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Short Communication

Electrochemical Behavior and Determination of four drugs using Multi-Wall Carbon Nanotubes Modified Glassy Carbon Electrode

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A glassy carbon electrode (GCE) that is modified with a thin film of multi-wall carbon nanotubes (MWCNT) is a useful tool for determining concentration, and a new method for obtaining this type of electrode with excellent determination characteristics is presented. In this paper, the electrochemical behavior of picoplatin, caffeic acid, ferulic acid, and breviscapine on the electrode was studied by cyclic voltammetry and showed effective improvements in terms of the sensitivity of measurement. The optimum conditions for the determination were investigated. Differential pulse voltammetry was used to determine the content of four drugs in the actual sample. The electrochemical detection method based on MWCNTs/GCE has a low detection limit, good recovery, and precision in pharmaceuticals determination. Therefore, the method is simple, rapid, accurate, and reliable to apply in pharmaceuticals field.

Keywords: MWCNTs/GCE; Pharmaceuticals determination; Electrochemical Behavior; Detection limit

1. INTRODUCTION

Due to excellent electrical and catalytic properties a number of electrochemists pay more attention to nanostructure materials [1]. The catalytic capabilities of electrode modified nanostructures, such as nanowires and carbon nanotubes (CNTs), can reduce the excess voltage needs for a redox reaction to become kinetically feasible [2, 3]. A current-voltage system can be produced by this phenomenon, and it is more reversible than that of the same materials in traditional backgrounds [4-5].

Considering these advantages in the field of material science and electrochemistry, CNTs are used as a new type of materials [6] and bring significant influence on a wide range of applications [7]. Excellent characteristics of CNTs, such as closed topology [8] and tubular structure [9], make them more distinguished from other carbon forms and provide more convenience for chemical and electrochemical researches. Many scientists believe that CNTs has also feature electrically, which is similar with semiconductor and metal on the base of atomic structure [10]. In many studies CNTs used as an electrode, because reaction of charge-transfer can be improved by it [11]. In other words, many advantages of CNTs-modified electrodes, such as small size, high electrical and thermal conductivity, mechanical strength, specific surface area and chemical stability, are better than other forms of carbon electrodes [12].

Simple, fast and sensitive methods for its determination in pharmaceutical and biological samples are very important. To determinate concentration of some drugs a lot of analytical techniques, such as chemiluminescence [13], spectrofluorimetry [14], liquid chromatography [15], capillary electrophoresis with electrochemiluminescence detection [16], liquid chromatographic-mass spectrometry [17], and voltammetric methods [18], have been reported. Nevertheless, some incomplete processes often affect accuracy of experiment result. For example, analytic time may be very long for derivatization steps, even some purely organic solvents must be employed in some situations. Obviously, some advantages of electrochemical methods, such as high sensitivity, low expense and simplicity, have been attractive to many people [19, 20].

Cis - two chloro - one, (2 - methylpyridine) and platinum is a new generation of platinum group metal antitumor drugs after cisplatin, carboplatin and oxaliplatin (Figure 1, A). It is mainly used for the treatment of small cell lung cancer, prostate cancer, colorectal cancer and ovarian cancer. Moreover, II phase clinical research has been carried out in the worldwide, showing the performance of platinum depended anticancer drugs that are displayed as carboplatin and cisplatin. Because of some advantages, such as broad-spectrum, high efficiency, oral administration and low toxicity, it can improve the shortage of traditional platinum group anticancer drugs that resist cross resistance [21].

Some agricultural products, such as potatoes, vegetables, cereals and coffee beans, contain rich antioxidants, so calcium and other nutritional compounds were easily transferred into the organs after oral administration, then in urine and plasma specific metabolites can found [22]. Caffeic acid [3 - (3,4- two hydroxyphenyl) -2- acrylic acid, Ca] is one of derivative from hydroxyl cinnamic acid (Figure 1, B).

