Simultaneous Determination of Paracetamol, Ascorbic Acid and Codeine by Differential Pulse Voltammetry on the Aluminum Electrode Modified by Thin Layer of Palladium

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Abstract
In the present work an aluminum electrode was modified with thin layer of metallic palladium. The ability of the electrode for electrooxidation and subsequent differential pulse voltammetric determination of paracetamol (PCT), ascorbic acid (AA) and codeine (CO) was evaluated. The results obtained indicated that a linear range from 0.1 – 3 mM and a detection limit of 5 μM for both three compounds is accessible. The peak separation of AA, PCT and CO is more than 300 mV large enough, allowed simultaneous determination of these compounds. The proposed method was applied for determination of AA, PCT and CO in some real samples.

Keywords: Modified aluminum electrode, Paracetamol, Ascorbic acid, Codeine, Palladized aluminum surface, Palladium

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1. Introduction

Electroanalytical measurement using chemically modified electrodes has become of growing importance in different applications in medicine and pharmaceutical analysis. Dicyano-bis(1,10 phenantroline) modified glassy carbon electrode was used for electrochemical detection of PCT after its liquid chromatographic separation from urine [1]. Determination of PCT via its oxidation on a bore-doped diamond electrode was reported [2]. A carbon film resistor electrode for amperometric determination of acetaminophen in pharmaceutical formulations [3]. Selective voltammetric determination of AA has been a major target of electroanalytical research. It has been demonstrated that AA can undergo mediated oxidation via a homogeneous process by electrogenerated ferricinium derivatives [4]. In addition some chemically modified electrodes with various conductive polymers [5 – 7] and active mediators [8 – 18] immobilized at the electrode surface for the catalytic oxidation of AA have been used. Y. Shih et al. reported the determination of CO using a nontronite clay-modified screen-printed electrode by both square-wave voltammetry and flow injection analysis [19]. Also the amperometric detection of CO and its metabolite, morphine following capillary zone electrophoretic separation has been described [20]. A carbon-disk electrode used as working electrode for CO and morphine exhibited a good response at 0.90 V (vs. Ag/AgCl). Recently we have reported an electrochemical method for simultaneous determination of CO and morphine in pharmaceuticals using a Prussian blue modified aluminum electrode [21].

New pharmaceutical preparation and clinical diagnosis appearing require fast, inexpensive and specific method for the simultaneous determination of some drugs. Computer-controlled instrumentation and multivariate calibration methods are playing a very important role in the multicomponent analysis of mixtures [22 – 24].

Various analytical techniques for the simultaneous determination of PCT, aspirin and caffeine or CO, including liquid chromatography [25 – 27], spectrophotometry [25, 28, 29] spectrofluorometry [30] FT-Raman spectroscopy [31] have been reported. Also some studies about the simultaneous determination in binary, ternary or multicomponent pharmaceuticals by spectrophotometry in combination by chemometry have been performed. Two new methods for the simultaneous determination of acetylsalicylic acid, PCT and caffeine based on total absorbance measurements and their processing by multiple linear regression and partial least-squares regression were proposed [32]. An analytical procedure proposed for the simultaneous determination of caffeine, aspirin and PCT in pharmaceutical preparations by partial least-squares treatment of a flow-through multisensor [33]. A micellar electrokinetic capillary chromatographic method has been developed to analyze the pharmaceutical preparations containing ternary combination of PCT, caffeine and propyphenazone [34]. At last a near infrared spectroscopic method for the simultaneous determination of the active principles PCT, AA, dextrometor-

phan hydrobromide, caffeine and chlorpheniramine maleate in a pharmaceutical preparation was developed [35]. The five active principles are quantified, using a partial least-squares regression method. Simultaneous determination of AA, PCT and caffeine in drug formulations by differential-pulse voltammetry using a glassy carbon electrode was also reported [36]. A paper on the development of the spectrophotometric and cyclic voltammetric methods for simultaneous determination of ascorbic acid and acetaminophen and their applications in the analysis of effervescent dosage forms is previously published [37]. The simultaneous determination of PCT and AA at a boron-doped diamond electrode by differential pulse voltammetry [38] and chronoamperometry in acidic Britton – Robinson buffer solution is reported [39]. Recently a carbon paste electrode (CPE) modified with thionine immobilized on multi-walled carbon nanotube (MWCNT), was prepared for simultaneous determination of ascorbic acid and acetaminophen in the presence of isoniazid [40]. To our knowledge there are no reports on the simultaneous electrochemical determination of PCT and CO. or PCT, AA and CO.

