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# Detection of mercury by a new sensor based CPE modified with extract of takaout plant

**Abdelaziz Ait sidi mou *, Aicha Ouarzane and Mama El Rhazi**

Laboratory of Physical Chemistry and Bioorganic Chemistry Mohammedia (FSTM), University Hassan II Mohammedia, Morocco

**Abstract**: In this work, carbon paste electrode (CPE) modified with extract takaout was used for the determination of mercury using square wave voltammetry (SWV). Compared with unmodified carbon paste electrode, the anodic peak current had a significant increase at the modified electrode. Under the optimized conditions (amount of modifier 3%, 0.1 M acetate buffer pH 2, accumulation potential -0.6 V, accumulation time 300 s, resting time 10 s, frequency 25 Hz, pulse amplitude 0.050 V, step height 2 mV), a linear response was obtained in the concentration range from 3.1 to 11 µM Hg(II) and the detection limit was 0.42 µM. The results indicate that this electrode is sensitive and effective for determination of $Hg^{2+}$ in the tap water sample.

**Keywords**: Carbon paste electrode; extract of takaout plant; mercury (II); square wave voltammetry.

## Introduction

The takaout plant is a nontoxic natural product derived from galls of tamarix orientalis used by Moroccan women for dyeing and coloration of hairs [1-3]. It is also used in the treatment of hypertension and heart disease for men and women [4,5], but the research about this plant is not sufficient for determination of their properties.

Mercury is naturally occurring in the environment in ores, rocks, and soils in limited quantities. This metal is of the more toxic metals. Although it is found at low concentrations, their toxicity can be dangerous [6]. Mercury one of the most important endocrine disrupters has been reported as poisonous to human body [21]. It can impair the human senses because it is a potent nerve toxin. Mercury evaporates readily and travels long distances in the atmosphere causing local and global pollution. Therefore knowledge of the mercury content in various matrixes, together with the development of fast, reliable and sensitive analytical methods for determination at trace level are very important [7,8].

The analytical techniques which are frequently used for the determination of mercury includes gaz chromatography coupled with mass spectrometry (GC-MS) [9-11], electrothermal atomic absorption spectrometry (ETAAS) [12], cold vapor atomic florescence spectrometry (CV-AFS) [13], cold vapor atomic absorption spectrometry (CV-AAS)[14], inductively coupled plasma atomic emission spectrometry (ICP-AES)[15] and Infrared Fluorescent (IF) [16,17]. Compared with the expensive optical detection method, electrochemical methods, particularly stripping voltammetry, have many advantages such as simple, economical and rapid for the practical trace analysis and suitable for onsite monitoring [18].

Several voltammetry methods especially coupled with chemically modified electrodes (CME) can be used for metals determination providing high sensitivity and precision with relatively low instrumental costs [19]. Generally carbon paste electrode is used in voltammetric methods, including square wave anodic stripping voltammetry (SWASV) [20,21], anodic stripping voltammetry by differential pulse polarography (ASV-DPP) [22-25], Cathodic adsorptive stripping voltammetry (CASV) [26] and chronoamperometric [27], potentiometric (CP) [28-30] for the determination of trace levels of metal ions such as mercury.

Following our work with carbon paste electrode modified by takaout plant for the determination of metal [31]. Takaout extract is used as a modifier for the preparation of the modified electrode and the method of square wave voltammetry is used for determining of mercury in the tap water sample.

## Experimental

### Apparatus

Electrochemical experiments were carried out with an autolab (Metrohm-Autolab, Utrecht Netherlands) PGSTAT302N potentiostat/galvanostat

**Corresponding author: Abdelaziz Ait sidi mou*
*Email adress : [aitsidimou_aziz@yahoo.fr](mailto:aitsidimou_aziz@yahoo.fr)*
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controlled by GPES 4.9 software. A three-electrode cell was employed for all electrochemical measurements. Carbon paste electrode (4 mm diameter) served as the working electrode, a platinum plate as counter electrode, and saturated electrode calomel (SEC) as reference electrode.

### Reagents

All chemicals were of analytical reagent grade, except the modifier (takaout plant). All solutions were prepared with distilled water. The mercury nitrate, acetic acid and sodium acetate powder were obtained from Riedel-de häen. The graphite powder was obtained from Fluka. Acetate buffer served as the supporting electrolyte for the determination of mercury.

