The Analytical Applications of Square Wave Voltammetry on Pharmaceutical Analysis

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Abstract: Compared to other voltammetric techniques a square wave voltammetry (SWV), which is presented in this minireview, has a several advantages such as high speed, increased analytical sensitivity and relative insensitivity to the presence of dissolved oxygen. Also it is an electrochemical technique used in analytical applications and fundamental studies of electrode mechanism. This paper delivers both the underlying theory and the practical guidance needed to apply square wave techniques and also provides a wide collection of data for the description of diverse tendencies that characterize several electrochemical reactions analyzed by SWV. This review summarizes some of the recent developments and application of direct and stripping SWV for drug compounds in their dosage forms and biological samples as reported in the period from 1997 till 2010 year.

Keywords: Square wave voltammetry, electrochemistry, drug analysis, nanoscale determination, electrode design.

1. INTRODUCTION

The pharmaceutical and biomedical analysis is among the most important branches of applied analytical chemistry. Analytical measurement procedures should have a critical role in drug analysis as well as in biological samples.

The scope of drug analysis includes the analytical investigation of bulk drug materials, the intermediates in their synthesis, products of drug research, drug formulations, impurities and degradation products of drug substances, biological samples containing the drugs and their metabolites with the aim of obtaining data that can contribute to the maximal efficacy and maximal safety of drug therapy and maximal economy of the drug production of pharmaceuticals. It is necessary that the early analytical methods and results comply with the following requirements: 1) the analytical techniques used provide reliable results with a fast turnaround time; 2) the obtained results provided will remain consistent throughout the development cycle of the drug product; and if possible, 3) the techniques are transferable to laboratories doing more repetitive testing.

Electrochemistry has always provided analytical techniques characterized by instrumental simplicity, moderate cost and portability [1-20]. Electroanalytical techniques can easily be adopted to solve many problems of pharmaceutical interest with a high degree of accuracy, precision, sensitivity and selectivity, often in spectacularly reproducible way by employing this approach. First examples of the pharmaceutical analysis using by polarographic methods were described in the 1930s and 1940s. Most of the pharmaceutical active compounds were found to be as an electrochemically active.

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Modern electrochemical methods are now sensitive, selective, rapid and easy techniques applicable to analysis in the pharmaceutical fields, and indeed in most areas of analytical chemistry. They are probably the most versatile of all trace pharmaceutically active compound analysis. Electroanalytical methods are also widely used in specific studies and monitoring of industrial materials, biological samples and the environment. It is apparent that the electroanalytical techniques at varying levels of sensitivity are required to solve analytical-pharmaceutical problems. This kind of assays require high specificity, low detection and determination limits and capable of determining drugs and their metabolites with nanogram or picogram level simultaneously. Voltammetric techniques have been extremely useful in measuring blood levels, metabolites and urinary excretion of drugs following low doses, especially when coupled with chromatographic methods. In many cases, modern electroanalytical techniques like square wave voltammetry (SWV) can be available alternative to more frequently used spectrometric or separation methods.

2. OVERWIEW OF SWV

Square wave voltammetric (SWV) technique is among the most sensitive means, for the direct evaluation of concentrations; it can be widely used for the trace analysis, especially on pharmaceutical compounds. This method is the source of a fair amount of confusion. The problem arises from the number of waveforms employed, which are frequently described as simply square wave voltammetry. In this context it will be consider three basic groups: the Kalousek, Barker, and Osteryoung formats. Square wave voltammetric technique originates from the Kalousek commutator and Barker's square wave polarography. Kalousek constructed an instrument with a rotating commutator which switched the potential of the dropping [1]. Kalousek square wave technique is a lower frequency method, which measures the current only on the reverse half cycle of the square wave (SW). The Barker format is the simplest to visualize. The waveform is a direct analog to

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sinusoidal ac voltammetry with a symmetric square wave of frequency and amplitude riding on either a ramp or slow staircase waveform. Osteryoung format is the most common form of SW techniques. This waveform differs from the other SW techniques in that the base potential increases by amplitude for each full cycle of the square wave. The current is measured at the end of each half cycle. This wave form can be applied to a stationary electrode or static mercury drop electrode. In this case the time interval is arranged to allow the drop to grow to a pre-determined size. The response consists of discrete current-potential points separated by the potential increment ΔE. Hence ΔE determines the apparent scan rate, which is a number of current-potential points within a certain potential range. The currents increase proportionally to the scan rate. Frequently, the response is distorted by electronic noise and a smoothing procedure is necessary for its correct interpretation. In this context, it is better if ΔE is as small as possible [1, 2]. In this technique, the net current is generally compared with theoretical predictions of a dimensionless current. The experimental and dimensionless currents are related by the Cottrell factor for the characteristic time:

$$i = (nFAC^*(D/\prod t_p)^{1/2})\psi \quad (1)$$

where ψ is the dimensionless current, tp = r/2 pulse width and the other symbols have their usual meaning [3].

The advantage of SWV is that a response can be found at a high effective scan rate, thus reducing the scan time. For this reason SWV is employed more often than normal pulse voltammetry (NPV) and differential pulse voltammetry (DPV) techniques. Whereas NPV and DPV function with effective sweep rates between 1 and 10 mVs^{-1}, SWV can reach 1 Vs^{-1}. There are advantages: greater speed in analysis and lower consumption of electroactive compounds in relation to DPV, and reduced problems with blocking of the electrode surface. Also, in comparison to both linear sweep and cyclic voltammetry, it as a much broader dynamic range and lower limit of detection because of its efficient discrimination of capacitance current. Analytical determinations can be made at concentrations as low as 10 nM. SWV is 4 and 3 times higher than the DPV response, for reversible and irreversible systems, respectively. Therefore, typical SWV measurements take only 1-5 s whereas DPV requires much longer analysis times at about 2-4 min. [1-5]. Frequencies of 1-100 cycles per second permit the use of extremely fast potential scan rates. This speed, coupled with computer control and signal averaging, allows for experiments to be performed repetitively and increases the signal-to-noise ratio.

The other advantage of SWV, the difference of current is larger than either forward or reverse currents, so the height of the peak is usually quite easy to read, thus increasing the accuracy. The forward current i_2, reverse current i_1, or difference current ($i = i_2 - i_1$) can be used as the response in this technique. The net current has only very small charging current contributions, and in typical experiments the total faradaic charge is much less than equivalent to a monolayer of material. That is, the system is charged very little by the perturbation. The position and shape of the net current response are remarkably insensitive to size and shape of electrode [3]. A further advantage of the current difference output is that, when the signal lies in the oxygen reduction plateau, the response due to the reduction of oxygen is subtracted out. The two components of the net response, the current of the forward and the reverse series of pulses, are also displayed. The sensitivity increases from the fact that the net current is larger than either the forward or reverse components. Also, the sensitivity of SWV is higher than that of NPV and DPV.

Square wave voltammetry is a powerful electrochemical technique that can be applied in both electrokinetic and quantitative determination of redox couples strongly immobilized on the electrode surface [6].