Considering that the physical and chemical properties of a metal thin layer on a foreign substrate are different from those of bulk metal [41], recently we have reported the modification of Al substrate with metallic palladium particles [42].

In the present paper we report an electroanalytical strategy, based on the electro oxidation of PCT, AA, and CO at Pd/Al modified electrode for the simultaneous differential pulse voltammetric determination of the three compounds.

2. Experimental

2.1. Chemicals

The commercial aluminum bar with purity of $99.9 \pm 0.9\%$ was used as substrate for electrode matrix. Palladium chloride, ammonia, acetic acid, sodium hydroxide, caffeine, codeine, starch, acetaminophen, analytical grade were used as received. The following commercial pharmaceuticals available from local sources were subjected to the analysis. Tablets containing PCT or AA as the single component; or combined with aspirin or with CO or with AA purchased from local sources.

2.2. Electrode Preparation

The aluminum surface fitted in a Teflon tube [43] was polished, first by a medium emery paper (320-grit) and then by a fine grade (1500-grit) to expose a relatively mirror surface. The polished surface is cleaned by dipping in 1 M HNO_3 for about 1 min and then rinsed with doubly distilled water. The electroless deposition of metallic palladium was carried out by dipping the cleaned surface in 2 mM $PdCl_2$ dissolved in 25% ammonia solution with forming Pd $(NH_3)_2Cl_2$ complex (plating solution) for 4 min [42].The electrodes were characterized by cyclic voltammetry using a potentiostat/galvanostat AUTOLAB, model PGSTA30 and by scanning electron microscopy (SEM) using a LEO 440i Oxford instrument.

2.3. Differential Pulse Voltammetry

Ten mL of 0.25 M KNO_3 solution buffered with 0.5 M acetic/acetate at pH 5 transferred to a voltammetric cell, an accurate volume of the individual or binary or ternary mixture standard solutions of PCT, CO and AA or pretreated real sample solution was added to the cell and subjected for individual or simultaneous differential pulse voltammetry (DPV) with a sweep rate of 10 mV s^{-1} on the Pd /Al modified electrode The amount of analytes were determined by means of standard addition method to the cell. All voltammograms were recorded with a three-electrode system. A polarograph E626 was used (from Metrohm) for polarographic measurements.

2.4. Analysis of Tablets

An accurately weighed portion of finely powdered sample obtained from three tablets, equivalent to about 75 mg of drugs was transferred to a 10 mL assay tube and was extracted with two 5 mL portions of 0.5% acetic acid in doubly distilled water. The extracts were combined in a 25 mL flask and diluted to volume. A 0.1 mL portion of extract was diluted with 10 mL of 0.25 M KNO_3 solution buffered with 0.5 M acetic/acetate at pH 5 in a voltammetric cell and subjected for DPV measurement.

2.5. Interference Study

In order to investigate the interference of some species frequently found with the analytes a 10 mL portion of 4 mM analyte dissolved in electrolyte solution was transferred into an electrochemical cell, then the differential pulse voltammetric signal was measured as described in section 2.3. The interference of the desired substance was investigated by gradual addition of its standard solution to the cell until a tolerated concentration (i.e. causing a maximum error of 2% in voltammetric signal of analyte is achieved.

3. Result and Discussion

3.1. Cyclic Voltammetry of AA, PCT and CO

We have reported a detailed and perfect study on the individual electrochemical behavior and kinetic characteristic of AA, PCT and CO on the PB/Pd-Al electrode as an improved electro-catalyst [44]. Here we describe only the voltammetric behavior of these compounds by cyclic

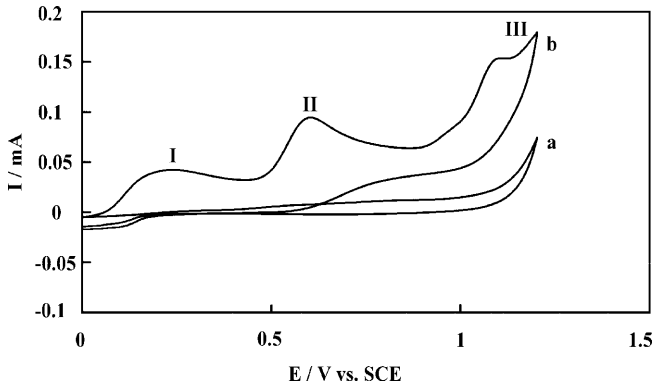

Fig. 1. Typical cyclic voltammograms of Pd/Al modified electrode in 0.25 M $KNO_3 + 0.5$ CH_3COO^- solutions of pH 6 (a) in the absence and (b) in the presence of 5 mM AA, PCT and CO, scan rate: 30 mV s^{-1} .