### Preparation the extract of takaout

1 g of takaout powder was weighed, dissolved in 50 mL ethanol and placed in a rotavapor for 2 h, followed by filtration with a vacuum pump. Finally, the solvent was evaporated with a rotavapor, and the extract was obtained in powder form to make final use.

### Samples preparation

Tape water samples were collected from our laboratory and analysis without any further treatments. The real sample was mixed with the supporting electrolyte (0.1 M acetate buffer solution, pH 2.0) in the ratio of 1:1.

### Preparation of the electrode

The modified carbon paste electrode was prepared by thoroughly mixing weighed amount of extract takaout (15 mg), dissolved in a small quantity of acetonitrile, with 0.5 g of graphite powder and 80 µL of paraffin oil until a uniformly wetted paste was obtained.

### Mercury determination

The electrode was placed in the measurement cell containing a selected concentration of mercury in 0.1 M acetate buffer, pH 03. An initial potential of -0.9 V (vs. ECS) was applied for 120 s. Following the preconcentration step, the rotation of the electrode was stopped and the solution was left to equilibrate for 10 s. The electrode potential is stepped reversibly between -0.2 V to 0.3 V at 50 mV $s^{-1}$ using square wave voltammetry. Cleaning of the electrode surface was carried out by applying a potential of 0.3 V for 30 s.

## Results and discussion

### Electrochemical behavior of modified electrode

The cyclic voltammetry behavior of modified electrode was studied using 0.1 M acetate buffer, at a potential scan rate of 50 $mVs^{-1}$. Fig. 1 show the first scan obtained at carbon paste electrode (a) and carbon paste electrode modified by extract of takaout (4%) (b). At CPE modified by extract of takaout, an anodic peak was observed at 0.52 V with a current of 83 µA. This response is attributed to aromatic compound contained in takaout, may be explained by the presence of paraphenylenediamine in this plant. Similar results were found at pH 3 on the two electrodes, with the anodic peak of 0.6 V for the electrode modified.

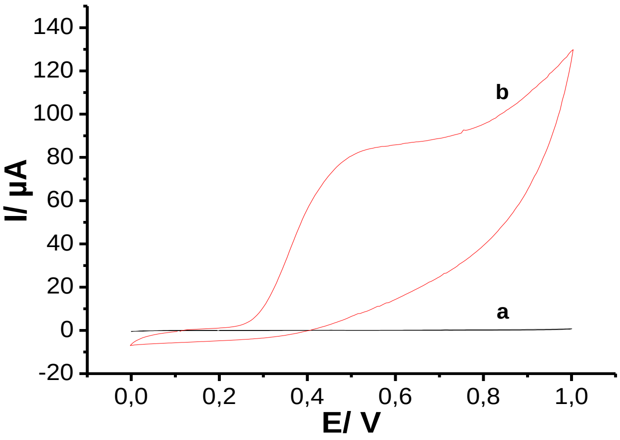

**Figure 1.** CVs of the CPE (a) and CPE modified by extract takaout (a), in 0.1 M acetate buffer at a scan rate of 50 mV $s^{-1}$.

### Electrochemical behavior of mercury on modified electrode

The electrochemical behavior of mercury on modified electrode by extract of takaout was evaluated in 0.1 M acetate buffer, contains 4 µM Hg (II) at pH 3, used the square wave voltammetry and the results were shown in Fig. 2. An anodic peak of mercury was recorded at 0.13 V and 0.12 V for carbon paste (a) and carbon paste modified by extract of takaout (b) respectively. The difference observed of currents, indicate that extract of takaout play an important role in accumulation of mercury process on electrode surface and significantly increase of sensitivity for mercury determination.

