Dedicated to the memory of Professor Sorin Roşca (1938–2021)

SIMPLE VOLTAMMETRIC ANALYSIS OF SULFAMETHOXAZOLE AT A DISPOSABLE PENCIL GRAPHITE ELECTRODE

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This paper presents the cyclic (CV) and differential pulse (DPV) voltammetric investigation of sulfamethoxazole (SMX) at the disposable, bare pencil graphite electrode (PGE). The working solution stability, the influence of the electrode material, the ethanol content of the stock solution, the nature and pH of the supporting electrolyte, and the potential scan rate on SMX voltammetric behavior were studied. Under optimized working conditions (B type PGE, Britton Robinson Buffer pH 7.96) SMX presented an anodic signal at about 0.850 V due to an irreversible diffusion controlled, pH-dependent process involving $2e^-$ and $1\ H^+$. The DPV method presented a linear range of $1.00 \cdot 10^{-5}$ - $2.50 \cdot 10^{-4}$ M with limits of detection and quantification of $4.04 \cdot 10^{-6}$ M and $1.22 \cdot 10^{-5}$ M SMX, respectively. The method presented good repeatability and was successfully applied (recoveries of $99.64 \pm 0.52\%$) to the assessment of the SMX content of pharmaceutical preparations containing both the analyte under study and trimethoprim.
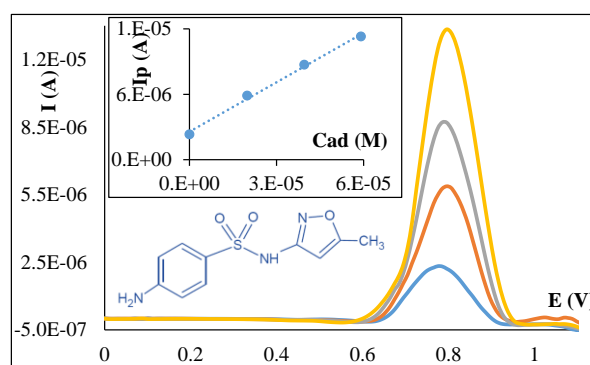
INTRODUCTION

Sulfonamides are broad spectrum antibacterial agents employed for decades in the treatment of human and animal infections due to their low cost and high efficiency.[1] Considering their poor solubility, the use of sulfonamides in animal husbandry without proper withdrawal periods could lead to their accumulation in food causing antibacterial resistance and endanger human health by favoring allergies, thyroid cancer and some other diseases. Therefore, USA and the EU set a maximum residue limit of 100 µg/kg edible tissue.[2]

One of the main representative of this family of antibiotics is sulfamethoxazole (4-Amino-N-(5-methyl-3-isoxazolyl) benzenesulfonamide, SMX) used in the treatment of urinary-tract infections, chronic bronchitis, pneumocystis pneumonia, meningococcal meningitis, acute otitis media, toxoplasmosis, skin and soft tissue infections. Nevertheless, SMX can have a series of side effects like gastro-intestinal and hematological disturbances, hypersensitivity[3] and hepatic failure due to drug-induced liver injury.[4] In order to increase the bacteriostatic effects, pharmaceutical products contain SMX and the potentiator,