voltammetry that lead us to the choice of a convenient electrochemical technique for their simultaneous determination. The cyclic voltammograms of the Pd/Al modified electrode recorded at a potential scanning range 0 to 1 V in the absence and presence of PCT, AA and CO in 0.25 M $KNO_3 + 0.5$ M acetate buffer of pH 6 showed that in the absence of these compounds no peak was observed . While upon the addition of 5 mM AA, PCT and CO an anodic peak at 0.2 V, 0.6 and 0.95 V appeared at less positive potentials range, compared with those obtained at bulk noble metals or carbon base electrodes (Figure 1) [2, 12, 37]. This behavior is consistent with an electrocatalytic effect on the electrooxidation of these compounds. The anodic peak current for the three compounds increased with scan rate (not shown). The plot of I_p versus square root of the scan rate $v^{1/2}$ is linear suggesting that the reaction is mass transfer controlled. On the other hand the peak current increased with increasing the analytes concentration and the calibration graph is linear in the concentration range about 0.5 – 30 mM, with a correlation coefficient of 0.999 (not shown). As seen in Figure 1 the potential separation between AA, PCT and CO peaks is more than 300 mV, permits the simultaneous voltammetric measurement of three component of the solution.

3.2. Individual Differential Pulse Voltammetry

Differential pulse voltammograms recorded for AA and PCT show a well-defined peak with $E_p = 0.2$ and 0.6 mV, respectively. The calibration graphs constructed over concentration range $10^{-4} - 3 \times 10^{-3}$ M. and $10^{-4} - 5 \times 10^{-3}$ M. are linear with correlation coefficient of 0.997. The detection limit for both compound was 5×10^{-5} M and the relative standard deviation for three replicate determinations of 5×10^{-4} M of AA and PCT was 1.5%. Similar study has been carried out in the case of CO and a detection limit of 2×10^{-5} M was found.

3.3. Simultaneous Differential Pulse Voltammetry of PCT, AA and CO

The simultaneous voltammetric determination of AA and PCT has been carried out by more sensitive electrochemical technique i.e. DPV. Figure 2 and 3 show the DP voltammograms of the solutions having the mixture of AA and PCT with same concentration at Pd/Al electrode. As can be seen in Figures 2 and 3, two well defined oxidation peaks of AA and PCT at about 0.2 and 0.6 V observed respectively. The results show that the peak potential separation of 400 mV and the peak current of AA or PCT in the presence of fixed concentration of each other is linearly dependant on their concentrations (Inset in Figures 2 and 3) .This permit the simultaneous differential pulse voltammetric determination of AA and PCT. Similar result was obtained for a solution having the mixture of PCT and CO with same concentration at Pd/Al electrode. As seen in Figure 4 the peak separation of PCT and CO is 300 mV large enough, allowing simulta-

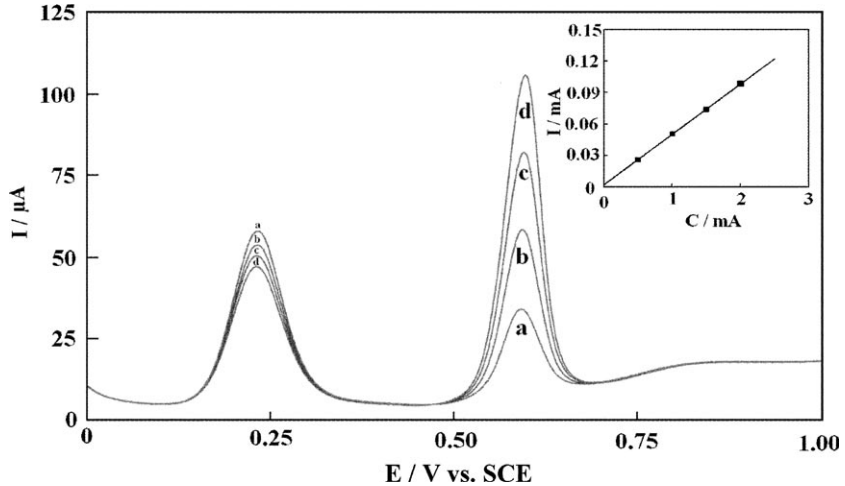

Fig. 2. Differential pulse voltammogram of 0.5 mM AA in the presence of 0.5 – 2 mM PCT, inset Fig calibration graph for PCT.