In general, computer-based data acquisition may revolutionize the whole area of data collection in electrochemistry since more complex waveforms and current gathering techniques may be employed. This technique requires the power and flexibility of the mini-computer for its development and modern microprocessors for its commercial implementation [5, 7-16]. Microprocessors have been used to compensate for the practical problem of solution resistance and recently menu-selectable software has been incorporated in a stand-alone instrument which allows background subtraction and signal differentiation. The inherent speed of SWV can greatly increase sample throughput in batch and flow analytical operations. The method can be quite rapid and lends itself to the monitoring of rapid processes such as liquid chromatography. Simplex optimization to maximize peak current by varying the waveform parameters has been examined and SWV has also been used in thin lays. Because of the sensitivity and rapidity SWV is useful for drug analysis in their dosage forms and biological samples. The low detection and determination limits permit the analysis of trace amount of drug compound. SWV method was applied to numerous drug active compounds. In addition, SWV detection can also be used to resolve co-elution or co-migrating species for LC and CE methods.

Electroanalytical applications of drugs using SWV technique can be consider into direct and stripping measurements. Some pharmaceutical compounds that were analyzed directly, i.e. without accumulation of reactant or product of the electrode reaction, are listed in Table **1**. The stripping methods are based either on the accumulation of amalgams and metal deposits, or on the adsorptive accumulation of pharmaceutical compounds and metal complexes. Several of them are listed in Table **2**.

3. EXAMPLES OF SWV ANALYSIS IN DIRECT MODE

Uslu *et al*. [17] have designed differential pulse (DP) and square wave (SW) at boron-doped diamond eelctorde and glassy carbon electrodes. The peak current is found to be linear over the range of concentration 2×10^{-6} to 2×10^{-4} M in 0.5 M H_2SO_4 at about 1.20 V for DPV using boron-doped diamond electrode (BDDE). No electroactive interferences from the excipients and endogenous substances were found in the pharmaceutical dosage forms and biological samples.

A simple, rapid voltammetric method has been developed for the quantitative determination of albendazole by De Oliveira and Stradiotto [33]. A well defined irreversible oxidation peak current was obtained at 1.00 V. The detection limit was found 6.2×10^{-5} M for albendazole.

Table 1. Selected Examples of Direct SWV on Pharmaceutical Compounds in their Dosage Forms and Biological Media

Drug	Electrode type	Medium	LOD/LOQ	Applications	Ref.
Pefloxacin	BDDE	0.5 M H_2SO_4	1.54×10^{-7} M	Pharmaceutical dosage forms, serum	[17]
Abacavir	HMDE	1 M H_2SO_4	2.69×10^{-8} M	Pharmaceutical dosage forms	[18]
Fluvastatin sodium	BDDE	pH 10.0 BRb	1.37×10^{-7} M	Pharmaceutical dosage forms, human serum	[19]
Atorvastatin calcium	BDDE, GCE	0.1 M H_2SO_4	2.27×10^{-7} M 2.11×10^{-7} M	Pharmaceutical dosage forms, human serum, human urine	[20]
Simvastatin	GCE	0.1 M H_2SO_4	2.71×10^{-7} M	Pharmaceutical dosage forms, biolgical fluids	[21]
Quetiapine	GCE	pH 3.5 acetate buffer	4.0×10^{-8} M	Pharmaceutical dosage forms, human serum, human urine	[22]
Valacyclovir	GCE	pH 10.0 BRb	1.04×10^{-7} M	Pharmaceutical dosage forms, human serum, gastric fluid	[23]
Primaquine	GCE	pH 4.0 BRb	4.2 μg mL^{-1}	Pharmaceutical dosage forms	[24]
Flupenthixol	GCE	pH 7.02 BRb	1.17×10^{-7} M	Pharmaceutical dosage forms, human serum	[25]
Vardenafil	GCE	pH 2.0 phosphate buffer	2.3×10^{-8} M	Pharmaceutical dosage forms, human serum	[26]
Cefixime	GCE	pH 4.5 acetate buffer	6.4×10^{-7} M	Pharmaceutical dosage forms, urine, breast milk	[27]
Amisulpride	GCE	pH 7.0 and 3.0 BRb	2.2×10^{-8} M	Pharmaceutical dosage forms, serum, urine, gastric fluid	[28]
Fenbendazole	GCE	Tetrabutylamonium tetrafluorborate	5.0×10^{-6} M	Pharmaceutical dosage forms	[29]
Lacidipine	GCE	0.5 M H_2SO_4	3.12×10^{-7} M	Pharmaceutical dosage forms	[30]
Nefazodone	GCE	0.1 M H_2SO_4	2.1×10^{-7} M	Pharmaceutical dosage forms, human serum	[31]
Fluvastatin sodium	GCE	pH 10.04 BRb	1.07×10^{-6} M	Pharmaceutical dosage forms, biological fluids	[32]
Albendazole	GCE	1 M HCl	4.0×10^{-5} M	Pharmaceutical dosage forms	[33]
Sertindole	GCE BDDE	pH 3.5 acetate buffer	1.0×10^{-6} M	Pharmaceutical dosage forms, serum	[34]
Ceftazidime	CPE	pH 2.7 phosphate buffer	1.0×10^{-6} M	urine	[35]
Indapamide	CPE	pH 4.0 BRb	5.0×10^{-6} M	Serum	[36]
Abacavir	GCE	pH 2.0 BRb	2.2×10^{-7} M	Biological fluids	[37]
Formeterol fumarate	GCE	0.5 M H_2SO_4	8.0×10^{-6} M	Pharmaceutical dosage forms	[38]
Etodolac	GCE	pH 2.15 BRb	6.8×10^{-7} M	Pharmaceutical dosage forms, serum	[39]
S-adenosyl-L-methionine	GCE	pH 2.04 phosphate buffer	2.6×10^{-6} M	Pharmaceutical dosage forms	[40]
Alfuzosin	GCE	pH 6.0 phosphate buffer	1.6×10^{-7} M	Pharmaceutical dosage forms, serum, gastric juice	[41]
Cisapride	GCE	pH 3.5 acetate buffer	1.9×10^{-7} M	Pharmaceutical dosage forms	[42]
Piribedil	GCE	0.1 M H_2SO_4 and pH 5.7 asetate buffer	5.6×10^{-7} M	Pharmaceutical dosage forms, serum	[43]
Tamsulosin	GCE	pH 4.5 acetate buffer	3.3×10^{-7} M	Pharmaceutical dosage forms, serum	[44]
Sildenafil citrate	GCE	pH 2.0 phosphate buffer and pH 3.5 acetate buffer	6.9×10^{-7} M 1.05×10^{-6} M	Pharmaceutical dosage forms	[45]

(Table 1) contd…..

