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Mercury Thin Film at Glassy Carbon Electrode for Adsorptive Stripping Voltammetric Determination of Captopril in Pharmaceutical Samples

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Abstract- A simple square-wave adsorptive voltammetric (SWAV) method was developed for determining Captopril (CAP) in pharmaceutical formulations. The proposed method was based on the electrochemical reduction of CAP at a mercury thin film electrode (MTFE). The preparation of the TMFE/Glassy carbon electrode was very simple; also, this electrode had very good reproducibility and regeneration of its surface was very easy. This kind of electrode has the advantages of mercury electrode and a negligible amount of mercury. In this study, the MTFE in situ produced on glassy carbon electrode to the adsorptive voltammetric quantification of trace amount of CAP. MTFE was shown to be extremely useful for the voltammetric measurements of CAP at μM level. Under optimized conditions, the SW adsorptive stripping voltammetric peak current showed linear correlation with drug concentration over the range of 4.6–64.5 μM with the correlation coefficient of 0.992. The detection limit at the S/N ratio of 3 was 0.6 μM for CAP (n=6) and the relative standard deviation for 23 μM of CAP (n=6) was 6.9%. The film electrode had the advantages of acceptable sensitivity, reproducibility, and simple preparation. The MTFE applied to determination of CAP in tablet samples with satisfactory results.

Keywords- Glassy carbon electrode, Thin mercury film, Captopril, Voltammetric determination

1. INTRODUCTION

Captopril (CAP) (Fig. 1) is an orally active antihypertensive drug, chemically known as ([2S-1-(3-mercapto-2-methylpropioniyl)-L-proline], is an effective angiotensin I converting enzyme inhibitor which is used to treat hypertension and congestive heart failure. It is sometimes prescribed for angina pectoris (crushing chest pain), Raynaud's phenomenon (a disorder of blood vessels that causes fingers to turn white when exposed to cold), and rheumatoid arthritis [1-3]. CAP is marketed under the brand name of Capoten® as tablets in dosages of 12.5, 25, 50, and 100 mg. The literature describes some methods that quantify CAP in pharmaceutical formulations, such as polarography [4], high-performance liquid chromatographic [5], spectrophotometry [3,6–8], atomic absorption spectrometry [9], electrochemical methods based on modified electrodes [10-18], and derivative UV spectrophotometry [19]. Most of these methods are the time-consuming procedures that involve several consecutive steps of double derivatization and double liquid-liquid extraction, and require sophisticated equipment that may not be readily available in laboratories. Thus, the development of a new, sensitive, and fast detection method still remains to be a great challenge.

Electrochemical analysis has growing importance in industrial process control, environmental monitoring, medicine, and biotechnology. Use of bare electrodes in electrochemical detection exhibits low sensitivity and reproducibility. On the other hand, modification of the surface of electrodes increases their performance in analytical applications [20-22].

Electrodes consisting of thin metal films are commonly employed in voltammetric analysis, since their elaboration is simple and regeneration of their surface is possible [23-27]. These electrodes such as mercury [22,24,28,29], antimony [30], tin [31], bismuth [32], and lead [33] are commonly employed in analyses. The film electrodes have shown extremely useful advantages for highly adsorptive stripping voltammetric measurements of chemical species. For many years, the dropping mercury electrode (DME) and hanging mercury drop electrode (HMDE) have gained wide acceptance in electroanalytical chemistry for trace analysis owing to their high sensitivity, reproducibility, and renewability [34]. However, because of the toxicity of mercury, alternative electrodes with a similar performance and lower toxicity are desirable. However, all of the thin film electrodes which were mentioned above are toxic; but, using the thin layer of this metal for analysis, with micro or nanometer thicknesses that is enough for the modification of electrode, can be reduce their danger and disposal. Specifically about MTFEs, there are the advantages of mercury electrode, while negligible amount of mercury is used. The application of TMFEs, in situ produced on GC, is widespread. The overall performance of these non-mercury electrodes has not approached that of mercury ones, in comparison mercury, some of them have low cathodic potential limit, short linear dynamic range, low hydrogen evolution, small

background contributions, or poor precision and resolution. To the best knowledge of the present authors, no works have been previously performed on depositing MTFE on the surface of GC by potential cycling method for CAP determination. Compared with other methods, the method of potential cycling method was found to be easier and make uniform film. The prepared MTFEs/GC showed more acceptable performance for the reduction of CAP than the unmodified electrode.