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trimethoprim (TMP), an antibiotic of the diamino-pyrimidine class, in a 5:1 ratio.[5] SMX-TMP combination has a synergetic effect on the inhibition of the bacterial folic acid metabolism increasing thus dozens of times the sulfa bacteriostatic effect and the antibacterial range is wider.[6] It was reported that about 85% and 30% of the original contents of TMP and SMX, respectively, are eliminated unchanged in urine and these drugs are among the three most abundant antibiotics in wastewater treatment plants.[7] Their persistence and accumulation in the environment may have severe eco-toxicological impacts. Considering the large use of these drugs, several chromatographic,[8,9] spectrometric,[10,11] lumines-cence[12] and electrochemical (Table 1) methods have been already reported for SMX quantification in various matrices like pharmaceuticals, foodstuff and environmental samples. Some of these methods are laborious, involve long analysis times and large sample volumes, need trained personnel and expensive apparatus, but the electroanalytical ones have some certain advantages like sensitivity and selectivity (especially when using modified electrodes), simplicity, fast response, reduced reagents consumption, low-cost instrumentation and possibility of miniaturization, allowing in-field applications. Having in mind the importance of pharmaceuticals in our daily life and the increasing production of generic drugs as well as of the number of the companies that manufacture and distribute these compounds, there is a real need to develop simple analytical systems and methods to be used in the reliable routine analysis like the pharmaceutical quality control with high-analytical frequency. Voltammetric methods can fulfill these requirements. Their main drawback is related to the possible fouling of the electrode surface during the measurements and the need to regenerate the electroactive surface in order to obtain reproducible results. This obstacle can be overcome by using low-cost disposable sensors like the pencil graphite electrode (PGE) whose electroactive part is represented by the composite material contained in the commonly available pencil graphite leads.[13] This type of electrode either bare,[14-17] electroactivated[18,19] or modified[20-22] was largely used in the analysis of pharmaceutical important compounds. A literature search pointed out that despite the fact that there are several reports on SMX voltammetric analysis, only PGE modified with overoxidized polypyrrole (OPPy)[20] or molecularly imprinted OPPy[21] were used as working electrodes. Therefore, the present work describes for the first time the voltammetric behavior of SMX at the bare disposable PGE and, based on this, a differential pulse voltammetric method (DPV) for the simple, rapid and reliable SMX quantification from pharmaceutical preparations.

Table 1

Performance characteristics of voltammetric methods reported in the literature for SMX analysis

Technique	Electrode	Linear range (M)	LOD (M)	Sample	Ref
SWV	CPE	$7.90 \cdot 10^{-6} - 2.40 \cdot 10^{-5}$	$2.30 \cdot 10^{-6}$	-	23
SWV	GCE	$5.50 \cdot 10^{-5} - 3.95 \cdot 10^{-4}$	$8.52 \cdot 10^{-6}$	Pharmaceuticals	1
DPV	Ag-MWCNT/MTOAC/GCE	$5.00 \cdot 10^{-8} - 7.00 \cdot 10^{-5}$	$1.00 \cdot 10^{-8}$	Pharmaceuticals, urine	24
DPV	SBA/AgNP/CNTPE	$6.00 \cdot 10^{-8} - 7.00 \cdot 10^{-5}$	$1.90 \cdot 10^{-8}$	Urine	4
DPV	oxMWCNTs/MI-OPPy/GCE	$1.99 \cdot 10^{-6} - 1.09 \cdot 10^{-5}$	$4.13 \cdot 10^{-7}$	Milk	25
Amp	g-C$_3$N$_4$/ZnO/GCE	$2.00 \cdot 10^{-8} - 1.10 \cdot 10^{-3}$	$6.60 \cdot 10^{-9}$	Blood	3
DPV	GR-ZnO/GCE	$1.00 \cdot 10^{-6} - 2.20 \cdot 10^{-4}$	$4.00 \cdot 10^{-7}$	Serum, urine, water	7
DPV	Fe$_3$O$_4$/ZIF-67/IL/CPE	$1.00 \cdot 10^{-8} - 5.20 \cdot 10^{-4}$	$5.00 \cdot 10^{-9}$	Urine, water	2
DPV	PSP(rGNR)CE	$1.00 \cdot 10^{-6} - 1.00 \cdot 10^{-5}$	$9.00 \cdot 10^{-8}$	Tap water	8
DPV	MIP/H-GNs/GCE	5.00 - 1000.00 ng/mL	1.2 ng/mL	Milk, honey, serum	26
DPV	SHL-GP/WP	$5.00 \cdot 10^{-6} - 1.00 \cdot 10^{-4}$	$4.00 \cdot 10^{-7}$	Milk, well and tap water	5
DPV	OPPy/PGE	$2.50 \cdot 10^{-5} - 1.50 \cdot 10^{-3}$	$8.35 \cdot 10^{-7}$	Pharmaceuticals	20
DPV	OPPy-MIP/PGE	$2.50 \cdot 10^{-5} - 7.50 \cdot 10^{-4}$	$3.59 \cdot 10^{-7}$	Pharmaceuticals	21