Drug	Electrode type	Medium	LOD/LOQ	Applications	Ref.
Mefloquine	GCE	pH 11.10 BRb	4.5×10^{-7} M	Pharmaceutical dosage forms, serum, urine	[46]
Lamivudine	GCE	pH 4.5 acetate buffer	6.3×10^{-8} M	Pharmaceutical dosage forms, serum	[47]
Nabumetone	GCE	pH 3.7acetate buffer	2.31×10^{-7} M	Pharmaceutical dosage forms, serum, urine	[48]
Verapamil	GCE	pH 3.7 acetate buffer	1.33×10^{-7} M	Pharmaceutical dosage forms, serum	[49]
α-tocopheryl acetate	Platinum microelectrodes	Acetic acid with $NaClO_4$	6×10^{-5} M	Pharmaceutical dosage forms	[50]
Etofibrate Fenofibrate Atorvastatin	HMDE	-	0.037-0.21 μg mL^{-1}	Pharmaceutical dosage forms, plasma	[51]
Opipramol	GCE	pH 3.5 acetate buffer	2.7×10^{-7} M	Pharmaceutical dosage forms, serum, urine	[52]
Donepezil	GCE	pH 7.0 BRb	-	Pharmaceutical dosage forms, serum	[53]
Sertraline	HMDE	pH 8.2 borate buffer	1.98×10^{-7} M	Pharmaceutical dosage forms	[54]
Verapamil	Graphite-polyurethane composite electrode	pH 5.3 acetate buffer	0.7 μmol L^{-1}	Pharmaceutical dosage forms	[55]
Isoniazid	SPCE modified with poly-L-histidine	pH 5.0 phosphate buffer	1.7×10^{-7} mol L^{-1}	Human urine	[56]
Cefotaxime	GCE	pH 2.0 BRb	2.8×10^{-7} M	Pharmaceutical dosage forms, serum	[57]
Necrodil sodium	GCE	pH 4.0 BRb	2.7×10^{-6} M	Pharmaceutical dosage forms	[58]
Amlodipine besylate Atorvastatin calcium	GCE (ratio voltammetric method)	pH 5.0 BRb	8.53×10^{-7} M 4.70×10^{-7} M	Pharmaceutical dosage forms	[59]
Azidothymidine	HMDE	pH 8.0 phosphate buffer	1 nM	Biological materials	[60]
Cefoperazone	Mercury electrode	pH 4.4 BRb	0.5 nmol L^{-1}	Pharmaceutical dosage forms, milk, urine	[61]
Cladribine	Graphite electrode	pH 6.0 BRb	75 nM	Biological samples	[62]
Quinapril	HMDE	pH 10.0 BRb	0.22 μg mL^{-1}	Pharmaceutical dosage forms	[63]
Chlorpromazine Propericiazine Thioridazine	GCE	0.1 M $HClO_4$ and pH 2.0 phosphate buffer	N.D.	Pharmaceutical dosage forms	[64]
Resveratrol	CPE	0.1 M HNO_3 (pH=1)	5×10^{-9} M	Pharmaceutical dosage forms, urine	[65]
Azitromycin	CPE	pH 4.6 acetate buffer	0.463 ppb	Pharmaceutical dosage forms, urine	[66]
Tramadol	GCE	pH 9.3 borate buffer	2.2 μM	Pharmaceutical dosage forms	[67]
Prednisone Prednisolone	SWNT EPPGE	pH 7.2 phosphate buffer	0.45×10^{-8} M 0.90×10^{-8} M	Pharmaceutical dosage forms, body fluids	[68]
Acetylsalicylic acid	BDDE	0.01 M H_2SO_4	2.0 μM	Pharmaceutical dosage forms	[69]
Adrenaline	Poly(1-methylpyrrole)mCPE	pH 4.0 phosphate buffer	1.68×10^{-7} M	Pharmaceutical dosage forms	[70]
Lidocaine	BDDE	pH 2.0 BRb	10 μgm L^{-1}	Pharmaceutical dosage forms	[71]
Dopamine	Mercury electrode	pH 7.5 citrate buffer	0.02 μg mL^{-1}	Pharmaceutical dosage forms	[72]
Ticlopidine	HMDE	pH 5.0 phosphate buffer	5.17×10^{-7} M	Pharmaceutical dosage forms	[73]
Fluoxetine	GCE	pH 9.0 borate buffer	1.0μM	Pharmaceutical dosage forms	[74]
Penicillamine	GCE	pH 5.0 acetate buffer	0.08 μM	Pharmaceutical dosage forms	[75]
Pantoprazole	HMDE	pH 5.0 BRb	0.048 μg mL^{-1}	Pharmaceutical dosage forms, plasma	[76]

(Table 1) contd…..

Drug	Electrode type	Medium	LOD/LOQ	Applications	Ref.
Captopril	SMDE	sodium sulfide	$6.28x10^{-3}$ µg mL^{-1}	Pharmaceutical dosage forms, serum	[77]
Trepibutone	PGE	pH 1.81 BRb	20 ng mL^{-1}	Pharmaceutical dosage forms	[78]
Fenofibrate	HMDE	pH 9.0 borate buffer	0.025 µg mL^{-1}	Pharmaceutical dosage forms	[79]
Estradiol	Au electrode	pH 7.4 phosphate buffer	18 pg mL^{-1}	biosensor	[80]
Captopril	modified CPE	aqueous buffer solution	9.1×10^{-8} M	Urine sample	[81]
Cilazapril Quinapril Ramipril	HMDE	pH 9.5 borate buffer	0.5 µg mL^{-1}	Pharmaceutical dosage forms	[82]
Dihydrocodeine	GCE	pH 3.0 acetate buffer	4 µM	Pharmaceutical dosage forms	[83]
Codeine	GCE	pH 3.0 acetate buffer	5 µmol L^{-1}	Pharmaceutical dosage forms	[84]
Thiamine	Self-assembled gold electrode	pH 11.40 BRb	5.5×10^{-9} mol/L	Pharmaceutical dosage forms	[85]
Codeine	Chemically modified electrode	0.05 M $HClO_4$	10 nM	Pharmaceutical dosage forms, plasma	[86]
Riboflavin Folic acid	SMDE	pH 5.89 buffer	1 x 10^{-7}M	Pharmaceutical dosage forms	[87]
Levodopa	Dysprosium nanowine modified CPE	pH 7.0 acetate buffer	4.0×10^{-9} M	Serum, urine	[88]
6-Tioguanine	p-aminophenol modified CPE	pH 9.0 universal buffer solution	0.08 µM	Pharmaceutical dosage forms	[89]
Mosapride citrate	Pt electrode	pH 6.0 phosphate buffer	0.05 µgm L^{-1}	Pharmaceutical dosage forms	[90]
Salbutamol	NGITO	pH 7.4 phosphate buffer	75 ng mL^{-1}	Pharmaceutical dosage forms, plasma, urine	[91]
Ketorolac Tromethamine	Polypyrole modified CE	pH 5.5 acetate buffer	1×10^{-12} M	serum	[92]
Dipyridamole	HMDE	pH 3.0 phosphate buffer	1.88×10^{-8} M	Pharmaceutical dosage forms	[93]
Ligustrazine	Pyrolytic graphite electrode	pH 7.0 phosphate buffer	8.0×10^{-8} M	Pharmaceutical dosage forms	[94]
Atrazine	HMDE	pH 1.9 BRb	0.08 µgm L^{-1}	Pharmaceutical dosage forms	[95]
Sulfonamids	Poly(3-methyl thiophene) GCE	pH 6.26 BRb	2.6×10^{-9} M – 4×10^{-6} M	Pharmaceutical dosage forms	[96]
Cefaperazone	GCE	pH 2.00 phosphate buffer	1.31×10^{-7}M	Pharmaceutical dosage forms, human serum	[97]
Nitrofurantoin	BDDE	pH 4.00 BRb	8.15×10^{-9}M	Pharmaceutical dosage forms	[98]
Dexamethasone	fullerene-C60-modified edge plane PGE	pH 7.2 phosphate buffer	5.5×10^{-8} M	Pharmaceutical formulations, human blood plasma	[99]
Methyprednisolone	single-wall carbon nanotubes modified EPPGE	pH 7.2 phosphate buffer	4.5×10^{-9} M	Pharmaceutical dosages and human blood plasma	[100]

