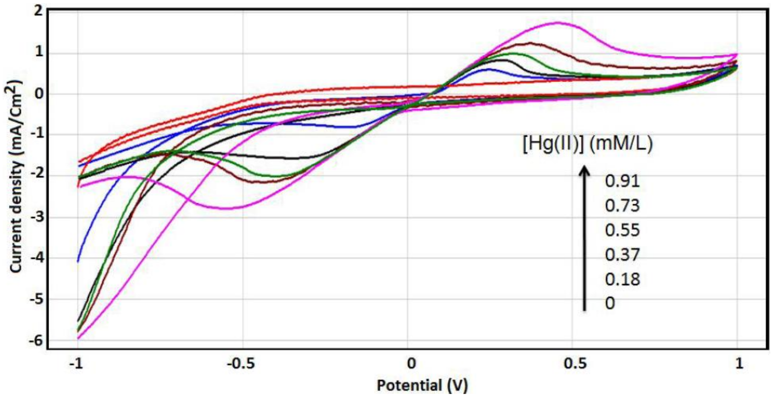

Figure 5 : Cyclic Voltammograms of different concentration of Hg(II) at NP-CPE in 0.1 M Na_2SO_4, Scan rate 100 mV/s

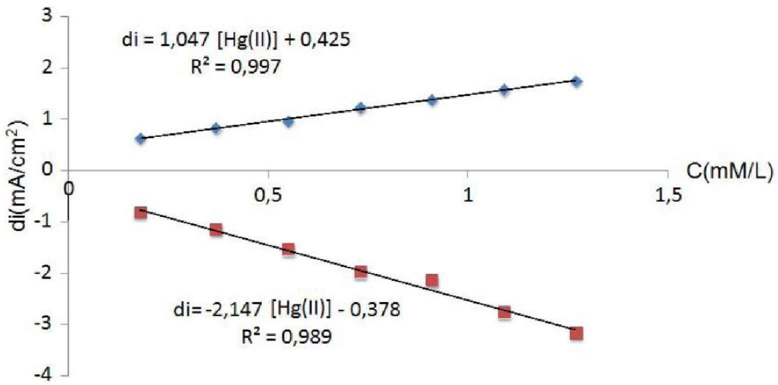

Figure 6 : Plot of peaks area versus added concentration of Hg(II)

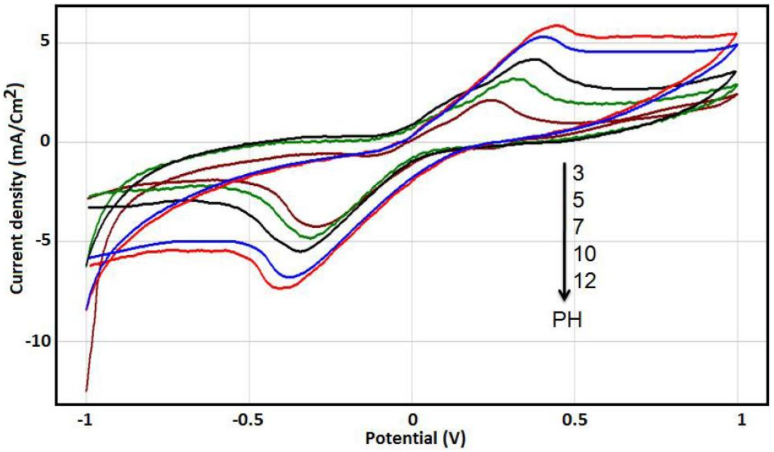

Figure 7 : Effect of pH on the redox of Hg(II) at the NP-CPE

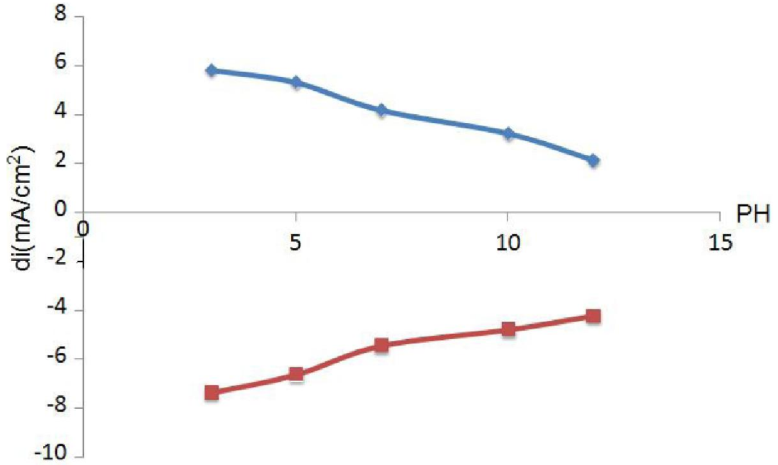

Figure 8 : Plot of the relationship between solution pH and the redox peak current