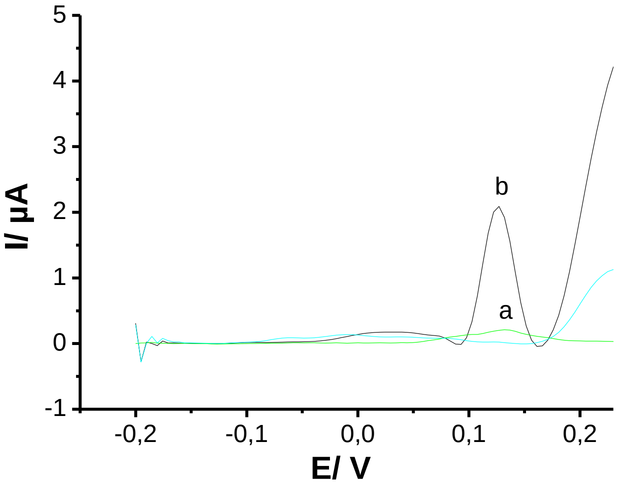

**Figure 2.** Determination of 4 µM Hg (II) by carbon paste (a) and carbon paste modified by extract of takaout (b), $E_{acc}$= - 0.9 V, $t_{acc}$= 120 s, equilibrate time= 10 s, frequency = 25 Hz, scan rate= 50 mV/ s, supporting electrolyte 0.1 M acetate buffer, pH = 3.

### Effect of parameters

Voltammetric behavior of the modified CPE was evaluated in terms of the influence of accumulation and stripping parameters such as the effect of amount of modifier, supporting electrolyte, pH of the accumulation medium, accumulation potential and accumulation time.

### Effect of electrode composition

The effect of the ratio of extract takaout to graphite powder was evaluated within the range of 1% to 10% (w/w). Fig. 3 shows an increase in the peak current from 1% to 3% of modifier to graphite powder ratio. Current value increases due to greater number of sites available for adsorption of mercury at the electrode surface. At greater than 3% a decrease in the peak current value was observed. 3% was chosen the value optimum for the further work

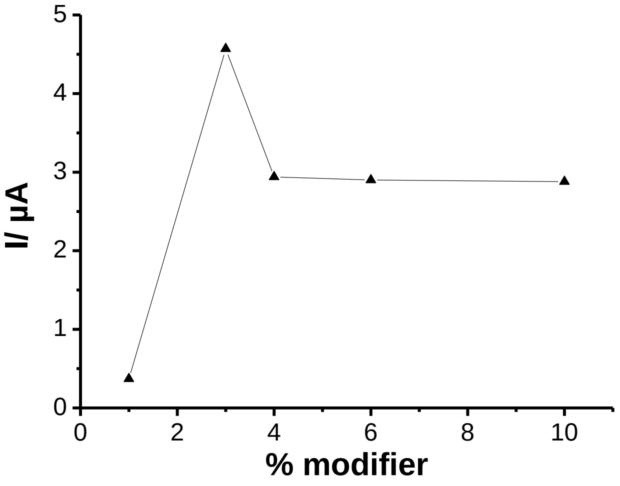

**Figure 3.** Determination of 4 µM Hg (II) for the carbon paste modified by different amount for the extract of takaout, $E_{acc}$= - 0.9 V, $t_{acc}$= 120 s, equilibrate time=10 s, frequency= 25 Hz, scan rate= 50 mV/ s, supporting electrolyte 0.1 M acetate buffer pH= 3.

### Effect of pH

The influences of various types of supporting electrolyte including hydrochloric acid, sodium hydroxide, phosphate buffer and acetate buffer were investigated. In acetate buffer the anodic peak currents were higher and better defined peak shapes were observed, which it is found to be the most suitable supporting electrolyte for mercury determination which is according to the previously reported literature[21].

The effect of pH on the SWV response of the electrode was studied in a pH range from 1.5 to 6.0 in a solution containing mercury. The anodic peak current for mercury was decreased as the pH is changed from 2.0 to 3.4 (Fig. 4). no response in the currents at pHs lower than 2.0 can be due to the competition between proton ion and the metal ions for binding to the donating atoms at the surface of the electrode. Also, at pH values below 2.0, the ligand can slowly dissolve in the solution and lose its ability for immobilizing $Hg^{2+}$ ions. The decrease in current at pH values higher than 2.0 for $Hg^{2+}$ is expected, because hydrolysis of this cation takes place at pHs higher than 2.5. Therefore, acetate buffer of pH 2.0 was chosen for further studies. The pH optimum found in this work is in accordance with previous investigations [32].