2. EXPERIMENTAL

2.1. Chemicals and reagents

All the chemicals and reagents used in this work were of analytical grade. CAP was purchased from Sigma. H₃PO₄ (84-85%) was purchased from Fluka (Fluka, Buchs, Switzerland). H₃BO₃, HgNO₃, K₃Fe(CN)₆ powder,CH₃COOH, NaOH, and HCl (37%) solutions were purchased from Merck (Darmstadt, Germany). All the aqueous solutions were prepared with doubly distilled deionized water. The stock solution of CAP was freshly prepared. The stock 0.2 M phosphoric (pH=2) and 0.1 M CH₃COOH (pH=4) buffer solutions of the required pH were prepared by adding appropriate amounts of phosphoric acid or acetic acid in water and adjusting the pH value with NaOH (0.2 M). The stock solution of 1000 mg L⁻¹ mercury (II) was prepared by dissolving the appropriate amount of mercury(II) nitrate salt (Merck) in water and diluting to 100 mL in 0.1 M CH₃COOH buffer solution (pH=4). All the experiments were performed at ambient temperature (25±3 °C).

2.2. Apparatus

Voltammetric measurements were performed using a computerized potentiostat and a galvanostat (Autolab TYPE III, Netherlands) connected to a personal computer. Test conditions for voltammetric measurement were controlled using General Purpose Electrochemical System (GPES) software. All the electrochemical studies were made at 25±2 °C with a three-electrode assembly with a carbon paste working electrode (unmodified or modified), an Ag/AgCl/KCl (3 M) electrode as the reference electrode, and a platinum counter electrode. pH measurements were taken with a pH-meter (model 632 Metrohm, Herisau, Switzerland) and a GCE (diameter of 0.4 cm in and geometry surface area of 0.125 cm².

2.3. Procedure for mercury film deposition

The simple construction of the applied electrode allows the mercury film to be refreshed before each measurement. The procedure of refreshing the outer mercury film involves two steps: polishing and cleaning up of GCE and mercury film deposition. At first, the GCE was rinsed thoroughly with water to obtain a clean electrode surface. Then, the electrode was

connected to the potentiostat and placed in the HNO₃ solution (0.1 M). Afterwards, the potential +1.0 V *versus* Ag/AgCl was applied for 100 sec. After each experiment for the removal of mercury film, the electrochemical pretreatment was only repeated.

It is known that in the second step, deposition of mercury has the main impact on voltammetric responses. So, mercury deposition on the GCE was done by the conventional procedures described in the literature with slight modification [24,36]. For this purpose, 25.0 mL of 100 μg mL⁻¹ mercuric nitrate solution in the acidic medium of 0.1 M acetate buffer (pH 4.5) was prepared and added to the electrochemical cell. For modification surface of GCE, two modes of applying potential were used: (a) with potential sweep rate with a constant scan rate, and (b) with constant potential at different times. In the first method, the solution was previously deoxygenated by nitrogen gas flow for 20 sec. Subsequently, the scan potential of 0.0 V to -1.0 V *versus* Ag/AgCl was applied with scanning rate (0.05 V/sec) for 30 scans. In the second method, the solution was previously deoxygenated by nitrogen gas flow for 20 sec. Subsequently, the constant potential of -1.0 V *versus* Ag/AgCl was applied for different deposition times (300 to 1100 sec). Applying potential with cyclic voltammetery mode for modification had better results. Therefore, this method was chosen and used for GCE modification.