centration of Hg(II) at NP-CPE was increased from 0.18 mM to 0.91 mM in 0.1 M Na_2SO_4 buffer solution at pH=7 at a sweep rate of 100 mVs^{-1}. Both the anodic and cathodic peak current increases linearly with the concentration of Hg(II). It was also observed that the cathodic peak potential shift towards negative values and anodic peak potential shift towards positive side. This kind of shift in Ep in the cathodic and anodic direction with increasing concentration of the Hg(II) indicates that the ion of Hg are adsorbed over the electrode surface. The Figure 6 shows the linear relationship between the Concentration anodic and cathodic peak currents of Hg(II) at NP-CPE.

Influences of pH

The Figure 7 a shows the cyclic voltammograms

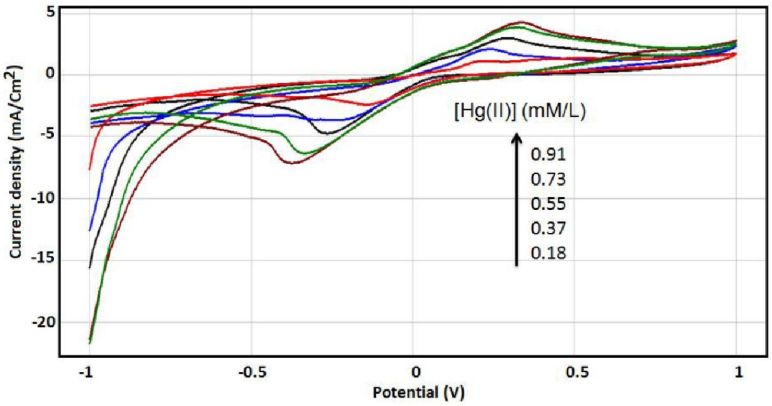

Figure 9 : Cyclic Voltammograms of different concentration of Hg(II) at NP-CPE in 100mL juice apple, Scan rate 100 mV/s

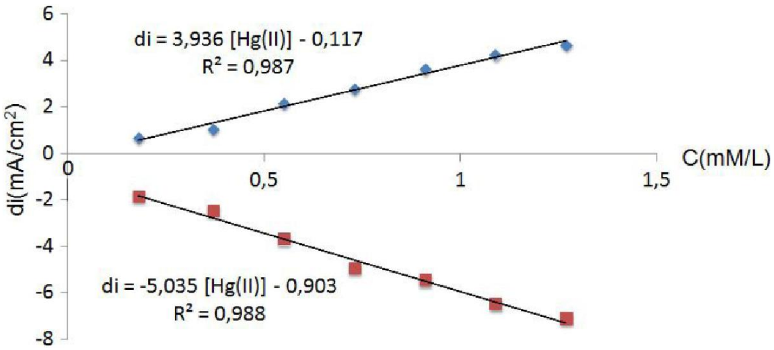

Figure 10 : Plot of peaks area versus added concentration of Hg(II)

of the Hg(II) at different pH. The current of the peak depend on the solution pH. The Figure 8 shows the graph of different pH versus peak current, it could be confirmed that the current density decreases with increased PH.

Analytical application

Under the optimized conditions, the analytical system was used for mercury determination in juice apple sample without any pretreatment. The analytical curves were obtained by CV experiments in supporting electrode (Figure 9). It was founded that the peaks currents increase linearly versus Hg(II) added into the juice apple (Figure 10).

CONCLUSION

This work demonstrated that carbon paste electrode modified with natural phosphate is a feasible alternative for the analytical determination of mercury. In the present work, the influence of Hg(II) peak current has been evaluated. The oxidation of this compound on the modified electrode occurs in an reversible manner. The modified electrode was successfully applied in juice apple samples. The method could be improved in a simple way without introducing additional procedures.

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