Abbreviations: BDDE: boron doped diamond electrode; BRb: Britton-Robinson buffer; CGMDE: controlled growth mercury drop electrode; CPE: carbon paste electrode; EPPGE: modified edge plane pyrolytic graphite electrode; GCE: glassy carbon electrode; HMDE: hanging mercury drop electrode; NGITO: nano-gold particles modified indium tin oxide; PGE: pencil graphite electrode; SMDE: static mercury drop electrode; SPCE: screen-printed carbon electrode; SWNT: single wall carbon nanotube.

Abacavir has an antiretroviral activity against human immunodeficiency virus (HIV) and is oxidizable at the glassy carbon electrode (GCE). Uslu and Ozkan [37] developed SWV and DPV methods for abacavir in pharmaceuticals and biological fluids. These two voltammetric methods for the determination of abacavir in Britton-Robinson buffer at pH 2.0, which allows quantitation over the $8 \times 10^{-7} - 2 \times 10^{-4}$ M range in supporting electrolyte for both methods, were proposed. The linear response was obtained in Britton-Robinson buffer (BRb) in the ranges of 1×10^{-5} to 1×10^{-4} M for spiked urine samples at pH 2.0 and 2×10^{-5} to 2×10^{-4} M for spiked serum samples at pH 3.0 for both techniques.

Electroanalytical characteristics of piribedil (PR) and its square wave and differential pulse voltammetric determination in pharmaceuticals and human serum were investigated by Uslu and Ozkan [43]. The redox behavior of PR was found irreversible. For analytical purposes, a very well resolved diffusion controlled voltammetric peak was obtained in 0.1 M H_2SO_4 and pH 5.7 acetate buffer. The determination peaks are obtained 1.29 and 0.97 V for SWV in 0.1 M H_2SO_4 and pH 5.7 acetate buffer, respectively.

Korany *et al*. [51] developed SWV and DPV techniques determination of etofibrate, fenofibrate, and atorvastatin in pharmaceutical preparations and plasma. The proposed

Table 2. Selected Examples of Stripping SWV on Pharmaceutical Compounds in their Dosage Forms and Biological Media

Drug	Electrode Type	Medium	LOD/LOQ	Applications	Ref.
Doxazosin	Tenax-modified CPE	pH 6.6 BRb	5.18×10^{-11} M	Pharmaceutical dosage forms, human urine	[101]
Candesartan	GCE	pH 5.03 phosphate buffer	7.94×10^{-6} M	Pharmaceutical dosage forms	[102]
Nitrofurantoin	HMDE	pH 10 BRb	1.32×10^{-10} M	Pharmaceutical dosage forms, human serum and human urine	[103]
Haloperidol	HMDE	pH 9 – 10 BRb	3.83×10^{-10} M	Pharmaceutical dosage forms, human biological fluids	[104]
Warfarin sodyum	HMDE	pH 5 BRb	6.50×10^{-10} M	Pharmaceutical dosage forms, human serum and urine	[105]
Sildenafil citrate	HMDE	pH 2.0 $HClO_4$	3.40×10^{-8} M	Human serum and urine	[106]
Pefloxacin	HMDE	pH 7.0 BRb	1.65×10^{-10} M	Pharmaceutical dosage forms, human serum	[107]
Ketolorac	HMDE	pH 5.0 acetate buffer	1.0×10^{-11} M.	Human serum	[108]
Cefonicid	HMDE	pH 4.0 BRb	4.0×10^{-8} M	Human urine	[109]
Nifedipine	HMDE	pH 9.0 borate buffer	1.21×10^{-9} M	Human plasma	[110]
Amlodipine	GCE	pH 11 BRb	1.40×10^{-8} M	Pharmaceutical formulation, human serum and urine	[111]
Amiloride	HMDE	pH 8 BRb	1.90×10^{-10} M	Pharmaceutical dosage forms, human serum.	[112]
Levofloxacin	GCE	pH 5.0 acetate buffer	5.0×10^{-9} M	Human urine	[113]
Trimetazidine	GCE	pH 5.0 acetate buffer	2.0×10^{-8} M	Pharmaceutical dosage forms and human urine	[114]
Isoniazid	HMDE	pH 5.5 acetate buffer	1.18×10^{-10} M	Pharmaceutical dosage forms, human serum and urine	[115]
Sildenafil	HMDE	pH 2.0 $HClO_4$	5.0×10^{-9} M	Pharmaceutical dosage forms	[116]
Clozapine	HMDE	pH 7 BRb	4.50×10^{-10} M	Pharmaceutical dosage forms, human serum	[117]
Entacapone	HMDE	pH 2.5 BRb	0.13 ng mL^{-1}	Pharmaceutical dosage forms	[118]
Lamotrigine	HMDE	pH 5.50 acetate buffer	5.02×10^{-9} mol mL^{-1}	Pharmaceutical dosage forms and human plasma	[119]
Ethinylestradiol	HMDE	pH 7 BRb	5.90×10^{-10} M	Pharmaceutical dosage forms, human serum and plasma	[120]
Celecoxib	HMDE	pH 7.0 BR b	1.86×10^{-10} M	Pharmaceutical dosage forms, human serum	[121]

(Table 2) contd…..