2.4. Determining electrode surface area (A)

The area of the electrode was obtained by cyclic voltammetry using 1 mM hexacyanoferrate ($K_3Fe[CN]_6$) as a probe in different scan rates. The Randles-Sevcik formula (1) is generally used.

$$I_{Pc} = 2.69 \times 10^{5} n^{\frac{3}{2}} AD^{\frac{1}{2}} v^{\frac{1}{2}} C_{0}$$
 (1)

In the Randles- Sevcik formula, I_{pa} (A) is the anodic peak current, n is electron transfer number, A (cm²) is surface area of the electrode, D (cm² s⁻¹) is diffusion coefficient, and v (V s⁻¹) is scan rate, and C₀ (mol cm⁻³) is the concentration of K₃Fe(CN)₆. For 1 mM K₃Fe (CN)₆ in the 0.1 M KCl electrolyte, n=1 and D_R=7.6×10⁻⁶ cm² s⁻¹. Also, from the slope (slop=7×10⁻⁵) of the I_{pc} – v ¹¹² relation, the active surface area can be calculated. The electrode surface area was nearly 0.092 cm², which was used for the following calculations.

2.5. Procedure

For CAP determination, the MTFE was prepared before each measurement. After plating was completed, the voltammetric electrodes were washed smoothly with distillated water before immersing in analyte solution and the common parameters for the square wave cathodic stripping voltammetry (SWCSV) were fixed as follows: purge nitrogen: 20 sec, deposition potential:-0.05 V, deposition time of 50 sec, initial potential of 0.0 V, final

potential of -1.0 V, SW amplitude of 40 mV, SW frequency of 25 Hz, and potential step of 0.6 mV. Then, the accumulation potential at -0.05 V versus Ag/AgCl was applied to a fresh MTFE and the accumulation was carried out in a stirred solution (100 rpm) for a period of 50 sec. Afterward, SW voltammogram was recorded from 0.0 to -1.0 V after 10 sec as a rest time without stirring. The blank voltammogram was recorded by the phosphoric buffer solution in the absence of CAP. Figure 1 displays the mechanism of detecting CAP by TMFE.

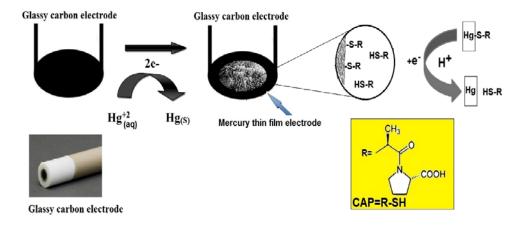


Fig. 1. MTF preparation on GCE and proposed mechanism for CAP reduction at the surface of the electrode

2.6. Preparing real samples (tablet samples)

Two different samples of tablet from different companies (labeled with the amount of 25 mg per tablet, Soha Pharmaceutical Company, Tehran, Iran and labeled with amount of 50 mg per tablet, Exir Pharmaceutical Company, Tehran, Iran) were purchased from a local pharmacy and analyzed using standard addition method.

3. RESULTS AND DISCUSSION

The behavior of the MTFE in the presence of CAP was studied by CV and SWV techniques

3.1. Mechanism

The high affinity of thiol group to react with mercury is well known. Figure 2-a displays the SW voltammograms for the system. A blank solution (phosphate buffer at pH=2.0) did not show any peak current in the potential range of 0.0 V to -0.8 V. But, by the addition of

CAP, a large cathodic peak was obtained at the potential of about -0.20 V, which was related to CAP. This phenomenon suggests that CAP was adsorbed before undergoing electrode reaction. The adsorption of CAP on the surface of electrode and reduction of CAP can be summarized as follows:

$$R-SH_{(aq)} + Hg \leftrightarrow R-S-Hg + H^{+}_{(aq)} + e^{-}(Hg \text{ electrode})$$

Where R-SH and Hg are CAP and MTFE, respectively. The protonated thiols (R-S-H) were adsorbed by the oxidative process to the Hg surface, which is a widely accepted reaction for thiol compounds at mercury and gold electrodes [35-37].