SWV: square wave voltammetry; CPE: carbon paste electrode; GCE: glassy carbon electrode; DPV: differential pulse voltammetry; Ag-MWCNT/MTOAC: silver filled multiwalled carbon nanotube nanocomposite/methyltrioctyl ammonium chloride; SBA/AgNP/CNTPE: Santa Barbara Amorphous material decorated with silver nanoparticles modified carbon nanotube paste electrode; oxMWCNTs/MI-OPPy-MIP: oxidized multiwalled carbon nanotubes / molecularly imprinted overoxidized polypyrrole; Amp: amperometry; g-C$_3$N$_4$/ZnO: graphitic carbon nitride and zinc oxide nanocomposite; GR-ZnO: graphene and zinc oxide nanorods; Fe$_3$O$_4$/ZIF-67/IL: Fe$_3$O$_4$/ZIF-67 nanocomposite and ionic liquid; PSP(rGNR)CE: paper based screen printed reduced graphene nanoribnons carbon electrode; MIP/H-GNs: molecularly imprinted polymer/hemin/graphene hybrid nanosheets; SHL-GP/WP: polymer Shellac-graphite water proof electrochemical sensor; PGE: pencil graphite electrode; OPPy: overoxidized polypyrrole; OPPy-MIP: molecularly imprinted OPPy.

RESULTS AND DISCUSSION

Selection of the working electrode

Influence of the electrode material: The first step in the electrochemical investigation of an analyte is the selection of the working electrode as the material of the electroactive surface influences the voltammetric behaviour of the species. Therefore, SMX voltammetric response at the two well-known solid electrodes (glassy carbon electrode-GCE and Pt) and at the disposable PGE (composite material containing graphite, high polymer and wax) using pencil leads of different hardness[13] was evaluated using differential pulse voltammetry (DPV). No SMX oxidation signal was obtained at Pt, whereas the highest SMX anodic peak was observed at B type PGE. The peak height depends also on the electroactive surface area. Due to the fact that GCE and the disposable electrode had different geometrical surface areas (see section "Experimental-Equipment and reagents"), in order to characterize and compare the electrode materials, the sensitivities (S, expressed as $A/cm^2 \cdot M$) of the electrodes were assessed. The GCE sensitivity was lower than that of the PGEs which varied as follows for the graphite leads with different hardness: B (1.225) > 2B (0.775) > 2H (0.750) > H (0.567) > HB (0.566). The highest sensitivity towards SMX was obtained at B type PGE and therefore this electrode (B_PGE) was used for all further SMX electrochemical investigations.

Influence of the electrode surface electroactivation: Changing the nature of the electroactive surface may enhance the sensitivity and selectivity of the voltammetric determination. The simplest way to modify the carbon-based electrode surfaces is electroactivation at high negative or positive potentials. During this processes the electroactive surface is cleaned and its structure can be also modified by the generation of oxygen containing groups that can interact with the analyte improving the electrode performance characteristics.[13] In this study, the influence of B_PGE electroactivation on the SMX oxidation signal was tested by performing the electrode pretreatment in four different media (4.00 N H_2SO_4, acetate buffer solution (ABS) pH 4.00, phosphate buffer solution (PBS) pH 7.00 and 0.20 N NaOH) and employing two techniques, one consisting in the maintaining of the electrode for 60 s at 2.000 V and one realised by applying to the working electrode ten potentials cycles from -0.500 to 2.000 V with a scan rate of 0.100 V/s. The obtained results pointed out that the PGE electroactivation did not improve the SMX oxidation signal and thus, the bare, unactivated PGE was used for subsequent investigations.