In traditional Chinese medicine many researchers always concern in woody, angelica and cimicifuga heracleifolian because the effective components, ferulic acid (4- hydroxy -3- methoxy cinnamic acid), play a key role in Chinese medicine (Figure 1, C). It can be found in many plant regions and can be absorbed by the small intestine and then into the urine [23].

Breviscapine is a mixture of scutellarin and apigenin -7- O-B-D- glucuronic acid but the number of scutellarin is more than 95%. Breviscapine, as an important component of flavonoids, origin from Erigeron breviscapus (Figure 1, D). Due to the prevention and treatment of various microcirculatory disorders and cardiovascular diseases Erigeron breviscapus has become very popular in main Asian regions. Breviscapine has good effect to reduce the inflammatory symptoms of many disorders. The degree of liver fibrosis in streptozotocin induced diabetic rats can dramatically decline by the drugs [24].

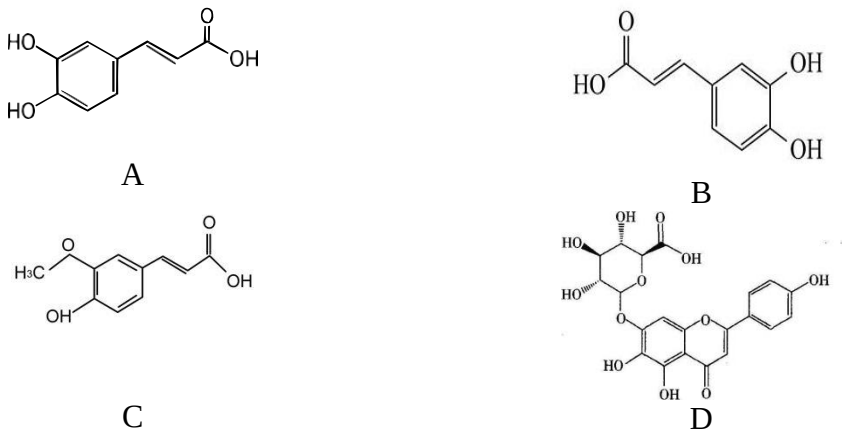

Figure 1. Chemical structure of four drugs A: Picoplatin, B: Caffeic acid, C: Ferulic acid, D: Breviscapine

In this paper MWCNTs/GCE which is a glassy carbon electrode (GCE) modified with an MWCNT thin film is as an important tool to determinate concentration of four drugs. Depended on the change of electrochemical behavior MWCNTs/GCE can enhance the oxidation peak current of these drugs and increase the sensitivity of determination. All parameters of the experiments were optimized and developed a set of determination method for the measurement of these drugs according to voltammetric technique. The method displays many advantages such as rapid response, high sensitivity and low cost.

2. EXPERIMENTAL

2.1. Reagents and chemicals

Carboxyl functionalized multiwalled carbon nanotubes (MWCNTs, TNMH3 type, 10-20 nm, wt > 95%, Chengdu Organic Chemistry Institute of Chinese Sciences Academy); picpolatin standard product (content >99.9%, Guiyan pharmacy Co.Ltd of Kunming, China); caffeic acid (content >99.9%, Mansite biology technology Co.Ltd of Chengdu, China); ferulic acid (content >99%, Qianjinxiang pharmacy Co.Ltd of Hunan, China); breviscapine (content > 99%, Longjin pharmacy Co. Ltd of Kunming, China). Other reagents were of analytical grade and double-distilled water was used to dissolve relate reagents in the experiment

The standard solution of 1×10^{-3} M four drugs was prepared with different buffer. These solutions were placed at 4℃ with refrigerator and in darkness with silver paper.

2.2. Apparatus

Three-electrode system include a glassy carbon electrode modified with MWCNTs as the working electrode, a saturated calomel electrode (SCE) as the reference electrode and a platinum electrode as auxiliary electrode. Multifunction electrochemical analysis system (MEC-12B) was produced by JIANGFENG electroanalytic technologies Co. Ltd from Jiangsu in China.