Also, during the cathodic potential scanning, at high concentration of CAP and low scan rate, the continuous sulfur-Hg bond formations occurred within a few seconds. At the higher local concentration of CAP at the surface of TMFE, after the reductive desorption, its readsorption would occur rapidly within a few seconds [35-37]. Therefore, another cathodic peak can be seen. At higher scan rate and lower concentration, it was not observed.

3.2. Effect of pH

Since H⁺ has an effect and participates in the reduction of thiol group on MTFE (see Section 3.1), the influence of pH on the peak current of CAP was studied in the pH range of 1–6. Figure 2-b illustrates the dependence of the peak currents on pH of the solution containing CAP. In the acidic solutions, CAP was more adsorbed and electroactive. Maximum peak current was obtained in the pH about 2.0. The results showed that the peak currents were increased from pH of 1.5 to 2.5. However, by increasing pH from 2.5 to 5.0, the peak currents decreased. For pH values of higher than 4, no reduction peak was observed. In this work, the pH value of 2.0 was selected for further experiments. Therefore, phosphate buffer with pH=2.0 was prepared and used as the buffer in all determinations. A study of the influence of concentration of buffer on the voltammetric peak revealed that the highest peak was obtained in 2.5 mM phosphate buffer.

3.3. Effect of variation of the deposition potential and time

The potential (E_{dep}) and time (t_{dep}) of deposition have the main impact on peak height in the voltammetry. Figure 2-c shows the dependence of the deposition potential on the peak current over the range of +0.10 to -0.10 V (vs. Ag/AgCl) for 23 μ M CAP. The deposition potential was varied between -0.1 and 0.1 V (vs. Ag/AgCl) using the constant deposition time of 50 sec (by stirring). Each CSV scan was initiated after 10 sec of equilibration (without stirring). The peak high for CAP increased with more deposition potentials up to -0.05 V and showed a decrease at higher positive potentials. Thus, the deposition potential of -0.05 V was selected. Also, the deposition time dependence of the peak height for CAP was examined for

deposition times in the range of 50-200 sec in the presence of 23 μ M CAP. Figure 2-d shows the peak currents versus deposition time. The peak currents were nearly constant and showed that the adsorptive equilibrium was reached at these times. According to the above results, the deposition time of 50 sec was selected for further experiments.

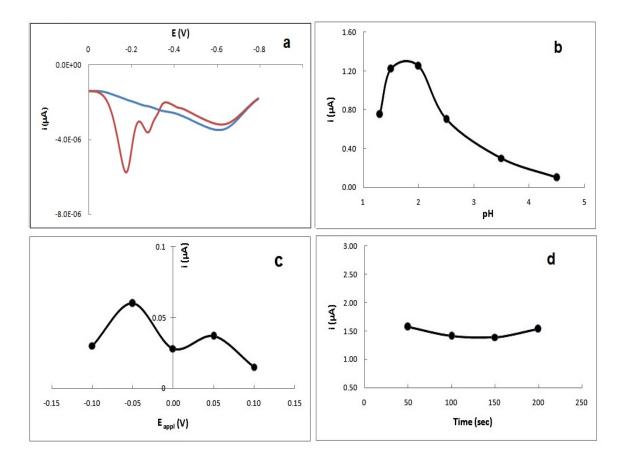


Fig. 2. (a) SW voltammograms of CAP at MTFE (red line) and pure GCE (blue line) in the presence of 1.0 mM CAP [conditions: phosphate buffer (pH:2): 1 mM; accumulation potential: 100 sec], (b) Dependence of the reduction peak current of 0.2 mM CAP in different pH values, (c) Effect of accumulation potential on the peak current [conditions: CAP: $23\mu\text{M}$, phosphate buffer (pH:2): 1 mM, accumulation potential: 50 sec], (d) Effect of accumulation time on the peak current [condition: CAP: $23\mu\text{M}$, phosphate buffer(pH:2):2 mM, accumulation potential=-0.05V]