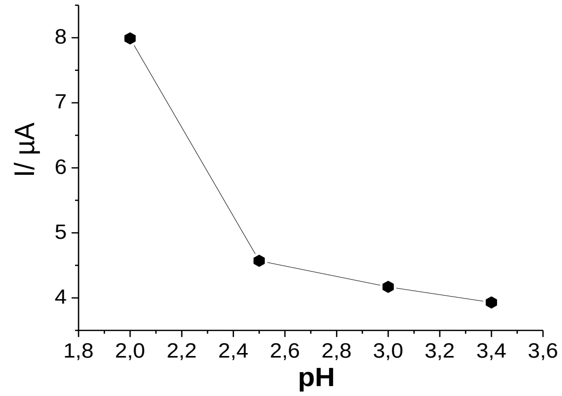

**Figure 4.** The effect change of pH between 2 and 3.4 on the intensity of the oxidation peak of 4 µM mercury. Condition: accumulation potential -0.9 V, accumulation time 120 s, equilibrate time 10 s, frequency 25 Hz, pulse amplitude 50 mV, step height 2 mV, acetate buffer 0.1 M.

Effect of accumulation potential

The accumulation potential is an important parameter for the analysis techniques, and has a significant influence on the sensitivity of the determination of heavy metals. The effect of accumulation potential on stripping peak response of the solution of 4 µM Hg (II), in pH 2 acetate buffer, was studied in the range −0.500 to −1.000 V. The investigation was performed by varying the applied accumulation potential recording a voltammogram at each point. The accumulation time for all points was 120 s. Fig. 5 shows the response of SWV for the mercury as a function of accumulation potential. The current for $Hg^{2+}$ increased with the accumulation potential shifting from −1.000 to −0.600 V. It was observed that for an accumulation potential at −0.60V, a decrease in the anodic peak current occur caused by an inefficient reduction of Pb(0) at the electrode surface. Therefore, −0.600 V was applied as the accumulation potential for the next studies.

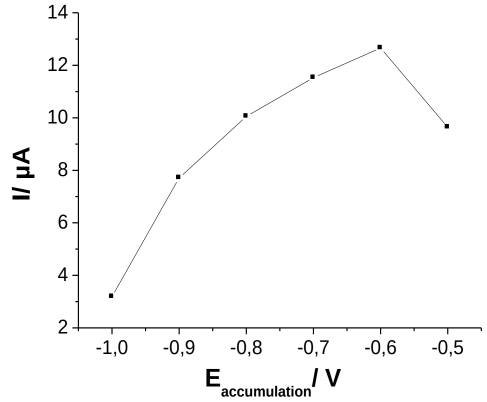

**Figure 5.** Effect of accumulation potential on the peak current of the solution of 4 µM $Hg^{2+}$. Condition: pH 2, accumulation time 120 s, equilibrate time 10 s, frequency 25 Hz, pulse amplitude 0.050 V, step height 2 mV.

Effect of accumulation time

The effect of accumulation time on the response of the solution of 4 µM $Hg^{2+}$, in pH 2 acetate buffer, in the range 30–600 s was studied. It is clear from Fig. 6 that initially the current value increase linearly with accumulation time which indicates that the mercury ions get adsorbed at the electrode surface rapidly while further prolonged accumulation time did not improve the peak height and a plateau was observed. A pre-concentration time of 300 s was selected as a compromise between length of analysis time and sensitivity. In addition, longer accumulation time could also damage the electrode surface that worsens the sensitivity and reproducibility of measurements taken.

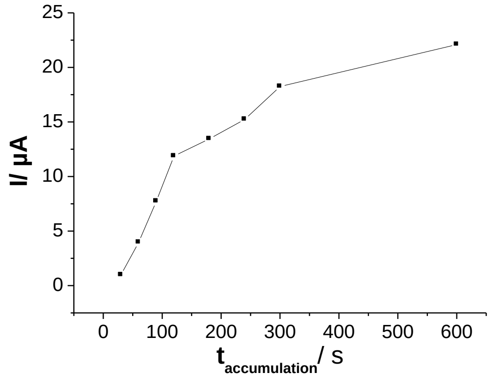

**Figure 6.** Effect of accumulation time on the peak current of 4 µM $Hg^{2+}$. Condition: pH 2 acetate buffer 0.1 M, accumulation potential -0.6 V, equilibrate time 10 s, frequency 25 Hz, pulse amplitude 0.050 V.