2.3. Preparation of MWCNT/GCEs electrode

To purify some MWCNTs they are exposed to concentrated HCl and ultrasound; then, these materials were circumfluenced at 140 ℃ about 8 hours. Doubly distilled water was used to clean MWCNTs and when pH value of the eluent became 7.0 MWCNTs was dried at 100℃in an oven. These MWCNTs was made to powder in a mortar and pestle.

First, 10.0mg of MWCNTs powder was suspended in water by ultrasonic equipment and become black solution. Then the glassy carbon electrode was polished to mirror face with 0.05μm Al_2O_3 powder and was cleaned in absolute ethyl alcohol and doubly distilled water under the exposure to ultrasound for 5 min. Finally, 8μL of suspension solution was added on the glassy carbon electrode and dried under the infrared lamp. This is MWCNTs/GCE electrode.

2.4. Preparation of four drugs

The standard solution of picoplatin was prepared with 0.05 M KCl (pH7.4) under exposure to ultrasound, the standard solution of caffeic and ferulic were prepared with B-R buffer solution (pH5.72), and the standard solution of brevisacapine ones was prepared with phosphoric acid buffer solution. The concentration of all the standard solutions was 1.0×10^{-4} M and placed at 4 ℃ in refrigerator and darkness immediately after prepared.

2.5 Analytic procedure

A certain amount of the stored solution of different drug was diluted with buffer solution to 10 mL volume, then transfer into the electrochemical cell. Under the condition of scanning rate of 50 $mV\cdot s^{-1}$ and potential range from -0.8V to 1.1V with the three-electrode system the cyclic voltammetry was conducted to record CV curve. At the same time the differential pulse voltammetry was also analysis in pulse weight of 250 ms, pulse range of 20 mV and pulse interval of 250 ms. To get rid of the adsorbate and receives renewable electrode surface, MWCNTs/GCE electrode was performed to sweep with eight successive cyclic voltammetry in the pure buffer solution after each measurement.

3. RESULTS AND DISCUSSION

3.1. Electrochemical Behavior of four drugs

In figure 2(a), the electrochemical behavior of picoplatin was analysis with cyclic voltammetry (CV) under the condition of 0.05 M KCl buffer with pH 7.4. Within the GCE picoplatin appeared slight peak of oxidation-reduction showing as curve (a). But picoplatin exhibited a couple of oxidation and reduction peaks strongly, which is a well-shaped and with low background. When oxidation peak potential (Epa) was 0.5 V and reduction peak potential (Epc) was -0.37 V, peak potential difference (△E) was 0.87 V. When oxidation peak current (Ipa) was 7. 35μA and reduction peak current (Ipc) was 5.66μA, ratio of oxidation and reduction peak current (Ipa/Ipc) is 1.30. So it is testified that the oxidation and reduction peak had quasi-reversible feature. Compared with GCE the oxidation and reduction peak

current of picoplatin became lager significantly in MWCNTs /GCE, and which can show that MWCNTs in modified electrode can play remarkable catalytic sensitization role to electrochemical action of picoplatin.