Drug	Electrode Type	Medium	LOD/LOQ	Applications	Ref.
Nitrofurantoin	HMDE	pH 6 phosphate buffer	0.06 ng mL^{-1}	Pharmaceutical dosage forms	[122]
Famotidine	A controlled growth mercury drop electrode	pH 6.7 MOPS (3-(*N*-morpholino) propanesulphonicacid) buffer solution	4.90×10^{-11} M	Human serum and urine	[123]
Chlordiazepoxide	HMDE	pH 8 BR b	4.40×10^{-10} M	Pharmaceutical dosage forms, human serum	[124]
Metoclopramide	CPE	pH~6.2 sodium acetate buffer	2.00×10^{-11}M	Pharmaceutical dosage forms and human urine	[125]
Rifampicin İsoniazid	CPE	pH 4.0 BR b	1.72×10^{-8} M 3.93×10^{-8} M	Pharmaceutical dosage forms and human serum	[126]
Terazosin	HMDE	pH 5.5 BR b	1.50×10^{-11}	Pharmaceutical dosage forms and human serum	[127]
Ofloxacine	HMDE	pH 7.5 BR b	1.10×10^{-8} mol L^{-1}	Pharmaceutical dosage forms, human urine and serum samples	[128]
Levonorgestrel	HMDE	pH 3 BR b	4.80×10^{-10} M	Pharmaceutical dosage forms, spiked human urine and real serum samples	[129]
Tianeptine	HMDE	pH 11 BR b	0.3 µg mL	Pharmaceutical dosage forms	[130]
Zopiclone	GCE	pH 7.08 BRb	1.70×10^{-7} M	Pharmaceutical dosage forms, spiked human urine	[131]
Triprolidine	HMDE	pH 11 BRb	8.80 ng mL^{-1}	Pharmaceutical dosage forms	[132]
Moxifloxacin	HMDE	pH 8.00 phosphate buffer	0.44 ng mL^{-1}	Pharmaceutical dosage forms, human urine	[133]
Cefaperazone	HMDE	pH 4.2 acetate buffer	4.50×10^{-10} M	Pharmaceutical dosage forms, human serum	[134]
Sildenafil	Lead film modified glassy carbon electrode	pH 5.0 acetate buffer	9.00×10^{-10} M	Pharmaceutical dosage forms	[135]
Dopamine	Carbon nanotube paste electrode	pH 3.5 0.1-M $NH_4H_2PO_4$	4.0 µg L^{-1}	Pharmaceutical dosage forms	[136]
Terbinafine	HMDE	pH 6.0 BR b	1.70×10^{-10} mol L^{-1}	Pharmaceutical dosage forms, human urine	[137]
Cefotaxime	HMDE	pH 2.8 BR b pH 9.25 BR b	1.73×10^{-9} M 6.27×10^{-9} M	Human urine	[138]
Aztreonam	Gelatin modified CPE CPE GCE Mercury electrode	pH 1–3, 0.1 M $HClO_4$	2.00×10^{-8} M	Human urine	[139]
Azithromycin	CPE	pH 4.6 acetate–acetic acid buffer	0.463 ppb	Pharmaceutical dosage forms, human urine	[140]
Nalidixic acid	HMDE	–	9.48×10^{-9} mol L^{-1}	Urine samples	[141]

(Table 2) contd…..

Drug	Electrode Type	Medium	LOD/LOQ	Applications	Ref.
Niclosamide	carbon nanoparticle/ chitosan film (CNP/CS) modified GCE	pH 7.0 phosphate buffer	7.7 nM	Pharmaceutical dosage forms, human serum	[142]
Cefadroxil	HMDE	pH 10.00 BR b	2.00×10^{-9} mol L^{-1}	Pharmaceutical dosage forms	[143]
Gatifloxacin	HMDE	pH 7.00 BR b	1.50×10^{-9} mol L^{-1}	Pharmaceutical dosage forms, human serum	[144]
Ornidazole	HMDE	–	3.40×10^{-8} mol L^{-1}	Pharmaceutical dosage forms	[145]
Candesartan	HMDE	pH 5.00 phosphate buffer	1×10^{-2} µg mL^{-1}	Pharmaceutical dosage forms	[146]
Glipizide	Mercury electrode	–	2.50×10^{-10} mol L^{-1}	Pharmaceutical dosage forms, human urine	[147]
Enrofloxacin	HMDE	pH 8.70, 0.4 mol L^{-1} ammonium chloride–ammonia solution	0.33 nmol L^{-1}	Pharmaceutical dosage forms, human plasma	[148]
Dexamethasone	HMDE	pH 3.00 BR b	3.10×10^{-9} M	pharmaceutical dosage forms, spiked human urine, bovine urine, protein-free bovine milk	[149]
Rutin	Lead film modified GCE (LF/GCE)	pH 4.6 Acetate buffer	2.50×10^{-10} mol L^{-1}	Pharmaceutical dosage forms	[150]
Ketotifen	ultra-gold microelectrode (Au UME)	pH 2.30 Phosphate buffer	0.7 pg mL^{-1}	Pharmaceutical dosage forms, biological samples	[151]
Diflunisal	montmorillonite-Ca-modified CPE	pH 5.0 acetate buffer	1.50×10^{-9} M	Pharmaceutical dosage forms, human serum	[152]
Vincamine	Nujol-based CPE	pH 5.00 BR b	6.00×10^{-9} M	Pharmaceutical dosage forms, human serum	[153]
Clarithromycin	Mercury electrode	–	1.50×10^{-8} mol L^{-1}	Pharmaceutical dosage forms, human urine	[154]
Acetaminophen Dipyrone Acetylsalicylic acid	sodium montmorillonite (NaMM) modified GCE	pH 1.00	0.02 µg mL^{-1} 0.04 µg mL^{-1} 0.02 µg mL^{-1}	Pharmaceutical dosage forms, human urine	[155]
Losartan	HMDE	pH 7.00 BR buffer	0.15 µg mL^{-1}	Pharmaceutical dosage forms	[156]
Simvastatin	mercury electrode	pH 7.00, 0.1 molL^{-1} $Na_2B_4O_7$-KH_2PO_4 buffer	4.50×10^{-9} mol L^{-1}	Pharmaceutical dosage forms, human serum	[157]
Losartan Triamterene	mercury electrode	pH 3.00 BR b	9.7 nmol L^{-1} 0.3 nmol L^{-1}	Pharmaceutical dosage forms, human urine	[158]
Fluvastatin	HMDE	pH 5.25	9.90×10^{-9} mol L-1	Pharmaceutical dosage forms	[159]
Astemizole	HMDE	pH 8.00 BR b	1.40×10^{-8} mol L^{-1}	Pharmaceutical dosage forms	[160]
Vitamin E (DL-α-tocopherol)	carbon nanotube powder with DNA and mineral oil	0.1 mol L^{-1} phosphate electrolyte solution	0.056 µg L^{-1}	Pharmaceutical dosage forms	[161]
Tetrazepam	mercury electrode	pH 11.0 BR b	3.0×10^{-9} mol L^{-1}	Pharmaceutical dosage forms, human serum	[162]

(Table 2) contd…..