**Calibration plot**

Under the optimized conditions described above, the amount of modifier of 3%, the supporting electrolyte of acetate buffer, the pH of 2, the accumulation potential of -0.6 V and the accumulation time of 300 s. Fig. 7 shows the square wave voltammograms for the oxidation of different concentrations of $Hg^{2+}$ obtained under the optimum conditions. The characteristics of the calibration graph are given in Table 1. The limit of detection, defined as LOD = $3S_b/m$, where LOD, $S_b$ and m are the limit of detection, standard deviation of the blank and the slope of the calibration graph, respectively.

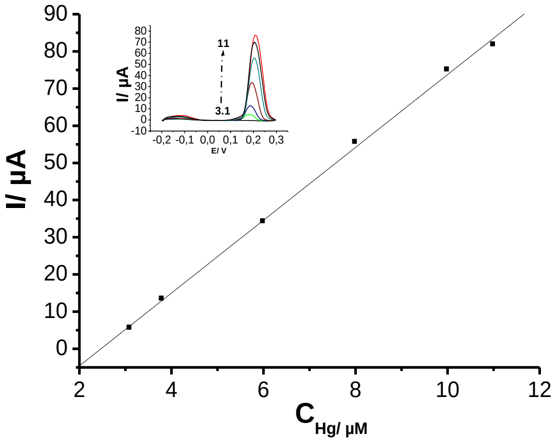

**Figure 7.** Square wave voltammograms for CPE modified by extract takaout in the solutions with different concentrations, from bottom to top, 3.1, 3.8, 6.0, 8.0, 10.0, 11.0 µM of Hg (II). Condition: 0.1 M acetate buffer pH 2, accumulation potential -0.6 V, accumulation time 300 s, equilibrate time 10 s, frequency 25 Hz, pulse amplitude 0.050 V, step height 2 mV.

The repeatability of the electrode in the determination of $Hg^{2+}$ was evaluated by performing seven determinations with the same standard solutions of $Hg^{2+}$. The relative standard deviation (RSD) for the response of electrode towards a 1.1 µM of $Hg^{2+}$ solution was 2.31%.

**Table 1.** Parameters of analytical curves for $Hg^{2+}$ obtained with SWV conditions.

| Cation | LR[a] (µM) | Linear regression equations for peak current $I_{pa}$ (µA) (C in µM) | Upper limit of linear range (µM) | Limit of detection (µM) | Correlation coefficient |
|---|---|---|---|---|---|
| $Hg^{2+}$ | 3.1-11 | $I_{pa}$= 9.79 C -24.18 | 11 | 0.42 | 0.999 |

[a] LR, linear range.

**Interference**

The influence of other metal ions, which can potentially introduce some competition with the ions of mercury (II) at the sites of complexation for the extract of takaout, were tested on their possible interfering effect on the determination of mercury under the same experimental conditions. Different interfering ions used for the study are lead, cadmium, copper and zinc. For the determination of mercury no effect was observed up to 15 fold of lead, 25 fold of cadmium, 5 fold of copper and no effect of zinc.

**Application**

To evaluate the applicability and feasibility of the proposed method for the analysis of real samples, modified electrode was employed to determine $Hg^{2+}$ ion in tap water. The results are given in Table 2. The obtained recoveries were in the ranges of 91-107% for $Hg^{2+}$. As shown in this Table, the recovery and RSD were acceptable.

**Table 2** Simultaneous determination of $Hg^{2+}$ after addition to water samples by the proposed method.

| Sample | Concentration added, µmol/L | Concentration found, µmol/L | Recovery (%) |
|---|---|---|---|
| Tap water | - | NV | - |
| | 4 | 4 .28 | 107 |
| | 6 | 5.46 | 91 |
| | 8 | 8.24 | 103 |

## Conclusion

In this study, carbon paste electrode modified with extract of takaout was prepared. The prepared electrode was found to have high affinity towards mercury. Square wave voltammetry was used to optimize the conditions for the determination of mercury. Maximum sensitivity of electrode was obtained from the pre-concentration conducted in solution with the acetate buffer as the supporting electrolyte of pH=2 for 5 min. Despite of some mutual interference effects, mercury can be reliably determined when the standard addition procedure is used, with low detection limits. Cleaning of the electrode surface was carried out by applying a potential of 0.3 V for 30 s. The proposed method is simple, sensitive, highly selective, accurate and applicable for the determination of $Hg^{2+}$ ion in real sample.

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