Influence of voltammetric recordings number: Despite the fact that PGE is a cheap (one graphite lead costed about 0.03 Euro), commonly available and disposable electrode, five successive cyclic voltammograms (CVs) were recorded in the same SMX solution in order to test the analyte electrochemical behaviour and to establish whether the same pencil graphite lead could be used for several repetitive voltammetric recordings. SMX was irreversible oxidized at PGE, presenting a single anodic signal (~0.952 V) whose intensity lowered with the increasing number of potential scans, the most significant decrease being after the first cycle. This behaviour indicated the passivation of the electrode surface, probably due to the formation of a less conductive polymer film. Therefore, if not stateted otherwise, in the next SMX investigation steps each voltammetric recording was performed employing a new graphite pencil lead.

Selection of the optimum conditions of the SMX working solution

The electrochemical behaviour of organic species usually depends on the solution pH. Thus, CVs (Fig. 1a) and DPVs (Fig. 1b) recorded at B_PGE for SMX in BRB with pH values from 1.81 to 11.58 pointed out that regardless of the solution pH, SMX was irreversible oxidized and the potential of the resulted anodic peak shifted linearly towards less positive values with pH increasing, indicating that the electron exchange was accompanied by protons transfer. Comparing the slopes of the regression equations describing the $E_p = f(pH)$ dependencies for SMX anodic peak obtained by CV ($E_{p,CV}$ = -0.0337pH + 1.159; R^2 = 0.9925) and DPV ($E_{p,DPV}$ = -0.0354pH + 1.082; R^2 = 0.9948) with the theoretical value of 0.059 x/n from the Nernst equation (x and n - the exchanged protons and electrons, respectively) resulted that in the SMX oxidation at B_PGE the ratio of transferred protons to electrons is 1:2.
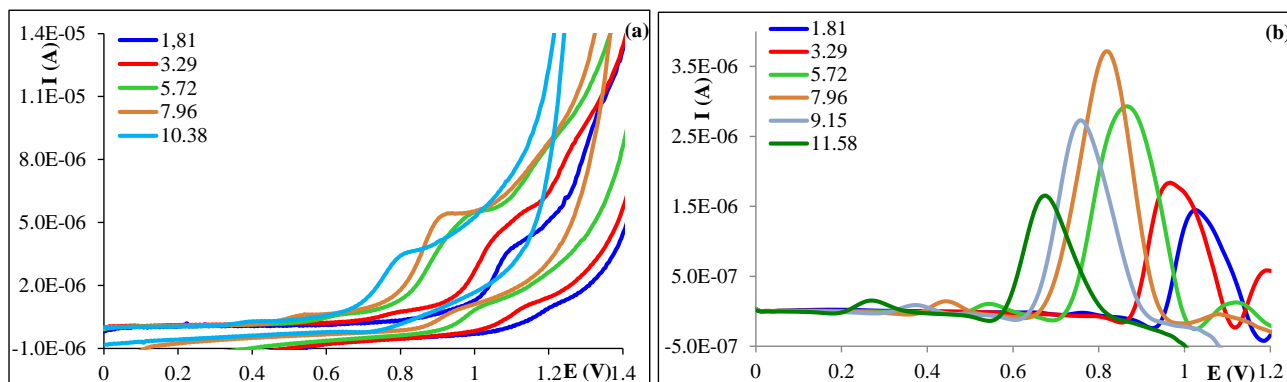
Fig. 1 – Selected CVs (a) and DPVs (b) obtained at B_PGE for $3.00 \cdot 10^{-5}$ M SMX in BRB of various pHs.

Considering that at B_PGE the best shaped and highest SMX oxidation signal was obtained at pH 7.96, both in CV and DPV (Fig. 1) other supporting electrolytes with similar pH values (PBS pH 7.40, 7.81 and 8.20) were investigated. The highest SMX oxidation signal was recorded in BRB pH 7.96. Therefore this medium was used in all subsequent electrochemical SMX investigations.

SMX has a low solubility in water, but it is soluble in ethanol. SMX stock solutions were prepared with various ethanol: water ratios. The most intense SMX oxidation signal was obtained when the stock solution was prepared totaly in ethanol.

Voltammetry allows multiple successive measurements on the same solution whitout changing the analyte concentration. Because this needs time, the stability of the SMX working solution in BRB pH 7.96 kept in the voltammetric cell was investigated by measuring the anodic DPV signal at certain time intervals. The SMX peak intensity did not vary up to 90 min, and decreased after this period of time. Thus, the SMX working solution

stability in ambiental conditions is sufficient for performing at least 20 measurements.