Drug	Electrode Type	Medium	LOD/LOQ	Applications	Ref.
Hydroxyzine	GCE	pH 4.0 BR b	3.0×10^{-9} mol L^{-1}	Pharmaceutical dosage forms, human serum	[163]
Spironolactone	HMDE	–	1.72×10^{-10} mol L^{-1}	Pharmaceutical dosage forms, human serum and urine	[164]
Dantralone	mercury electrode	pH 2.5-11.5 BR b	2.10×10^{-10}M	Pharmaceutical dosage forms	[165]
Tolmetin	HMDE	pH 2 perchloric acid	2.00×10^{-9} M	Pharmaceutical dosage forms, human serum	[166]
Piroxicam	HMDE	pH 4.00 Acetate buffer	5.40×10^{-11} mol L^{-1}	Pharmaceutical dosage forms, human serum	[167]
Terbutalin	GCE	pH 6.0 BR b	6.00×10^{-9}M	Pharmaceutical dosage forms, human serum	[168]
Riboflavin	-Plain Carbon paste electrode -Chemically Modified electrode with cyclam	pH 1.5 BR b	1.9 ng mL^{-1} 0.2 ng mL^{-1}	Pharmaceutical dosage forms and food samples	[169]
Flavoxate	Mercury electrode	pH 4.00 acetate buffer	1.0×10^{-9} M	Pharmaceutical dosage forms	[170]
Triamcinolone acetonide	HMDE	pH 2-11	3.0×10^{-10} mol L^{-1}	Pharmaceutical dosage forms and human serum	[171]
Fluoxetine	Mercury drop electrode	pH 12.00 phosphate buffer	6.50×10^{-8} mol L^{-1}	Pharmaceutical dosage forms and human serum	[172]
Oxcarbazepine	HMDE	pH 4.00 BR b	1.74×10^{-7} mol L^{-1}	Pharmaceutical dosage forms	[173]
Norethisterone	Mercury electrode	pH 5.00 universal buffer	1.50×10^{-9} M	Pharmaceutical dosage forms	[174]
Paroxetin	Mercury drop electrode	pH 8.8 borate buffer	6.20×10^{-8} mol L^{-1}	Pharmaceutical dosage forms	[175]
Danazol	HMDE	pH 3.00 BR b	5.70×10^{-9} mol L^{-1}	Pharmaceutical dosage forms	[176]
Citalopram	Mercury drop electrode	pH 12.00	5×10^{-8} mol L^{-1}	Pharmaceutical dosage forms	[177]
Pravastatin	HMDE	pH 4.50 BR b	3.6×10^{-8} mol L^{-1}	Pharmaceutical dosage forms	[178]
Carvedilol	GCE	0.2 M H_2SO_4	2.37×10^{-9}M	Pharmaceutical dosage forms and human serum	[179]
Cefazolin	Mercury electrode	pH 6.00 BR b	2.60×10^{-10} M	Pharmaceutical dosage forms	[180]
Zafirlukast	HMDE	pH 8.0 borate buffer	5 ng mL^{-1}	Pharmaceutical dosage forms	[181]
Lamotrigine	HMDE	pH 5.5 acetic–acetate buffer	5.02×10^{-9} mol L^{-1}	Pharmaceutical dosage forms and human serum	[182]
Sertraline	Mercury electrode	pH 8.2	1.50×10^{-7} mol L^{-1}	Pharmaceutical dosage forms	[183]
Thalidomide	SMDE	–	0.5 pg	Pharmaceutical dosage forms, human serum and urine	[184]

(Table 2) contd…..

Drug	Electrode Type	Medium	LOD/LOQ	Applications	Ref.
Fluvoxamine	SMDE	pH 2.0 phosphate buffer	4.70×10^{-9} mol L^{-1}	Pharmaceutical dosage forms, human serum	[185]
Trimethoprim	HMDE	pH 3.8, acetate buffer	10 nM	Pharmaceutical dosage forms	[186]
Flutamide	HMDE	pH 5 acetate buffer	9.70×10^{-9} mol L^{-1}	Pharmaceutical dosage forms, human serum	[187]
Imatinib	HMDE	pH 6-7 BR b	2.60×10^{-10} mol L^{-1}	Pharmaceutical dosage forms, human serum	[188]
Captopril	HMDE	pH 2.2 BR b	0.5 µg L^{-1}	Pharmaceutical dosage forms	[189]
Ketoprofen	Dropping Mercury electrode	pH 2.0 BR b	0.10 ng mL^{-1}	Pharmaceutical dosage forms, human plasma	[190]
Rifampicin	HMDE	pH 3.5 phosphate buffer	6.14×10^{-9} mol L^{-1}	Pharmaceutical dosage forms, human urine	[191]
Rofecoxib	HMDE	pH 9.0 BR b	1.0×10^{-9} M	Pharmaceutical dosage forms	[192]
Venlafaxine	HMDE	pH 8.7 boric acid/potassium tetrahydroxoborate buffer	0.124 mg L^{-1}	Pharmaceutical dosage forms	[193]
Doxazosin	HMDE	pH 5.75 BRb	2.20×10^{-11} M 6.40×10^{-10} M	Pharmaceutical dosage forms; human urine	[194]
Gestodene	HMDE	pH 4.50 buffer solution HOAc/NaOAc	3.00×10^{-8} M	Pharmaceutical dosage forms	[195]
Timolol	HMDE	pH 4.60 BRb	6.60×10^{-10} M	Pharmaceutical dosage forms	[196]
Rifamycine SV	HMDE	pH 3.48 phosphate buffer	1.23×10^{-8} M	Pharmaceutical dosage forms	[197]
Norfloxacin	GCE	pH 5.0 acetate buffer	1.10 µg. mL^{-1}	Human urine	[198]
Dapsone	GCE	pH 1.0 10% H_2SO_4 in 50% aqueous alcohol	0.0036 mg.mL^{-1}	Pharmaceutical dosage forms; human urine	[199]
Codein	Clay modified SPCE	pH 6.00 phosphate buffer	20 nM	Pharmaceutical dosage forms; human urine	[200]
Dipyridamole	HMDE	pH 8.00 BRb	4.0×10^{-11} M	Human serum	[201]
Melatonin	GCE	pH 6.70 BRb	5.0×10^{-8} M	Pharmaceutical dosage forms	[202]
Lansoprazole	HMDE	pH 9.0 BRb	0.25 nM	Human serum	[203]
Indomethacin	HMDE	pH 4.0 BRb	6.70×10^{-10} M	Human serum	[204]
Melatonin	HMDE	pH 5.00 acetate buffer	3.13×10^{-10} M	Pharmaceutical dosage forms; human urine; serum	[205]
Mifepristone	HMDE	pH 2.00 $HClO_4$	2.0×10^{-7} M	Human urine	[206]
Ethamsylate	SAM Au Electrode	pH 7.00 BRb	6.0×10^{-8} M	Pharmaceutical dosage forms	[207]
Cyclofenil	HMDE	pH 9.00 BRb	1.5×10^{-8} M	Pharmaceutical dosage forms; human urine	[208]

(Table 2) contd…..