3.4. Effect of scan rate on the peak currents and peak potentials

Cyclic voltammogram (CV) of CAP reduction at the MTFE and pH of 2.0 was studied. In the forward scan, one well-defined cathodic peak, owing to the reduction of thiol group, was observed and the very weak anodic peak was noticed in the reverse direction. This point indicates that reduction of the CAO peak was quasi-reversible in the scan rate range of 20–110 mV s⁻¹. CVs of CAP at the MTFE in various potential sweep rates in the range of 20–

110 mV s⁻¹ are shown in Figure 3. According to this figure, the reduction current of CAP on the MTFE surface increased linearly with the potential sweep rate (r=0.993), which indicated the adsorption controlled process.

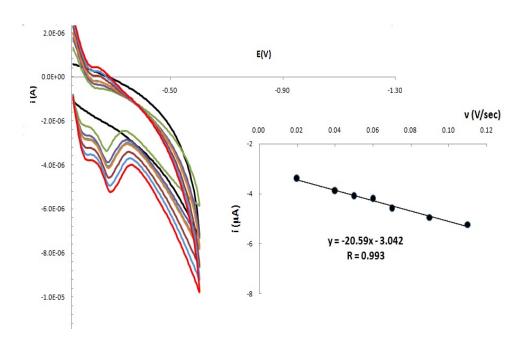


Fig. 3. Dependence of the CV responses at MTFE on sweep rate in buffer (pH 2.0); Scan rate: 20, 40, 50, 60, 70, 90, 110, mV s⁻¹ and 2.5 mM of CAP (Inset: Variation of the current with the sweep rate.)

3.5. Chronoamperometric study

Chronoamperometry as well as other electrochemical methods may be used to investigate processes at different electrodes. In this part of the process, reduction of CAP was also studied by chronoamperometry. Figure 4-a shows the chronoamperograms of CAP at the MTFE that were obtained by setting the potential of the working electrode at -300 mV for the various concentrations of CAP. Figure 4-b shows the linearity of chronoamperometry currents and concentration of CAP. In this section, chronoamperometry was used to estimate the diffusion coefficient (D) of CAP in the solution. For an electroactive material (such as CAP) with diffusion coefficient D, the current corresponding to the electrochemical reaction was described by Cottrell's law equation (2).

$$I_{p_c} = nFA\pi^{-1/2} D^{1/2} t^{-1/2} C$$
 (2)

Where C is bulk concentration of CAP (mM); in fact, the plots of I versus $t^{-1/2}$ (Figure 4-c) at three different concentrations (14, 28 and 42 μ M) produced straight lines (n=3); Using the slopes, the mean value of D was calculated 9.1×10⁻⁵ cm² s⁻¹ (n=1) for CAP.

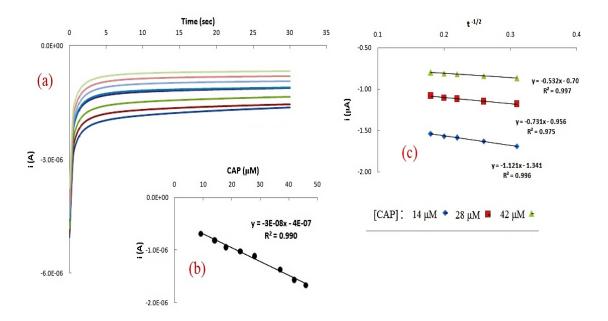


Fig. 4. (a) Chronoamperometric responses of the MTFE in buffer solution (pH 2.0) containing different concentrations of CAP for the potential step of -200 mV. The curves correspond to 9.2, 14, 18, 23, 28, 37, 42, and 46 μM of CAP, respectively. (b) Variation of chronoamperometric currents at t=30 sec vs. CAP concentration for 9.2–46 μM, (C) Plot of I vs. t ^{-1/2} obtained from chronoamperometric experiments for the MTFE in 2.5 mM buffer solution (pH 2.0) containing different concentrations of CAP: 14 μM, 28 μM and 42 μM, respectively