The influence of the potential scan rate

In order to assess the nature of SMX electrode process, CVs were recorded at different scan rates. It is obvious from Fig. 2a that by increasing the scan rate the SMX anodic peak shifted towards more positive potentials as it is typically for irreversible electrode processes and its current was enhanced. The non-linear dependence of the peak current on the scan rate, the linear variation of the peak current with the square root of the scan rate ($I_p = 4.00 \cdot 10^{-5} \cdot v^{1/2} + 4.00 \cdot 10^{-6}$; $R^2 = 0.9893$) and the slope of the logarithmic dependence between peak current and scan rate near to 0.5 ($\log I_p = 0.4024 \cdot \log v - 4.38$; $R^2 = 0.9890$) indicated that SMX oxidation at B_PGE was controlled by the analyte diffusion towards the electrode.
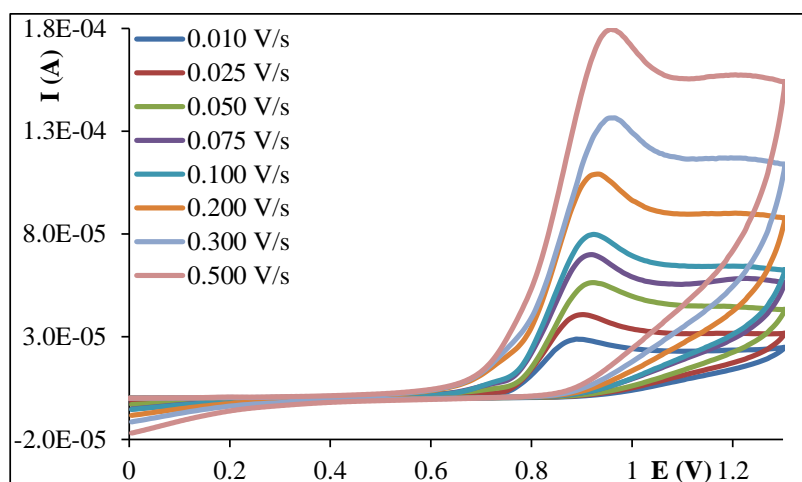

Fig. 2 – CVs recorded with different scan rates at B_PGE for $1.00 \cdot 10^{-3}$ M SMX in BRB pH 7.96.
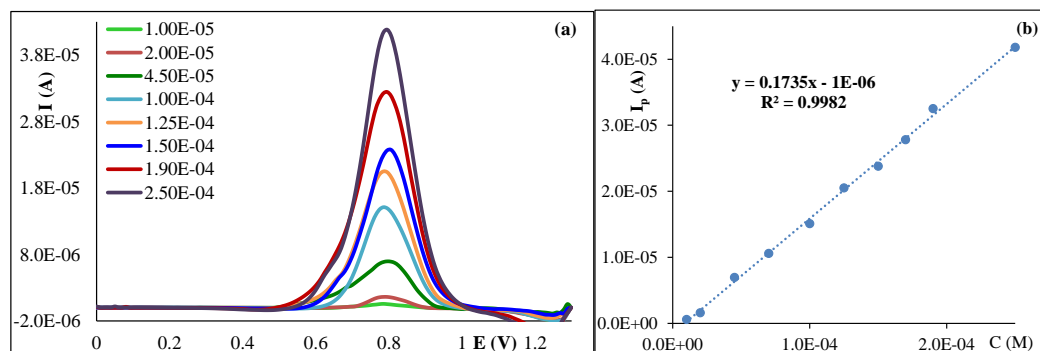
Fig. 3 – (a) Selected DPVs recorded at B_PGE for solutions with different SMX concentrations in BRB pH 7.96; (b) the corresponding calibration graph.