Drug	Electrode Type	Medium	LOD/LOQ	Applications	Ref.
Ambroxol	HMDE	–	0.2 $\mu g.mL^{-1}$	Pharmaceutical dosage forms	[209]
Imatinib	HMDE	pH 2.00 $HClO_4$	5.19×10^{-8} M	Human urine	[210]
Griseofulvin	HMDE	pH 10.00 BRb	5.80×10^{-10} M	Human urine; serum	[211]
Nitroxynil	HMDE	pH 6.00 BRb	8.40×10^{-10} M	Pharmaceutical dosage forms	[212]
Folic acid	Lead film electrode on GCE	pH 5.60 acetate buffer	7.0×10^{-10} M	Pharmaceutical dosage forms	[213]
Oxybutynin chloride	HMDE	pH 4.00 phosphate buffer	0.23 $\mu g.mL^{-1}$ 0.10 $\mu g.mL^{-1}$	Raw material; Pharmaceutical dosage forms	[214]
Trimethoprim	Lead film electrode on GCE	pH 5.8 acetate buffer	3.50×10^{-9} M	Pharmaceutical dosage forms; human urine	[215]
Testosterone	Lead film electrode on GCE	pH 5.2 acetate buffer	9.0×10^{-9} M	Pharmaceutical dosage forms; human urine	[216]
Rutin	Single-sided heated graphite cylindirical electrode	pH 5.00 phosphate buffer	1.0×10^{-9} M	Pharmaceutical dosage forms	[217]
Rifampicine	Lead film electrode	pH 5.00 acetate buffer	9.0×10^{-11} M	Pharmaceutical dosage forms	[218]

Abbreviations: BDDE: boron doped diamond electrode; BRb: Britton-Robinson buffer; CGMDE: controlled growth mercury drop electrode; CPE: carbon paste electrode; EPPGE: modified edge plane pyrolytic graphite electrode; GCE: glassy carbon electrode; HMDE: hanging mercury drop electrode; NGITO: nano-gold particles modified indium tin oxide; PGE: pencil graphite electrode; SMDE: static mercury drop electrode; SPCE: screen-printed carbon electrode; SWNT: single wall carbon nanotube.

methods proved to be accurate, precise, robust, and specific for determination of these three drugs. Limit of detection and quantitation were in the ranges of 0.037 - 0.21 and 0.12 - 0.71 $\mu g\ mL^{-1}$ respectively, indicating high sensitivity.

Dogan-Topal *et al*. [59] described first derivative of ratio voltammetric methods for determination of amlodipine and atorvastatin in tablets in the presence of the other compounds. Ratio derivative method involves calculating and plotting one of the mathematical derivatives of the curve, which offers an alternative approach to drug analysis. This technique depends on the measuring of first derivative of the ratio voltammograms of each concentration as a function of the increased concentration of analyte. DP and SW voltammetric methods depend on the first derivative of the ratio-voltammetry by measurements of the selected potentials for amlodipine and atorvastatin. The linear response was within the range of $4 \times 10^{-6} – 1 \times 10^{-4}$ M for amlodipine and 2×10^{-6} -1×10^{-4} M for atorvastatin.

Zidovudine is an antiproliferative and virostatic drug widely used in human immunodeficiency virus type 1 infection treatment. Vacek *et al*. [60] developed square wave voltammetry for determination of zidovudine. In phosphate buffer the SWV yielded the best zidovudine signal with the detection limit of 1 nM. The determination of zidovudine concentration in biological materials is affected by electroactive components, such as proteins and DNA. It has been shown that the SWV may be considered as useful tool for the determination of zidovudine concentration in cell cultures, and for monitoring zidovudine pharmacokinetics.

4. EXAMPLES OF SWV ANALYSIS IN STRIPPING MODE

Hamam [103] has described the fully validated, sensitive, and reproducible developed procedure for determination of the nitrofurantoin in bulk form, pharmaceutical formulation, human serum and human urine using, square-wave cathodic adsorptive stripping voltammetry. The cyclic voltammogram of the nitrofurantoin in Britton–Robinson buffers (pH 2 – 11) exhibited a single well-defined cathodic peak at the hanging mercury drop electrode, that due to the reduction of its nitro group to the amine stage. The optimal experimental parameters for the drug assay were: accumulation potential −0.4 V (*vs* Ag/AgCl/ KCls), accumulation time 40 s, frequency 120 Hz, pulse amplitude 50 mV and scan increment 10 mV in Britton–Robinson buffer (pH 10). A mean percentage recovery of 100.68 ± 0.17 (n = 5) and a detection limit of 1.32×10^{-10} M of bulk drug were achieved. Applicability to assay of the drug in pharmaceutical formulation, human serum and human urine was studied and illustrated. The mean percentage recoveries were found as: 101.49 ± 0.65, 103.94 ± 0.73 and 101.98 ± 0.52 (n = 5) in pharmaceutical formulation, human serum and human urine, respectively. Detection limits of 2.86×10^{-10} M and 5.77×10^{-10} M nitrofurantoin were achieved in human serum and urine, respectively.

The adsorptive and electrochemical behavior of trimetazidine hydrochloride on a glassy carbon electrode were investigated in acetate buffer solution by using cyclic and square-wave voltammetry by Ghoneim *et al*. [114]. Cyclic voltammetric studies indicated the oxidation of

trimetazidine hydrochloride at the electrode surface through a single two-electron irreversible step and fundamentally controlled by adsorption. The solution condition and instrumental parameters were optimized for the determination of the authentic drug using adsorptive square wave stripping voltammetry. Trimetazidine hydrochloride gave a sensitive adsorptive oxidative peak at 0.750 V (*vs* Ag/AgCl). The oxidation peak was used to determine authentic trimetazidine hydrochloride concentration in the range 5.0×10^{-8}–5.0×10^{-6} M with a detection limit of 2.0×10^{-8} M. The procedure was successfully applied for assay of trimetazidine hydrochloride in the tablet dosage form (Vastarel®). A mean recovery of 94.7% with a relative standard deviation (R.S.D.) of 0.88% was obtained. Applicability to assay the drug in urine samples was illustrated. The peak current was linear with the drug concentration in the range 17–85 µg per ml urine. The detection limit was 1.7 µg mL^{-1} in urine.

Adsorptive stripping voltammetric (AdSV) techniques were proposed for the direct quantitative determination of zopiclone (ZP) in spiked human urine and tablet dosage forms for first time by Yılmaz [131]. The electrochemical oxidation and determination of ZP were easily carried out on glassy carbon electrode (CGE) using a variety of voltammetric techniques. Different conditions were investigated to optimize the analytical determination of ZP. The dependence of the intensities of currents and potentials on pH, concentration, scan rate, deposition time, deposition potential, and nature of the buffer were investigated. Oxidation of ZP was found to be adsorptive-controlled and irreversible. The best results for the determination of ZP were obtained by using differential pulse adsorptive stripping (DPAdSV) and Osteryoung square wave voltammetric (OSWAdSV) techniques. Britton–Robinson buffer at pH 7.08 after a pre-concentration period of 120 s at 0.60 V were used. The peak current showed a linear dependence on the ZP concentration in the range of 6×10^{-7} to 2×10^{-5} mol L^{-1} for both techniques. The achieved detection and quantitation limits were 2.78×10^{-7} and 5.28×10^{-7} mol L^{-1} for DPAdSV and 1.70×10^{-7} and 5.78×10^{-7} mol L^{-1} for OSWAdSV, respectively. The proposed techniques were successfully applied to direct determination of ZP in tablet dosage form and spiked human urine samples. Excipients did not interfere with the determination. Precision and accuracy of the developed method were checked by recovery studies in tablet dosage forms and spiked urine samples [131].