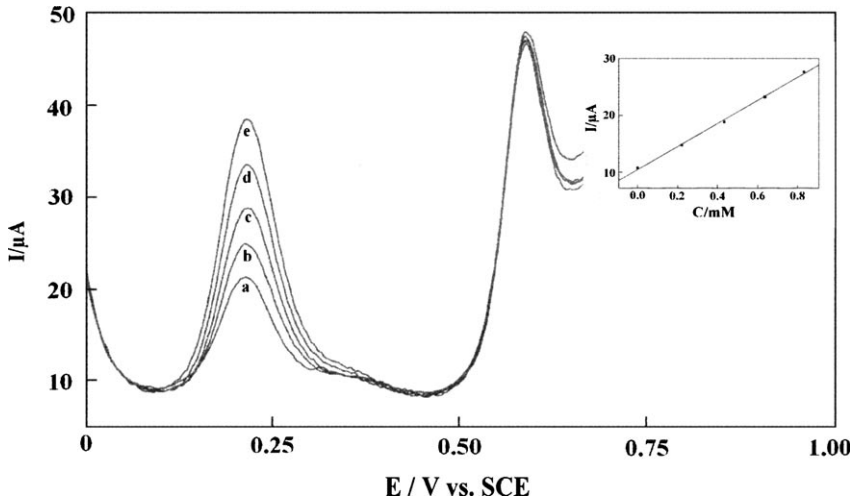

Fig. 3. Differential pulse voltammogram of 0.5 mM PCT in the presence of 0.5 – 1.3 mM AA, inset Fig. calibration graph for AA.

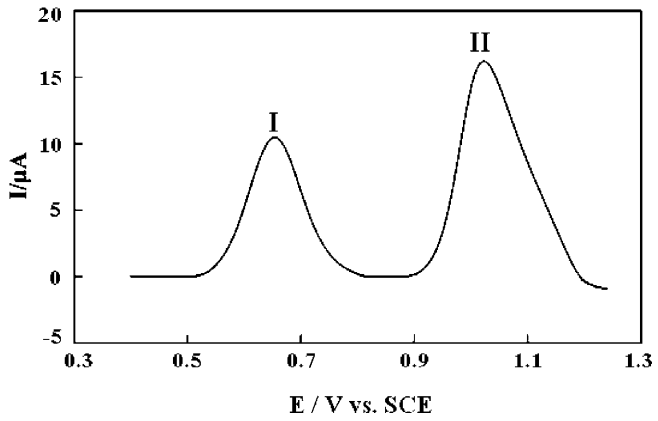

Fig. 4. Differential pulse voltammogram of 5 mM PCT in the presence of 5 mM CO. Experimental conditions as Fig. 2.

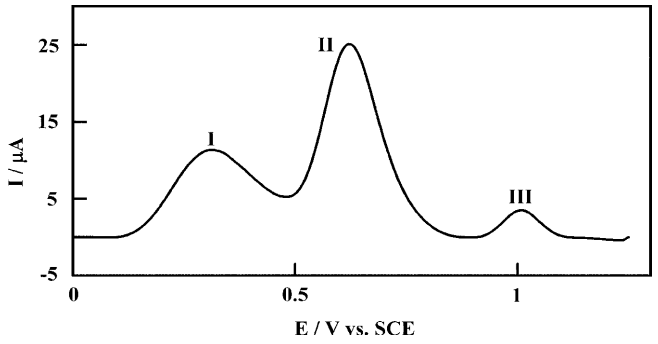

Fig. 5. Typical differential pulse voltammogram recorded in 5 mM PCT + 7mM AA + 3 mM CO. Experimental conditions as Fig 2.

neous determination of PCT and CO. Typical DP voltammogram for a solution having the mixture of AA and PCT and CO is also shown in Figure 5. This confirms that the simultaneous determination of the three compounds is easily possible in a mixture solution.

3.4. Interference Study

The possible interference in the pharmaceutical dosages containing AA, PCT or CO are N acetyl salicylic acid, caffeine, nicotinamide, folic acid, glucose, sucrose and starch was investigated. It is noteworthy, a foreign compound was considered to interfere seriously when it gave a determination error of more than 2%. The results obtained show that the presence of ten-fold excess of N-acetyl salicylic acid, caffeine and hundred-fold of nicotinamide, folic acid, glucose, sucrose, and starch did not significantly influence of the determination of PCT, AA and CO upon the experimental conditions. The absence of interference from these substances showed that the present strategy can be used for the simultaneous determination of PCT, AA and CO in the presence of common concomitant substances in real samples.