3.6. Chronocoloumetry study

Also, chronocoloumetry, as well as other electrochemical methods, was employed for the investigation of electrode processes at an MTFE. The one potential step chronocoloumetry on the modified electrode in a blank buffer solution and in the presence of CAP (28 μ M) showed symmetrical chronocolougrams (Figure 5). The analysis of the chronocoulometric data was based on the Anson equation [38] (Eq. 3):

$$Q = \frac{2nFD^{1/2}ACt^{1/2}}{\pi^{1/2}} + Q_{dl} + Q_{ads}$$
 (3)

Herein, Q represents the charge (coulombs), n and A represent the number of electrons transferred and the real electrochemical surface area of the electrode (cm²), respectively, and F is the Faraday's constant (96,485 coulombs/mole). Also, concentration of the mediator is denoted by C where the diffusion coefficient of the mediator (cm²/sec) and time (sec) are denoted by D and t, respectively, Q_{dl} is double-layer charge, and Q_{ads} is the Faradaic charge due to the reduction of adsorbed CAP. Q-t and Q-t¹/² plots were recorded and shown in Figure 5 Q_{ads} (the difference of the two intercepts) was produced by the adsorbed CAP. According to the formula given by Anson [38], the value of Q_{ads} and Q_{dl} were calculated as 4.8×10⁻⁶ C and

 2.13×10^{-6} C respectively. Using Laviron's theory of Q_{ads}= nFAΓ*, the saturating adsorption capacity of CAP on MTFE was calculated as 5.4×10^{-10} mol cm⁻¹.

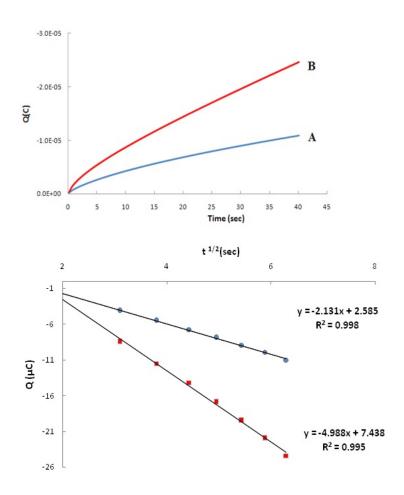


Fig. 5. Chronoamperograms and Q vs. $t^{1/2}$; Corresponding data were derived from Q vs. t obtained at the MTFE/GCE in the presence (red) and absence (blue) of CAP (28 μ M) in 2.5 mM buffer solution (pH 2.0)

3.7. Analytical parameters

Analytical features of the method such as linear range of the calibration curve, LOD, accuracy, and precision were examined in order to validate the proposed method. Figure 6 shows that CAP voltammograms are in the concentration range of 4.5 to 64.5 μ M. Under optimum conditions, the calibration graph for CAP determination was obtained using the correlation coefficient (R²) of 0.992. The regression equation for the line was i (μ A)=0.067X (μ M)+2.662 (n=9), where x is CAP concentration in μ M and (i) is peak current intensity in Ampere (Figure 6). Under optimum experimental conditions, LOD of the proposed method was based at three times. The standard deviation of the blank divided by the slop of

calibration curve ($3S_b/m$) [39] was 0.6 μ M for CAP (n=6). Also, relative standard deviation (RSD%) for determinations of 23 μ M of CAP (n=6) was 6.9%, respectively. Table 1 compares the response characteristics of the proposed electrode with some reported methods that have been reported for making CAP determinations.