Arranz *et al*. [137] have designed the voltammetric methods for the quantitative determination of terbinafine. Terbinafine is adsorbed on a hanging mercury drop electrode at pH 6.0 and gives a single wave at -1.47 *vs* Ag/AgCl reference electrode, due to olefinic double bond reduction. The electrochemical process is irreversible and fundamentally controlled by adsorption. A systematic study of the several instrumental and accumulation variables affecting the adsorptive stripping (Ads) response was carried out using square wave voltammetry (SWV, Osteryoung's method) and differential pulse voltammetry (DPV) as re-dissolution techniques. The limits of detection were 1.7×10^{-10} mol L^{-1} (Ads-SWV) and 6.3×10^{-7} mol L^{-1} (Ads-DPV). The coefficients of variation were 2.71% (Ads-SWV) and 2.63% (Ads-DPV) at 4×10^{-8} mol L^{-1} (n = 10). For the determination of terbinafine in formulations and spiked human urine samples, a method based on a pre-separation step at a solid phase C-18 cartridge and on the Ads-SWV procedure is proposed.

An easy, rapid and selective adsorptive stripping voltammetry (AdSV) method for the determination of vincamine in its formulation and human serum was developed and validated by Beltagi [153]. It was based on the oxidation of the drug onto a Nujol-based carbon paste electrode. The stripping step was carried out by using a square-wave (SW) potential-time voltammetric excitation signal. The optimal experimental variables as well as accumulation parameters were investigated as follows: frequency f = 120 Hz, scan increment ΔE_i = 10mV, pulse-amplitude ΔE_a = 25 mV and an accumulation potential E_{acc} of 0.0 V using a Britton-Robinson (BRb) universal buffer of pH 5 as a supporting electrolyte. After validation of the described method, it was applied for determination of vincamine in its formulation and human serum. Mean recovery of 100.41 ± 0.74 (n = 5) was achieved for assay of vincamine in Oxybral® capsules. Limits of detection and quantitation of 6.0×10^{-9} M (2.20 ng mL^{-1}) and 2×10^{-8} M (7.33 ng mL^{-1}) vincamine were achieved in human serum with a mean recovery of 99.5 ± 1.79%, without prior extraction of the drug. No interferences were observed in formulation and/or human serum. Due to high sensitivity and specificity of the developed method, it was successfully applied for evaluating some pharmacokinetic parameters of two healthy volunteers after administration of a single oral Oxybral® capsule.

The electrochemical oxidation of carvedilol was investigated using cyclic, linear sweep voltammetry at a glassy carbon electrode by Dogan and Ozkan [179]. In cyclic voltammetry, in all values of pH, the compound shows two irreversible oxidation peaks. These two peaks are related to the different electroactive part of the molecule. First and second peak currents were found as diffusion and adsorption controlled, respectively. Using second oxidation step, two voltammetric methods were described for the determination of carvedilol by differential pulse adsorptive stripping voltammetry (DPAdSV) and square-wave adsorptive stripping voltammetry (AdSSWV) at a glassy carbon electrode. Accumulation of carvedilol was found to be optimized in 0.2 M H_2SO_4 solution following 275 second accumulation time at open circuit condition. Under optimized conditions, the current showed a linear dependence with concentration in the range between 2×10^{-7} M and 2×10^{-5} M in supporting electrolyte and in the range between 2×10^{-7} M and 1×10^{-5} M in spiked human serum samples for both methods. These methods were successfully applied for the analysis of carvedilol pharmaceutical dosage forms and spiked human serum samples. The repeatability and reproducibility of the methods for all media were determined. Precision and accuracy were also found. No electroactive interferences from the tablet excipients and endogenous substances from biological material were found.

Determination of captopril (CPL) was studied by square wave cathodic adsorptive stripping voltammetry (SWCAdSV) on a hanging mercury drop electrode (HMDE) by Ioannides *et al*. [189]. CPL was adsorptively pre-concentrated on the mercury surface as a sparingly soluble

mercury salt under stirring of the solution and then the accumulated species was reduced by a cathodic square wave voltammetric scan. The reduction current was related to the CPL concentration in the sample. The chemical and instrumental parameters affecting the response were investigated and optimized for the CPL determination. The calibration curve was linear from 0.5 to 180 μg L^{-1} of CPL (depending on the preconcentration time), the limit of detection at a S/N ratio of 3 was 0.5 μg L^{-1} with 300 s of preconcentration and the relative standard deviation was 3.2% at the 20 μg L^{-1} level (with 120 s of preconcentration, n = 8). The method was applied to the determination of CPL in two pharmaceutical formulations with recoveries of 97.9 and 98.8 %. Finally, the potential for applying the proposed method to the determination of CPL in biological media was briefly discussed.

CONCLUSIONS

In years 1997-2010, to our best knowledge, the reported practical implementations of direct SWV technique for analysis of pharmaceuticals were refered to 95 drugs from variable therapheutical classes. The most often used variants of working electrode was a native- and/or modified-glassy carbon electrodes CGE (ca. 35% of reports). The BDDE and HMDE electrodes were second type of mostly applied electrodes (ca. 18 % of reports) in these direct SWV protocols for drugs determination. In case of stripping mode of SWV analysis the detailed reports on determination of more than 100 different drugs were reported in considered span of years. The use of HMDE electrode dominating in this type of SWV analysis (ca. 65% of all reviewed here reports). The GCE electrode with its modifications has been prefered as the second type of working electrode in stripping SWV mode (ca. 18% of reports). These facts means that working electrode design, its fabrication conditions and specific demanding characteristics of electrode materials used in production of working electrode are still critical factors to control such basic performace criteria of direct and stripping SWV analysis of drugs as the background currents, noise and measured signal level. However, the recently observed progress in the SWV technique indicated cleary that this mode of voltammetry meet successfully the still increasing requirements for precise and rapid determination and nanoscale quantification of variety of important ionisable drugs in pharmaceutical dosage forms and typical biological fluids. Thus further spreading of this highly prospective electrochemical technique in variety of laboratories for drugs research and analysis could be expected in coming years.

ABBREVIATIONS

AdSV = Adsorptive stripping voltammetry

AdSSWV = Square-wave adsorptive stripping voltammetry

BDDE = Boron doped diamond electrode

BRb = Britton-Robinson buffer

CGMDE = Controlled growth mercury drop electrode

CPE = Carbon paste electrode

CPL = Captopril

DP = Differential pulse

DPAdSV = Differential pulse adsorptive stripping voltammetry

DPV = Differential pulse voltammetry

EPPGE = Modified edge plane pyrolytic graphite electrode

GCE = Glassy carbon electrode

HMDE = Hanging mercury drop electrode

NGITO = Nano-gold particles modified indium tin oxide

NPV = Normal pulse voltammetry

OSWAdSV = Osteryoung square wave voltammetric adsorptive stripping voltammetry

PGE = Pencil graphite electrode

PR = Piribedil

SMDE = Static mercury drop electrode

S/N = Sinal-to-noise ratio

SPCE = Screen-printed carbon electrode

SW = Square wave

SWCAdSV = Square wave cathodic adsorptive stripping voltammetry

SWNT = Single wall carbon nanotube

ZP = Zopiclone

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