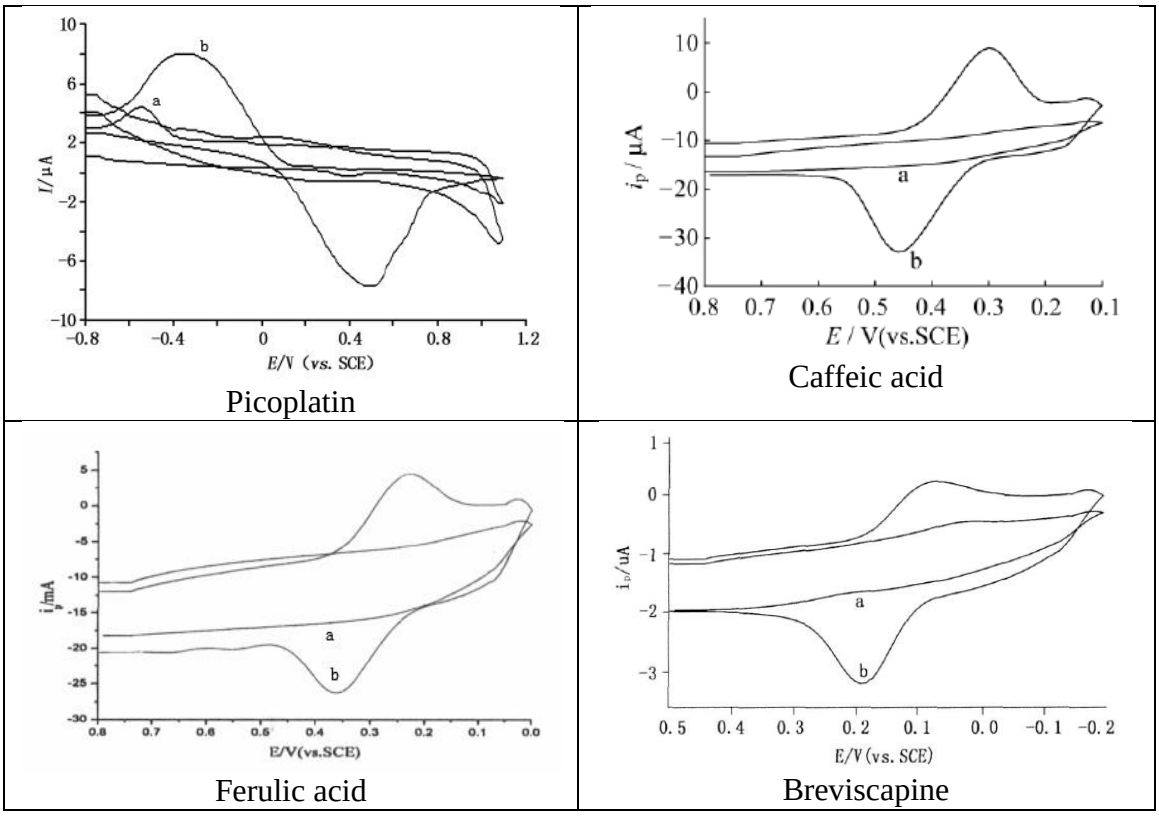

Figure 2. Cyclic voltammogram of four drugs in supporting electrolytes, GCE(a), MWCNTs/GCE(b), 0.05 mol L^{-1} HAc-NaAc buffer solution, PBS buffer solution and KCl buffer solution (picoplatin), 0.04 mol L^{-1} BR buffer solution (caffeic acid and ferulic acid), and 0.1 mol L^{-1} PBS buffer solution (breviscapine), and scan rate is 100 mVs^{-1}.

At the same time, potential and current of oxidation and reduction from other drugs had almost same tendency with picoplatin, that is as follows. Caffeic acid: Epa = 0.47 V, Epc =0.32 V, △E =0.15 V, Ipa =18.5 μA, Ipc =15.7 μA, Ipa/Ipc =1.2; Ferulic acid: Epa =0.36 V, Epc =0.23 V, △E=0.13 V, Ipa =4.68 μA, Ipc =6.44 μA, Ipa/Ipc =0.73; Breviscapine: Epa = 0.19 V, Epc =0.07 V, △E =0.12 V, Ipa =11.7 μA, Ipc =8.16 μA, Ipa/Ipc =1.43. These curves showed that characteristics of quasi-reversible is found in the electrode reaction process of four drugs at MWCNTs/GCE [25].