For an irreversible electrode process, the peak potential varies with the logarithm of the scan rate according to the Laviron equation.[27] For SMX peak obtained at B_PGE in BRB pH 7.96 the $E_p = f (\log v)$ dependence was described by $E_p = 0.0528\log v + 0.9901$ ($R^2 = 0.9811$). Considering that the charge transfer coefficient (α) for an irreversible electrode process is 0.5, from the slope of the $E_p = f(\log v)$ dependence ($0.0528 = 0.05916/\alpha n$) the number of exchanged electrons was found to be n = 2.26, which is ~2. Correlating with the results of the pH influence study it was concluded that SMX oxidation involved $2e^-$ and $1 H^+$.

Quantitative determination of SMX using DPV at PGE

The influence of SMX concentration on its DPV oxidation signal recorded at B type PGE was studied in BRB pH 7.96 by varying the analyte concentration in the range $2.00\cdot10^{-6}$ - $2.50\cdot10^{-4}$ M. At concentrations up to $1.00\cdot10^{-5}$ M SMX, the signal was very low and not reproducible. At higher concentrations, the peak current increased linearly with the analyte concentration up to $2.50\cdot10^{-4}$ M SMX. Thus, in the optimized working conditions the linear range of the DPV method was $1.00\cdot10^{-5}$ - $2.50\cdot10^{-4}$ M SMX (Fig. 3).

The limit of detection (LOD) and quantification (LOQ) were calculated using the regression data of the linear range as $3.3\cdot s_{x/y}/b = 4.04\cdot10^{-6}$ M and $10\cdot s_{x/y}/b = 1.22\cdot10^{-5}$ M SMX, where b is the slope of the regression equation describing the calibration curve and $s_{x/y}$ is the residual standard deviation.

Despite the fact that CV results emphasized the diffusion controlled SMX oxidation in BRB pH 7.96, the possible analyte accumulation at the at B_PGE surface was investigated in order to extend the linear range towards lower concentrations. No SMX accumulation was observed for periods of up to 120 min.

The repeatability of the SMX response at B type PGE, expressed as percentage relative standard deviation (RSD%), was assessed by carrying out ten DPV recordings at each of the three levels of SMX concentrations, the lowest ($1.00\cdot10^{-5}$ M), the highest ($1.90\cdot10^{-4}$ M) and a middle ($4.80\cdot10^{-5}$ M) concentration of the linear range. The obtained RSD% values of 7.10%, 5.50% and 3.60%, respectively, were within the accepted limits for the corresponding concentration level.[29]

Analytical applications of the developed DPV method

The analytical applicability of the developed DPV at PGE method was evaluated by the analysis of Sumetrolim tablets containing 400 mg SMX and 80 mg trimethoprim (TMP). The diluted pharmaceutical tablets sample was prepared as described in the section "Experimental- Sample preparation". To minimize the matrix interferences, the standard addition method was applied to assess the SMX content of the tablets. The DPVs obtained for the analyzed sample solution before and after each of the three additions of SMX stock solution (Fig. 4a) and the corresponding peak currents (Fig. 4b) were used to calculate the SMX content of the tablets. Comparing the obtained results with the content claimed by the producer, the average percentage recovery value of the SMX tablet content was found to be $99.64 \pm 0.52\%$.
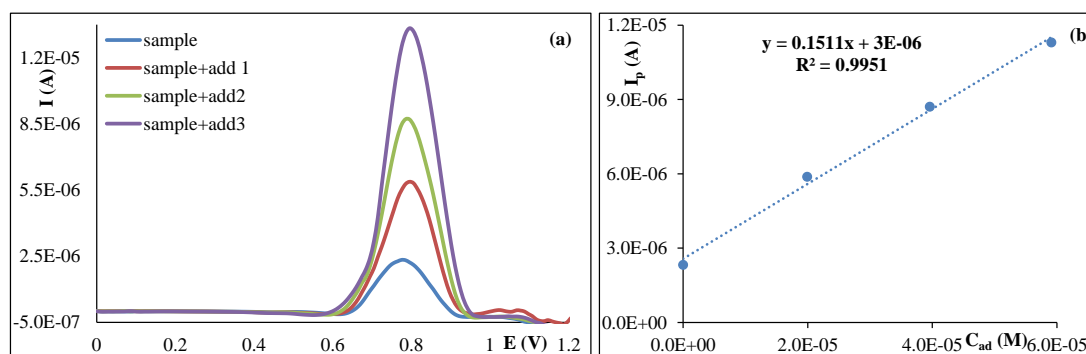
Fig. 4 – (a) DPVs recorded at B_ PGE for 10.00 mL tablet sample solution in BRB pH 7.96 before and after each addition of 0.05 mL $4.00 \cdot 10^{-3}$ M SMX standard solution; (b) the corresponding calibration graph.