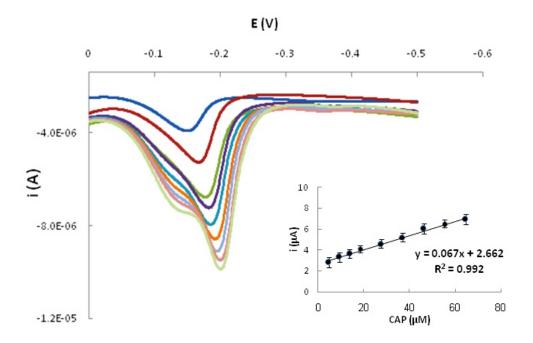


Fig. 6. SW voltammograms of CAP in 2.5 mM phosphate buffer solution (pH 2.0) containing different concentrations of CAP (up to down) 4.6, 9.2, 13.8, 14.8, 27.6, 36.8, 46.1, 55.3, and 64.5 μ M and calibration curve

3.8. Analytical application

Under optimum conditions, the proposed analytical procedure was applied to detect CAP in the samples of tablets (25 mg/tablet) and (50 mg/tablet) from different companies. The analytical results obtained by the standard addition method are listed in Table 2. Therefore, 3 tablets from each brand were accurately weighed and finely powdered separately. The appropriate amount of powder (equal to the weight of one tablet for each different brand) was accurately weighed and dissolved into 50 mL distilled water. The mixture was shaken for 30 min and filtered into a 100 mL volumetric flask. Then, the sample solutions of CAP tablets were analyzed by standard addition. The results obtained from this study were acceptable; thus, the proposed method can be recommended for making CAP determinations in the tablet samples. Results of the analysis are shown in Table 2.

Table 1. Comparison of the proposed method with some other reported methods in the literature for CAP determination

Analytical technique	LDR ^a (µM)	LOD b (µM)	Reference
Electrochemistry (Static mercury drop electrode)	2.3–230	0.029	4
Separation (High-performance liquid chromatographic)	42.8-690	0.008	5
Spectroscopy (Chemiluminescence)	0.1-6.0	0.037	6
Spectroscopy (Spectrophotometry–titrimetry)	552-2393	D.N ^c	7
Spectroscopy (Spectrophotometry)	1.38-13.8	0.18	8
Spectroscopy (Atomic absorption spectrometry)	4.6-184	D.N	9
Electrochemistry (Modified CPE electrode)	0.5-600	0.2 ^d	10
Electrochemistry (Modified CPE electrode)	4–110	1.1	12
Electrochemistry (Boron-doped diamond electrode)	50-3000	25	13
Electrochemistry (Modified CPE electrode)	0.8-65	0.3	14
Electrochemistry (CPE electrode)	50-10000	14	15
Spectroscopy (Colorimetric determination)	200-1400	D.N	16
Electrochemistry (Nano-composite electrode)	0.2-5.8	0.09	17
Electrochemistry (Supported manganese sensor)	3-0.3	0.9	18
Spectroscopy (Derivative UV spectrophotometry)	23-115	1.4	19
Electrochemistry (MTFE)	4.6-64.5	0.6	This work

^a Linear dynamic range (LDR)

Table 2. Determination result of CAP in real samples by standard addition method

Sample	Found (mg per tablet)	Added (μM)	Found (µM)	Recovery (%)
Tablet 1 ^a	23.81±0.02	0	27.40±0.02	-
	_	9.2	36.91±0.01	103.2
		18.4	45.40±0.02	97.9
Tablet 2 ^b	45.20±0.02	0	26.01±0.03	_
	_	9.2	35.21±0.02	100.1
		18.4	44.81±0.01	102.1

^bLimit of detection (LOD)

^c Data not available

^d Experimental detection limit

 ^a Tablet (25 mg CAP per tablet. product of Soha company).
^b Tablet (50 mg CAP per tablet. product of Exir company).

^c Average of three determinations.

4. CONCLUSION

In this paper, mercury was simply and successfully deposited onto the surface of GCE. The film electrode was shown to be extremely useful for highly adsorptive stripping voltammetric measurements of CAP. The fabricated sensor showed good precision, reproducibility, stability, and ease of preparation. The detailed electrochemical characters of CAP were studied and calculated. A reasonable reaction mechanism of CAP at the MTF/GCE was also proposed. Combining the advantages of MTFE such as its high surface area and conductivity and high intensity to thiol groups greatly improved the electrochemical response signal of CAP.

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