3.2. Effects of Scan Rate

When the range of scan rates started change from 40mV s^{-1} to 100 mV s^{-1}, the oxidation peak current of picoplatin (100mg/L) was measured by linear sweep voltammetry (LSV). It was found that the oxidation and reduction peak currents are proportional to the square root of the scan rate, indicating

that the oxidation and reduction of picoplatin at the MWNT-modified GCE is controlled by the diffusion of picoplatin from bulk solution to the MWNT film.

When scan rate ranging from 100mV $s^{-1}$to 400 mV s^{-1} the oxidation and reduction peak currents are proportional to the first power, indicating that the oxidation and reduction of picoplatin is controlled by the adsorption of picoplatin [26]. The change of ferulic acid is nearly the same tendency with picoplatin, but this is opposite to caffeic acid and breviscapine.

According to Laviron theory [27], Ip = nFQv/4RT, where Ip is electronic number of electrode reaction, F=96485 C·mol^{-1}, R=8.3145 J· K· mol^{-1}, T=298.15 K, v is scan rate, Q is power of electrode reaction. In which, Q = nFAΓT, A is electrode surface area, ΓT is adsorption capacity (mol·cm^{-2}).

Table 1. The relation of peak current density and scan rates from four drugs

Drugs	Range of scan rate (V·s^{-1})	Current density (μA)	R value	Reaction pr)ocess	The best scan rate (V·s^{-1})	The number of transferred electrons in oxidation peak
Picoplatin	0.04-0.10	I_{pa} = 13. 98$v^{1/2}$ + 1.169	0. 9919	diffusion-controlled	0.05	2.04
		I_{pc} = 10. 34$v^{1/2}$ + 4. 816	0. 9901			
	0.10-0.40	I_{pa} = 23.25v+1.436	0.9906	adsorption-controlled		
		I_{pc} =31.26v-1.036	0.9912			
Caffeic acid tablets	0.04-0.10	I_{pa} = 19.69v+1.2145	0.9995	adsorption-controlled	0.10	1.98
		I_{pc} = 122.16v-0.0122	0.9998			
	0.10-0.40	I_{pa} = 53.072$v^{1/2}$-3.1516	0.9996	diffusion-controlled		
		I_{pc} = 54.708 $v^{1/2}$-5.0538	0.9991			
Ferulic acid tablets	0.04-0.10	I_{pa} = 23.375 $v^{1/2}$-3.8037	0.9995	diffusion-controlled	0.10	1.16
		I_{pc} = 38.262 $v^{1/2}$-5.4196	0.9996			
	0.10-0.40	I_{pa} = 25.478v+2.3722	0.9984	adsorption-controlled		
		I_{pc} = 42.628v+2.1097	0.9990			
Breviscapine tablets	0.04-0.10	I_{pa} = 63.19v-0.5005	0.9996	adsorption-controlled	0.15	1.42
		I_{pc} = 43.18v+0.3141	0.9953			
	0.10-0.40	I_{pa} = 44.206 $v^{1/2}$-7.7125	0.9974	diffusion-controlled		
		I_{pc} = 19.012 $v^{1/2}$+1.3177	0.9986			

3.3. Calibration Graph

Table 2. The liner relation and detection limit of four drugs (n=5).

Drug	Range of concentration (mol·L^{-1})	Liner equation	r value	Detection limit (μg.mL^{-1})
Picoplatin	1.0×10^{-5}-5.0×10^{-4}	I_{pa} = 1.735c-0.0107	0.9997	1.0×10^{-5}
Caffeic acid tablets	5.0×10^{-7}-2.0×10^{-5}	I_{pa} = 11.143c+3.9025	0.9995	5.0×10^{-7}
Ferulic acid tablets	2.0×10^{-6}-1.0×10^{-5}	I_{pa} = 2.908c+0.84	0.9997	1.0×10^{-6}
Breviscapine tablets	2.0×10^{-7}-6.0×10^{-5}	I_{pa} = 0.6181c+0.359	0.9990	2.0×10^{-7}