EXPERIMENTAL

Equipment and reagents: All voltammograms were recorded with an Autolab PGSTAT electrochemical system equipped with a PC running the GPES 4.9 software. The employed three electrode voltammetric cell was build-up of a working electrode (glassy carbon electrode- GCE, Pt or PGE), a Ag/AgCl, KCl (3.00 M) reference electrode and a Pt auxiliary electrode. GCE and Pt (diameter of 3.00 cm; surface area of 0.071 cm^2) were polished with alumina before each voltammetric recording. The PGE (surface area of 0.159 cm^2) was obtained as already described.[14] SMX electrochemical behaviour was investigated by CV. DPV (step potential 0.005 V, modulation amplitude 0.150 V, modulation time 0.05 s and interval time 0.10 s) was used for optimum parameters selection and quantitative determinations.

All used reagents were of analytical grade and bi-distilled water was employed for the solutions preparation, if not stated otherwise. A $1.00 \cdot 10^{-3}$ M SMX stock solution was daily prepared in ethanol. Less concentrated solutions were obtained by dilution with the appropriate supporting electrolyte.

Sumetrolim (Egis Pharmaceuticals PLC., Hungary) with 400 mg SMX and 80 mg TMP per tablet was purchased from a local pharmacy. From the powder obtained by grounding 10 accurately weight Sumetrolim tablets an amount equivalent to obtain 20.00 mL solution with a concentration of ~$1.00 \cdot 10^{-3}$ M SMX was dissolved in 10.00 mL ethanol, ultra-sonicated for 15 minutes to assure the complete analyte dissolution and filtered using Whatman paper. The vessel and the filter paper were washed 3 times with 2.00 mL ethanol in order to minimise the analyte loss. The filtrate and the washing solutions were collected in a 20.00 mL volumetric flask which was brought to the mark with ethanol. A volume of 0.20 mL of this solution was diluted to 10.00 mL with BRB pH 7.96 so that the SMX concentration was situated within the linear range of the method. DPVs were recorded at B_PGE for the sample before and after each of the three additions of 0.05 mL of $4.00 \cdot 10^{-3}$ M SMX.

CONCLUSIONS

CV and DPV investigations at B_PGE in BRB pointed out that SMX was irreversible oxidized in a diffusion controlled, pH-dependent process involving $2e^-$ and $1 H^+$. Starting from these results, using the optimized conditions (BRB pH 7.96, B_PGE) a DPV method was developed for SMX quantitative analysis in the concentration range $1.00 \cdot 10^{-5} – 2.50 \cdot 10^{-4}$ M, with a LOD of $4.04 \cdot 10^{-6}$ M SMX. The method presented good repeatability and was successfully applied to the assessment of the SMX content of tablets containing SMX and TMP. However, when compared with the data already reported in the literature for SMX voltammetric quantification, the results obtained with the here described method are not as good as some of those obtained at modified electrodes, but they are comparable with those presented when bare sensors[1,23] were used or in the case of polymeric film modified PGE.[20,21] The DPV method at B_PGE developed during this study has a LOD and a linear range which are sufficient for SMX quantification in pharmaceuticals, when the analyte concentration in the working solution can be adjusted by the proper selection of the taken sample amount. Moreover, it has the main advantages of being simple (user-friendly), rapid, eco-friendly (minimum time and reagents consumption) and cheap (a disposable graphite pencil lead costed about 0.03 Euro), being thus adequate for high-throughput routine quality control analysis of pharmaceuticals.

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