3.5. Performance and Stability of the Pd/Al Electrode

Deposition of metallic Pd on the Al surface by simple and rapid dipping of polished Al surface in $Pd(NH_3)_4^{2+}$ solution, provides a good physical dispersion of the catalytic centers leading to a highly active electrode surface suitable for efficient electrocatalysis. This was confirmed by scanning electron microscopic (SEM) study of naked and Pd plated Al surfaces (not shown) [44]. Reproducibility of the electrode response with the electrochemical techniques used in the present work (e.g. *RSD* of 5 replicate DPV measurements of 0.8 mM of AA was 1.6%) confirmed that there was not any fouling phenomena, during the analytes (i.e. AA) reduction on the electrode and there was also no detachments of the catalyst (i.e. Pd particles).

The effect of various factors, including the exposing time of the electrode in air and in supporting electrolyte, on the stability and electrochemical behavior of the electrode were investigated We have found that the stability and reproducibility of the electrode response are less affected by the

Table 1. Results for the determination of AA, PCT and CO in pharmaceuticals.

Sample	Found amount (mg/mL) [a]				
	Proposed method	*RSD*%	Official method [b]	*RSD*%	*t*
Vitamin C tablet (chevable) 250 mg	262	0.3	261	0.57	0.73
Multivitamin syrup 60 mg/5 mL vitamin C	60.47	1.74	61.641	2.85	0.98
Acetaminophen tablet (325) mg	317.6	0.22	321.1	0.7	0.77
Acetaminophen (500 mg)	485	0.23	478.2	0.7	0.22
+ Codeine (8 mg) tablet	7.9	1.2			
Acetaminophen (162.5 mg) + aspirin	170.7	0.32	171.2	0.9	0.8
Synth. tablet Codeine (10 mg)	10.03	4.5	–	–	–
+ AA (150 mg)	150.6	1.3	151	0.8	–
+ Acetaminophen (250 mg)	255	0.06	248	0.6	–
Efferalgan efferverscent					
Tablet 200 mg vitamin C	203.6	1.4	206.2	2.1	0.9
+ 330 mg acetaminophen	344.2	0.25	332	1.2	–
Codeine (10 mg) + aspirin Tablet	10.03	4.5	–	–	–
Synth. tablet AA(150mg)	150.6,	1.3	151	0.8	–
+ Acetaminophen (250 mg)	255	0.06	248	0.6	–
Efferalgan efferverscent					
Tablet 200 mg vitamin C	203.6	1.4	206.2	2.1	0.9
+ 330 mg acetaminophen	344.2	0.25	332	1.2	–

[a] Average of three replicate determinations.
[b] For vitamin C USP iodometric titration [45], for acetaminophen spectrophotometry [46].

factors mentioned above. In addition the results obtained showed that the stability and consequently the current response of the electrode in AA, PCT and CO solutions in the absence and in the presence of some concomitant compounds did not change significantly for several uses (about 15 times). Furthermore at a constant potential under hydrodynamic conditions (stirred solutions), the oxidation current of the three compounds is proportional to their concentrations and the differential pulse voltammetric behavior of the electrode maintained almost constant for long times (about one week).

3.6. Application

The individual or simultaneous determination of PCT and AA in some real samples was carried out and the results are presented in Table 1. Similarly the amount of CO in the presence of PCT and acetyl salicylic acid was determined by standard addition method and is shown in Table 1. As a real pharmaceutical preparation containing simultaneously AA, PCT and CO was not available, the suitability of the method for their determination was investigated by analysis of a synthetic product. For this purpose we have prepared a synthetic Tablet (0.15 g AA, 0.25 g PCT 0.1 g CO and 0.3 g