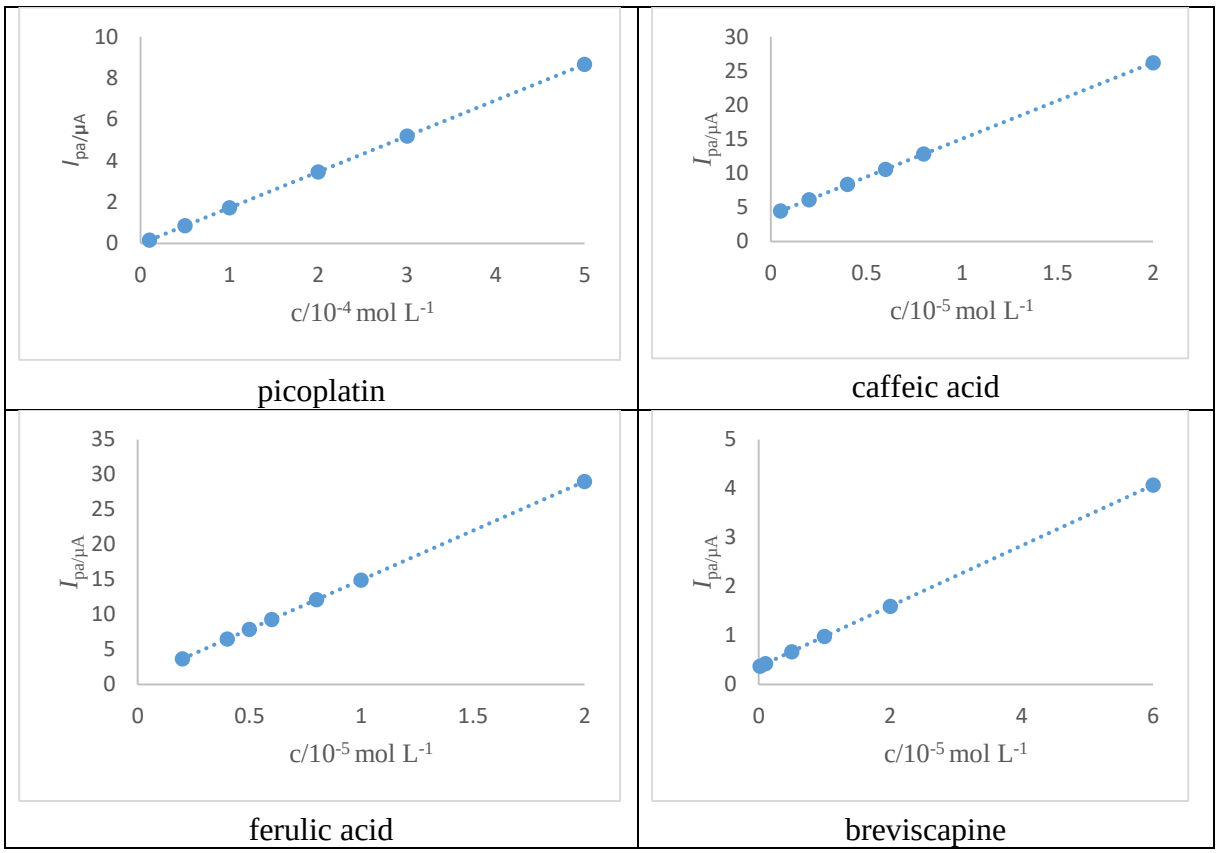

Figure 3. The calibration curve between oxidation peak current under the different concentration of four drugs.

According to calibration curve was measured by LSV [28] for different concentration of four drugs, the relation between concentration and peak current is a regression tendency (figure 3) and r value was also very high (table 2). Moreover, the detected limit of caffeic acid and breviscapine were reached 10^{-7} mol·L^{-1} and other two samples is less slightly. These results showed that the method of MWCNTs / GCE provide a good analysis concentration of some drugs.