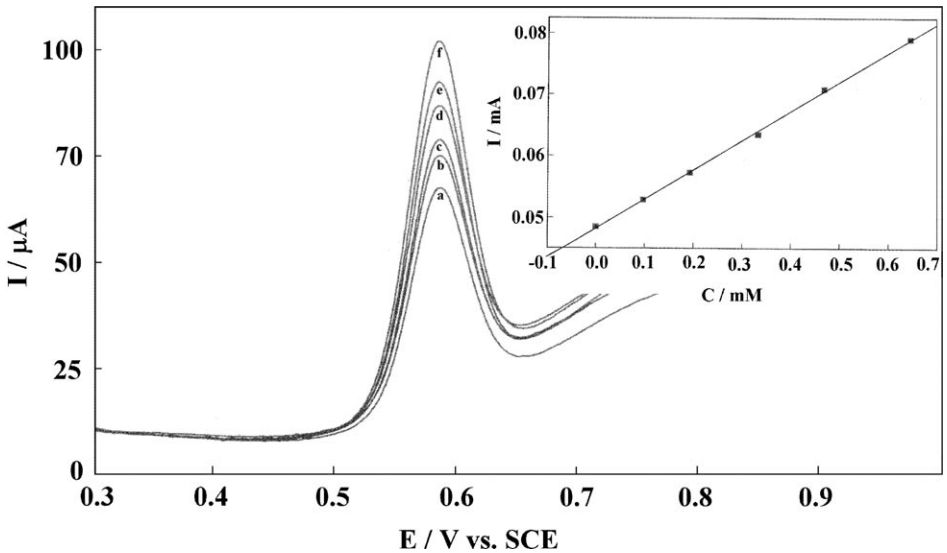

Fig. 6. Differential pulse voltammogram of 10 mL 0.25 M KNO_3 + 0.5 CH_3COO^- solutions of pH 6 after (a) addition of 0.1 mL acetaminophen sample solution (b – f) a + (0.1 – 0.7 mM) successively added standard PCT solution (10 mM), Inset: standard addition graph, experimental conditions as Fig. 2.

Table 2. Comparison of electroanalytical data for simultaneous determination of AA and PCT.

Electrode	Method	Dynamic range	Peak resolution	*LOD*	Reference
Modified CP	LSV	1 – 10 mM (AA) 3 μ M – 7.5 mM(PCT)	300 mV	–	[37]
Boron doped diamond	DPV	0.01 – 0.1 mM	250 mV	0.8 μM	[38]
Boron doped diamond	CA	0.01 – 0.07 mM	250 mV	1.4 μM	[39]
Modified CP	DPV	1 – 100 μM (AA) 0.1 – 100 μM (PCT)	303 mV	– –	[40]
Pd/Al	DPV	0.1 – 3 mM (AA) 0.1 – 5 mM (PCT)	400 mV	50 μM	This work

starch) according to a sample formulation reported in literature. After mixing this component in the porcelain mortar, a convenient amount of mixture was subjected for DPV measurement. The obtained results are given in Table 1. Typical pulse voltammograms related to the measurement of PCT in a Tablet by standard addition method are displayed in Figure 6.

3.7. A Comparative Study of Performances of the Existing Methods

The electrochemical methods used for simultaneous determination of AA and PCT in pharmaceutical are limited. There is also a lack of simultaneous determination of PCT and CO and both three compounds. The literature study in the introduction section involves the works reported. The analytical performances of published methods for simultaneous determination of AA and PCT are summarized in Table 2. As seen in Table 2 the dynamic range of the present method is comparable with those of other methods. Although the slightly high detection limit, the sensitivity of the present method is acceptable. The prepared modified electrode in the present work shows several advantages such as ease of preparation, long-time stability, and excellent reproducibility. The great advantage of the present differential pulse voltammetric method in comparison with the other electrochemical methods of the other electrodes, is the observation of a peak potential separation more than 400 mV for AA and PCT and about 300 mV for PCT and CO, permitting the more precise and selective simultaneous determinations of AA, PCT and CO in their mixture solutions.

4. Conclusions

Metallic palladium on an aluminum substrate can be used for the anodic oxidation of AA, PCT and CO at a potential rang 0.0 – 1.0 V. The differential pulse voltammograms recorded for the three compounds show that the peak are well defined and differential pulse voltammetry is suited for the individual determination of AA, PCT and CO at μM concentration level. Also the peak potential separation more than 300 mV between AA and PCT or between PCT and CO permits the simultaneous determinations of AA, PCT and CO. The ease of preparation of the electrode in combination with the relatively low detection limit and selectivity represent important factors for use of the present electroanalytical strategy in routine quantitative analysis of pharmaceuticals. Furthermore the method has a clear advantage over the spectrophotometric method for the analysis of samples, containing fine particles or deep color or high viscosity. These make the electrode usable in electroanalysis of the both analytes in biological real samples that is in progress in our laboratory .

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