Table 3. Comparison of some analytical methods toward four drugs detection performance

Samples	Detection method	Linear range (μM)	LOD (M)	References
Picoplatin	HPLC [a]	0.10–0.50	0.05	[29]
	MWNTs-[ODMIM]PF6/GCE [b]	2.66-532	1.33	[30]
Caffeic acid	Amperometric	0.5-130	0.524	[31]
	DPV [c]	0.01-46	0.004	[32]
Ferulic acid	SWSV [d]	9.71–194.18	0.19	[33]
	DPV	0.02–10.27	8.58×10^{-3}	[34]
Breviscapine	DPV	0.4-18	0.24	[35]

[a] high-performance liquid chromatography; [b] multi-walled carbon nanotubes ionic liquids modified glassy carbon electrode; [c] differential pulse voltammetry; [d] Square wave stripping voltammetry;

In the past many detection methods of these drugs have been reported, covering from high-performance liquid chromatography (HPLC) to electrochemical technique. Compared with some important analytical conditions, such as the linear range and LOD, the performance of MWCNTs / GCE was almost equal good as previously researches (Table 3).

3.4. Analysis of four Drugs

Table 4. Confirmation of four drug concentration with MWCNTs / GCE (n=5)

Drugs	Labeled (mg/g)	Detected (mg/g)	Average (mg/g)	RSD (%)	Added (mg/g)	Recovery (%)
Picoplatin	200.0	198.9	198.00	1.09	4.67	101.3
		197.6			8.52	98.7
		196.2			13.33	99.2
		198.3			16.35	99.4
		199.0			20.00	100.8
Caffeic acid tablets	100.0	97.16	98.46	0.82	20.0	103.7
		99.03			40.0	97.3
		98.24			60.0	99.3
		99.15			80.0	96.1
		98.74			100.0	101.1
Ferulic acid tablets	20.0	18.74	18.95	2.5	0.2	101.7
		19.26			0.4	98.9
		18.28			0.6	99.5
		19.53			0.8	98.1
		18.96			0.1	103.3
Breviscapine tablets	200.0	199.1	198.7	0.37	4.62	102.5
		198.3			9.24	96.3
		197.6			13.86	97.5
		198.8			18.48	98.6
		199.5			23.10	104.5

The ratio that is three times of blank standard deviation and gradient of calibration curve in the blank solution is as determination limit. A certain amount of drug was diluted to 100 mL with buffer solution for DPV determination. Every sample was determined five times in parallel, experiment of the sample recovery rate was carried out adopted the method of standard adding.

In table 4 with the determination of MWCNTs / GCE average content of four drugs were nearly to truth value, RSD value were less than 3% and the recovery rate of adding standard were between 96% and 105%. These data are highly similarity to value of HPLC determination. It is state clearly that MWCNTs / GCE can determined to drug quantitatively and the electrode possess high accuracy and excellent precision [36].

4. CONCLUSIONS

In this paper, with the use of MWCNTs/GCE the electrochemical behavior of picoplatin, caffeic acid, ferulic acid and breviscapine on the electrode was investigated by cyclic voltammetry. The results showed that the MWCNTs/GCE can effectively improve the sensitivity of measurement. The optimum conditions of the determination were investigated. Differential pulse voltammetry was used to determine the content of four drugs in the actual sample. The method is simple, rapid, accurate and reliable to apply in pharmaceuticals determination.

The study showed that the carbon nanotube has a large specific surface area and strong adsorption capacity, and has obvious catalytic sensitization function. The four kinds of drugs have good electrochemical behavior on the prepared carbon nanotube electrodes. The carbon nanotube modified electrode can significantly increases the peak current of the drug, and the current of oxidation peak is good linear relationship with the drug concentration. Therefore, the electrochemical detection method based on MWCNTs/GCE has low detection limit, good recovery and precision in pharmaceuticals content.

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